

Synthesis of PMMA/Polysiloxane Core-Shell Latex

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ABSTRACT: In this study, silicon-acrylic latex, consisting of poly (methyl methacrylate) (PMMA) as the core and modified polysiloxane as the shell, had been successfully synthesized via cationic emulsion polymerization. The structure of the silicon-acrylic latex was confirmed by means of DLS, FTIR and TGA. There was an increase of 24.74 nm in average particle size and a shift of the size distribution to large sizes for core-shell particles in comparison with the original PMMA core particles, which indicated the formation of core-shell structure. The typical absorption peaks of Si-O-Si and Si-O-C in infrared spectrum indicated that the hydroxyl groups on the PMMA surface had reacted with the silanol groups, which could be confirmed by heterogeneous two-component system form TGA test.

Keywords: silicon-acrylic latex; core-shell; cationic emulsion polymerization; size distribution; heat resistance

1 INTRODUCTION

By synthesizing the polymer particles with core-shell structure, the materials of excellent film-forming properties, mechanical properties and heat treatment properties can be obtained [1]. Therefore, the core-shell latex particles are widely used in many fields of point, adhesives, paper and coating industries [2]. As the differences in performance between polysiloxane and polyacrylate, the former can be used for modifying the latter to obtain new materials with superior performance [3]. Chen and coworkers synthesized silicon-acrylic latex with better heat and oxidation resistant property than acrylic latex through emulsion copolymerization using octamethyl cyclotetrasiloxane (D₄), active silicone and acrylate [4]. Fan et al. modified acrylate with active silicone of 3-methacryloxypropyltrimethoxysilane (KH570) to get silicon-acrylic latex whose film had high tensile strength and elongation at break [5]. Fan and coworkers obtained silicon-acrylic latex with stable performance by emulsion polymerization using triethoxyvinylsilane (VTEO) and polyacrylate as the seed emulsion [6]. The silicon-acrylic latex as mentioned above were mostly synthesized using compound emulsifier consisting of anionic and nonionic emulsifier. However, synthesis of silicon-acrylic latex using the compound emulsifier of cationic and nonionic emulsifier is still relatively rare.

In this study, we have successfully synthesized the silicon-acrylic latex which consists of PMMA as the core and modified polysiloxane as the shell, through cationic emulsion polymerization. Core-shell particles containing polyacrylate core and polysiloxane shell are the most favored type owing to their superiority in performance, which is determined by the activity of the surfactant in the water phase [7,8]. Throughout the whole experimental process, the PMMA core was

obtained by free radical emulsion polymerization using cationic 2, 2'-azobis (2-amidinopropane) dihydrochloride (AIBA) as the initiator and hexadecyltrimethylammonium bromide (CTAB)/primary alcohol ethoxylate (AEO-3) as the cationic/nonionic complex surfactant. With respect to modified polysiloxane shell, 3-methacryloxypropyltrimethoxysilane (KH-570) was employed as the silane coupling agent of octamethyl cyclotetrasiloxane (D₄) in combination with NaOH as the catalyst through ring-opening polymerization. The monomer mass ratio of core to shell was 1:2 to obtain a stable core-shell structure. More importantly, the copolymer significantly displayed heat resistance both of PMMA core and polysiloxane shell.

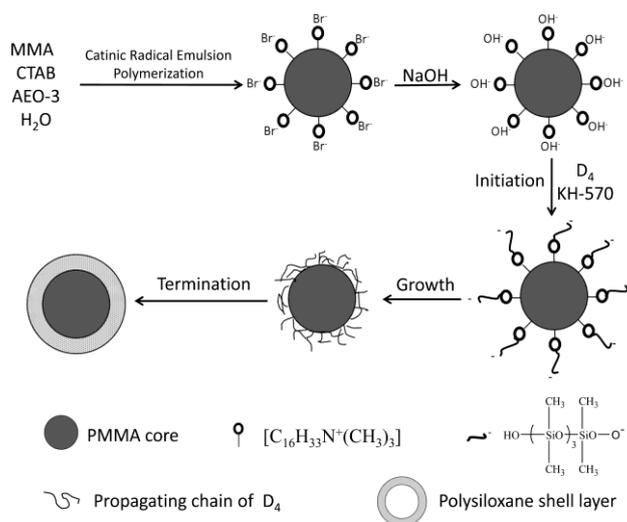
2 EXPERIMENT

2.1 Materials

Methyl-methacrylate (MMA), hexadecyltrimethylammonium bromide (CTAB), 2, 2'-azobis (2-amidinopropane) dihydrochloride (AIBA) and sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Octamethyl cyclotetrasiloxane (D₄) was purchased from Shenzhen OSBang New Material Co., Ltd (China). Primary alcohol ethoxylate (AEO-3) was purchased from Linyi Lusen Chemical Co., Ltd (China). Alkylphenol polyoxyethylene (OP-10) and sodium hydrosulfite were purchased from Shanghai Haoshen Chemical Reagent Co., Ltd (China) and 3-methacryloxypropyltrimethoxysilane (KH-570) was supplied by Evonik Industries AG (Germany).

All reagents were used as received except MMA which had been fractionated under reduced pressure before used to remove the inhibitor.

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Scheme 1. Schematic representation of the synthesis of silicon-acrylic latex

2.2 Synthesis of silicon-acrylic core-shell latex

The silicon-acrylic core-shell latex was obtained through cationic emulsion polymerization, using constant temperature water bath equipped with a 3-neck round bottom flask (500 mL), a stirred and reflux condenser. The cationic surfactant CTAB 0.25 g and nonionic surfactant AEO-3 0.25 g were firstly dissolved in the 20 g of distilled water. The MMA monomer 5 g was added into the emulsion drop by drop under a vigorous stirring rate of 1000 rpm, and pre-emulsified at 45 °C for 0.5h. The temperature was then raised to 80 °C. The initiator, AIBA, was prepared to 10 mL aqueous solution of 0.1 wt% and dropped into the mixture within 2 h, after which the reaction was maintained for 1 h for the sufficient polymerization of the PMMA. The as-obtained PMMA emulsion, as seed, was then cooled down to 70 °C and the pH value was regulated to 10–11 by using 1 mol/L NaOH. This was followed by adding the stable pre-emulsification of the shell monomer, previously prepared with OP-10 0.25 g, AEO-3 0.5 g, D₄ 10 g, KH-570 1 g and distilled water 20 g under a vigorous stirring rate of 1000 rpm at 45 °C for 0.5 h, into the core emulsion as-prepared above. The feeding time of shell monomer pre-emulsified would last 2 h at 70 °C. Kept the reaction for another 1 h at 70 °C and then raised the temperature to 80 °C, and maintained for 2 h for aging.

2.3 Characterization

Fourier transform infrared (FTIR) spectroscopy analysis, recorded in the 4000-400 cm⁻¹ reign, was performed on a Nicolet Avatar 380 FT-IR (America) using the KBr pellet technique to evaluate the special functional groups and formation of the silicon-acrylic core-shell latex. The sizes of PMMA particles, and in contrast, that recovered with modified polysiloxane

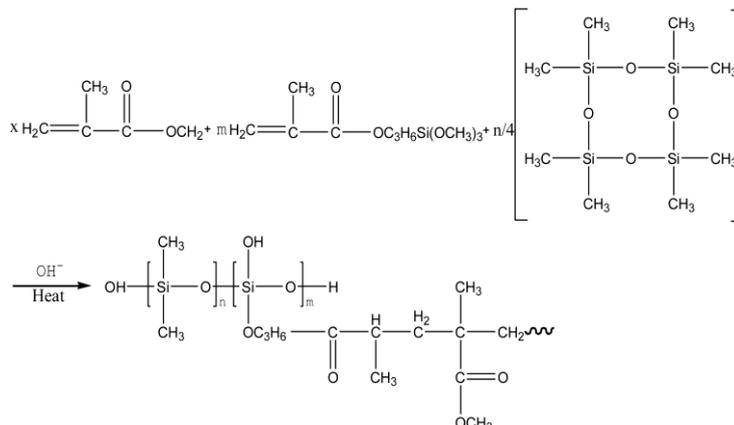
shell were determined by dynamic laser scattering measurement (DLS) using Nano-ZS90 (Malvern). The polymer content of the core-shell particles was determined through using the thermogravimetric analysis (TGA) using a TA Instruments Q500 by heating the sample up to 700 °C at 10 °C /min.

3 RESULTS AND DISCUSSION

3.1 Synthesis of silicon-acrylic core-shell latex

Scheme 1 shows the synthetic process of silicon-acrylic core-shell latex. Because of the cationic reaction system, which was different with synthesizing PMMA by anionic surfactant as usual, it was a great challenge to experiment for preparation formula and technology. While synthesizing the PMMA core, we took the AIBA as initiator instead of ammonium peroxydisulfate (APS). Because AIBA initiator with weak cationic would not react with cationic emulsifier, APS would and could lead to an unstable emulsion [9]. The amount of AIBA should be chosen well. When the concentration of initiator was low, it was hard to initiate the polymerization so that the reaction was not complete and no well-defined core was obtained. But too much AIBA would cause free polymer particles. It's because too much initiator would produce too many free radicals to go into aqueous phase to initiate more monomers for polymerization according to the classical emulsion polymerization [10].

As CTAB was used as cationic surfactant, it would be alkaline ring-opening polymerization in combination with using NaOH as the catalyst [11]. It is well known that CTAB would be highly ionized under alkaline condition to produce a large amount of ammonium and bromide ions. Therefore, the surface of PMMA particles could be fundamentally treated as



Scheme 2. Chemical reaction equation

cationic and the bromide ions could be entirely replaced by hydroxyl ions that would attack and break the Si-O bonds to initiate the polymerization of cyclic monomer D₄. In this case, silicone could be successfully coated on the PMMA core (Scheme 2).

Despite all this, the dosage of surfactant was still worth for discussion. At low surfactant concentration, unstable latex would be obtained because of the insufficient stabilization provided by surfactant. Increasing amount of surfactant produced stable core-shell latex. But too much surfactant would yield free micelles in the continuous phase, leading to separate free latex particles. What's more, KH-570, as the siloxane coupling agent, could react both with C=C unsaturated bonds of PMMA and hydroxyl terminated silicone so that it could also play a role of cross-linking agent between core and shell. Ring-opening polymerization of D₄ cyclic monomer was therefore expected to take place easily at the PMMA surface in the early stage of polymerization, resulting in a more closely packed layer of core-shell structural polymer.

3.2 Particle size distribution of silicon-acrylic core-shell latex

The dynamic light scattering analyses were performed on latex which was diluted to 1:100 with distilled water, as shown in Figures 1–2. In Figure 1, the size distribution by intensity is the same as that by number in Figure 2. The PMMA core showed a Z-average particle diameter of 63.9 nm with the polydispersity index (PDI) of 0.142, while the silicon-acrylic core-shell latex displayed a Z-average diameter of 88.64 nm with the PDI of 0.208. Obviously, there was a great increase in average particle size and a shift of the size distribution to large sizes for core-shell particles in comparison with the original PMMA core particles, which is indicating the propagation reaction of organosiloxane on the PMMA core surface and successful synthesis of core-shell structural latex.

As a matter of fact, the particle size of latex was

connected with the monomer content ratio of core and shell. Generally, the content ratio of core and shell was controlled within the scope of 1:1–1:3. It had been found during the experimental studies that when the monomer content ratio of core and shell was more than 1:3, the stability of the polymerization system would be bad and the viscosity would elevate dramatically, and finally the obtained latex production with large particle size would present as the state of jelly after lying for a time. These would be explained by that when the content of organic silicon was too high, part of the excess of polysiloxane existed in the emulsion with suspended state instead of reacting with PMMA, which could make the emulsion phase separation to occur. However, when the monomer content ratio of core and shell was less than 1:1, the stability of the polymerization system would also be bad. There was not enough polysiloxane around the core particle surface to react with PMMA. Thus, the latex particle size related to the core part was almost of no growth and no well-defined core-shell structure would be obtained.

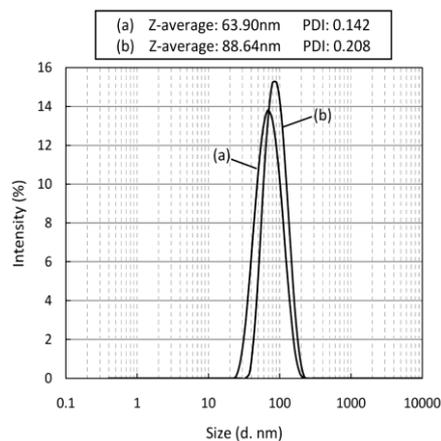


Figure 1. Size distribution by intensity of the latex: (a) PMMA core latex; (b) Silicon-acrylic latex

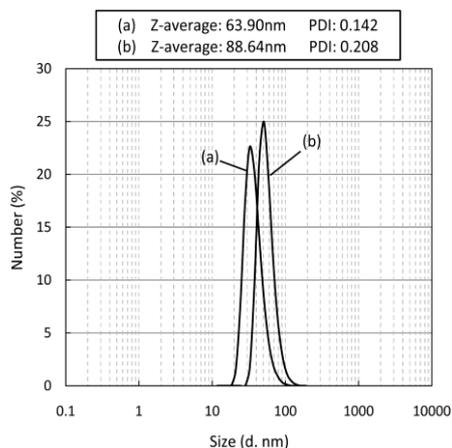


Figure 2. Size distribution by number of the latex: (a) PMMA core latex; (b) Silicon-acrylic latex

3.3 Chemical structure of silicon-acrylic copolymer

FTIR spectra of pure PMMA and silicon-acrylic co-polymer were shown in Figure 3. There were carbon dioxide absorption peaks in the range of 2257-2385 cm^{-1} both of curve (a) and curve (b) because of the air blank of the measurements. The FTIR spectrum of PMMA showed a sharp peak at 1722 cm^{-1} , which was attributed to the stretching vibration of C=O groups, and a peak at 1280 cm^{-1} , which is related to C-O stretching vibration of the acrylic moiety. Because of the conjugation effect with C=C, the peak was a little lower than that of the absorption peak of pure C=O (1735 cm^{-1}). Also, an absorption peak at 2923 cm^{-1} , which corresponded to C-H symmetric and asymmetric stretching of methyl and methylene groups, was observed; the presence of the group was

also confirmed by peaks at 1440 and 1385 cm^{-1} , which was associated with a bending vibration due to the C-H group. The broad band at 3429 cm^{-1} was due to alkanol groups (C-OH) which came from the hydrolysis of the acrylate monomer. The peak at 1633 cm^{-1} corresponded to the hydroxyl groups (O-H) of absorbed water. In addition to the peak characteristics of PMMA core, the FTIR spectrum of the silicon-acrylic latex showed peaks corresponding to the modified polysiloxane shell, formed during emulsion polymerization of the D₄ cyclic monomer onto the PMMA core emulsion. From curve (b), a peak at 495 cm^{-1} , which was attributed to Si-O-Si bending from dehydration and condensation, was observed. Besides, peaks at 1119 and 466 cm^{-1} , which were attributed to Si-O-C bonds and indicating that the hydroxyl groups on the PMMA surface had reacted with the silanol groups, were observed. Different with PMMA core, the peak at 1633 cm^{-1} was the typical signal of silanol groups (Si-OH), presented on the silica surface.

3.4 Thermal properties of silicon-acrylic core-shell polymer

A homogeneous polymer system had only one thermal degradation temperature or a broad temperature range of pyrolysis. While for not fully compatible polymer system, because of the micro phase separation, the heterogeneous system would form two-phase systems with relative independence due to the micro phase separation, each of it had their own pyrolysis temperature.

According to Figure 4, the TGA analysis for silicon-acrylic core-shell polymer consisting PMMA and polyorganosiloxane, showed a three-step degradation process indicating the heterogeneous two-component system in it. Before reaching 100 °C, the initial mass loss was observed and there was a slight weight loss

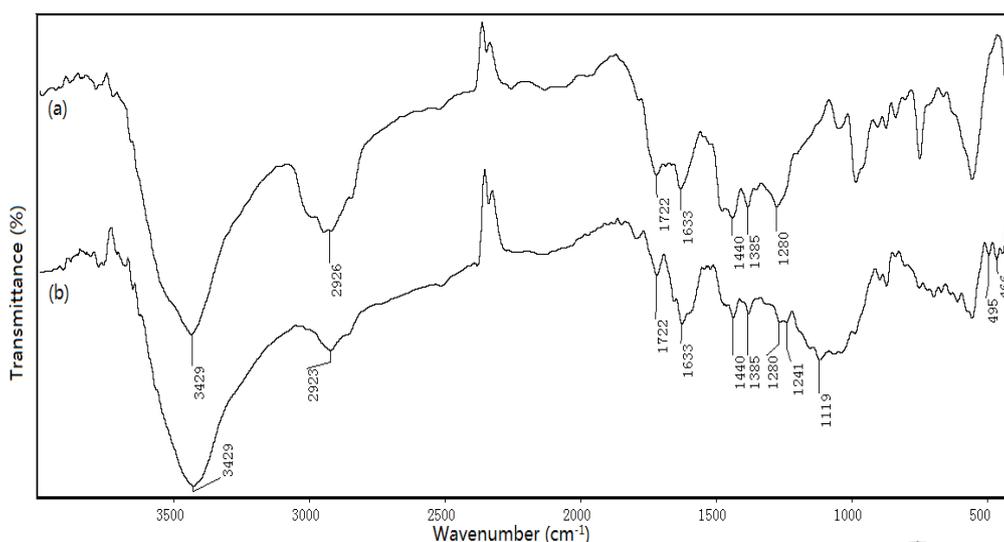


Figure 3. FTIR spectra of PMMA and silicon-acrylic copolymer: (a) PMMA; (b) silicon-acrylic copolymer

about 2%. This was caused by the evaporation of water, which was absorbed while the sample was weighed on the scale and placed at the crucible before testing. From 150 °C to 200 °C, the content decrease for oligomer could be observed. This might be caused by the methyl acrylic monomers that had been incompletely reacted or low molecular weight polymers and any other low molecular materials, such as emulsifiers, initiators and catalysts.

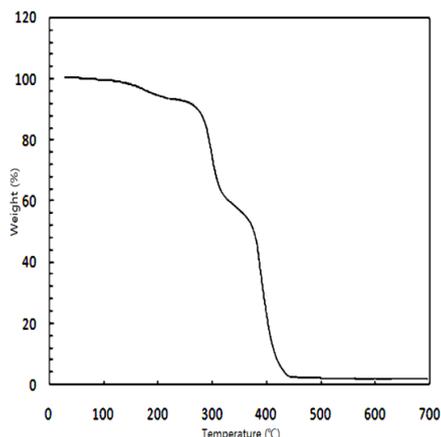
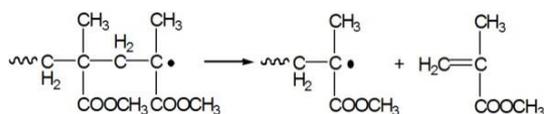


Figure 4. TGA curves of silicon-acrylic latex

And when the temperature reached to 280 °C, the first component was starting to decompose rapidly. This mass loss was attributed to the decomposition of the polysiloxane shell. The main decomposition process of polysiloxane shell, which occurred at 250 and 300 °C and containing polydimethylsiloxane and silane coupling agent, was attributed to the degradation of the polymer backbone.

PMMA firstly decomposed at 300 °C owing to the monomer formation from the macro-radical formed after rupture of a β -bond at the end unit containing unsaturated bonds, as shown in Scheme 3. The monomer recovery rate was high after the thermal degradation when there was quaternary carbon atom contained in polymer chain structure. Until the temperature reached to 380 °C, the content of sample was lowered to 58%. And finally, during 390 to 420 °C, the content of PMMA was completely decomposed, even the methyl methacrylate monomer (MMA) did not exist.



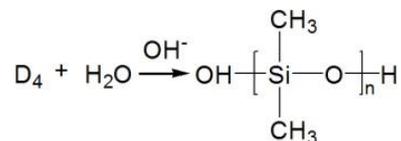
Scheme 3. Depolymerization reaction of PMMA

From this experiment, thus we showed the excellent heat resistance both of PMMA core and polysiloxane shell.

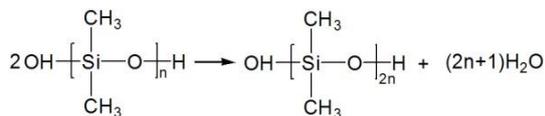
3.5 Oil separation during the cationic emulsion polymerization

As mentioned above in the second section of this chapter, when the content of organic silicon was too high, the emulsion phase separation would occur to cause the phenomenon of oil separation. In addition, improper control of many factors such as emulsifier, stirring speed, reaction temperature and catalyst and so on would result in oil separation.

According to the kinetics studies of emulsion polymerization of D_4 [12-14], the whole polymerization reacted in two steps in the presence of cationic emulsifier. First, the monomer of D_4 hydrolyzed, ring-opened and the hydroxyl-terminated linear oligomer was generated. Then the condensation reaction happened and the molecular weight of polymer increased rapidly.



Scheme 4



Scheme 5

The reaction speed of D_4 was determined by Scheme 4 and Scheme 5, while the growth of molecular weight was depended on Scheme 5. So the consumption speed of monomer did not equal with the growth rate of polymer molecular weight. As a matter of fact, the emulsion polymerization firstly happened on the surface of PMMA core latex particles, and was then gradually transferred to the surface of polymer particles which were formed later. The monomer of D_4 was firstly emulsified into "transition particles" during the emulsion polymerization, and then ring-opened to achieve the additional reaction. Finally, the stable and uniform polymer particles of low molecular weight were generated. If the "transition particles" weren't completely transferred into polymer particles during the reaction, they would collide with each other to get together into a larger particle, which would cause the oil separation.

Therefore, it was necessary to control the reaction conditions and polymerization rate to transfer the whole "transition particles" into stable polymer particles gradually. In order to solve the question of oil separation, many measures such as lowering the reaction temperature, reducing the amount of catalyst and slowing the stirring speed down could be adopted.

4 CONCLUSIONS

Silicon-acrylic core-shell latex with PMMA as the core and modified polysiloxane as the shell was successfully synthesized by a regular cationic emulsion polymerization process. Analysis from results of DLS, FTIR and TGA test showed that the new linkages between PMMA core and polysiloxane shell were formed and the particle size of latex is increased in comparison with the original PMMA core particles, which indicates the successful synthesis of core-shell structure. More importantly, the copolymer significantly displayed heat resistance both of PMMA core and polysiloxane shell.

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