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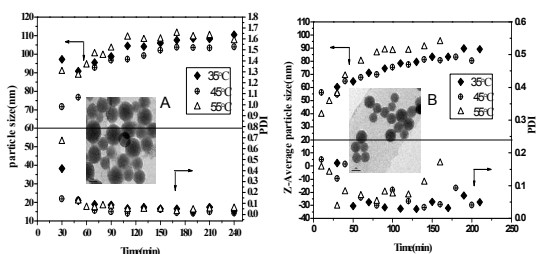
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Effects of feeding mode on synthesis of polyalkylsilsequioxane emulsion and latex properties

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Graphical abstract:



The stable polyalkylsilsequioxane emulsion was prepared by batch and semi-continuous method emulsion polymerization respectively. The influence of two methods on the emulsion was investigated.

ARTICLE

Effects of feeding mode on synthesis of polyalkylsilsequioxane emulsion and its properties

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The stable polyalkylsilsequioxane emulsion was prepared by batch and semi-continuous emulsion polymerization of methyl triethoxysilane (MTES) and n-propyltrimethoxysilane (PTMS). The influence of different feeding modes on emulsion particle size and morphology structure was discussed by dynamic laser scattering (DLS), transmission electron microscopy (TEM), scanning electron microscopy (SEM). The results indicated that the particle sizes of polyalkylsilsequioxane emulsion increased and finally tended to be constant as with the extension of reaction time. The latex particle size distribution index (PDI) decreased as with the extension of reaction time. The particle size prepared by batch was larger than that by semi-continuous, while the PDI was smaller. The actual solid content of emulsion was 15.6% (by batch) and 15.5% (by semi-continuous) when monomers mass fraction was 30% in the total system. The polymerization stability and storage stability of emulsion prepared by two methods are good. The morphologies of latex particles prepared by two methods were spherical. There was core-shell structure. There were some similar crystal structures in the molecular chain of polyalkylsilsequioxane prepared with alkyltrialkoxysilane. Thermal degradation weightlessness peak of polymer in nitrogen atmosphere was at 450-600°C, while in air atmosphere was at 250-300°C. The final residues were 68% in nitrogen, 65.1% in air atmosphere.

1 Introduction

Polysiloxane is widely used in textile finishing agent, waterproofing agent, adhesives and so on because of their specific physical and chemical properties.¹⁻² The methods for preparation the polysiloxane emulsion are generally classified in two categories: mechanical means and emulsion polymerization. Mechanical means usually entail taking the polysiloxane and using mechanical means such as homogenizers or vigorous agitation to emulsify the siloxanes in water.³⁻⁵ Emulsion polymerization typically entails combining a reactive silicone monomers or oligomers, emulsifiers, polymerization catalyst and water. (eg: octamethylcyclotetrasiloxane (D₄) emulsion).⁶⁻⁸ Emulsion polymerization method is much more flexible in raw material selection and much easier to control the polymer structure during preparing polysiloxane emulsion. For example, for this polysiloxane emulsion prepared by ring-opening polymerization of D₄, the molecular structure of polysiloxane is mainly linear structure. In order to increase the diversity of polysiloxane structure, a small amount of alkoxy silane monomer could be added into the D₄ ring-opening emulsion polymerization system. Silicone resin dispersions were synthesized by emulsion polymerization of three silicone monomers: D₄, methyltrimethoxysilane (METMS) and methacryloyltrimethoxysilane (MATMS) in the presence of

dodecylbenzenesulphonic acid playing the role of both surfactant and polymerization catalyst.⁹

The hydrolytic condensation mechanism of alkylalkoxysilane (R_nSiX_{4-n}, n = 1, 2, 3; R is alkyl, X for alkoxy) shows that the siloxy is easy hydrolysis and condensation in the acidic or alkaline aqueous medium.¹⁰⁻¹² Pühringer¹³ synthesized polyalkylsiloxane emulsion using alkylalkoxysilane monomer. During the emulsion polymerization, the reaction rate of alkylalkoxysilane was controlled using just the right amount of water and organic solvent. It has a negative impact to the natural environment to use organic solvent. However, a few reports are focused on the synthesis of polyalkylsilsequioxane emulsion via the hydrolysis/condensation of sole alkyltrialkoxysilanes.

In this paper, the stable polyalkylsilsequioxane emulsion was prepared by batch method and semi-continuous method emulsion polymerization of methyl triethoxysilane (MTES) and n-propyltrimethoxysilane (PTMS). The influence of different feeding modes on emulsion particle size was discussed. The thermal properties and X-ray powder diffraction (XRD) of polyalkylsilsequioxane was also analyzed.

2. Experimental

2.1. Materials

Methyltriethoxysilane (MTES) (99.2%), and n-propyltrimethoxysilane (PTMS) (99.2%) were purchased from Jingzhou Jiangnan Fine Chemical Co., Ltd. (China). Sodium dodecylsulfate (SDS) (CP) was purchased from Shanghai Maxam Co., Ltd. (China). Sodium dodecylbenzenesulfonate (SDBS) (CP) was purchased from Nanjing Tianxi Fine Chemical Co., Ltd. (China). Polyoxyethylene octylphenol ether (OP-10) (CP) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water was used throughout experiments.

2.2 Synthesis polyalkylsilsequioxane emulsion by batch

All the monomers (mole ratio of PTMS:MTES=1:1, mass fraction of total system $w=30\%$) and emulsifiers (mass ratio of SDS: OP-10: SDBS=2:3:1) were mixed with 50mL water at room temperature for 30minutes, and then the temperature was increased to a certain temperature and kept there for 3-5h.

2.3 Synthesis polyalkylsilsequioxane emulsion by semi-continuous

All the emulsifiers (mass ratio of SDS: OP-10: SDBS=2:3:1) were mixed with 50mL water at room temperature for 30minutes, and then the temperature was increased to a certain temperature. After that, the monomers (mole ratio of PTMS: MTES=1:1, mass fraction of total system $w=30\%$) were added into the system using semi-continuous process (feed rate=2-3seconds per drop). The polymerization was continued for about 2-5h after the monomer dripping off.

2.4 Characterization

2.4.1 Latex solid content

The sample of polyalkylsilsequioxane emulsion obtained was dried in a vacuum oven at 105°C to stable weight. The latex solid content (ω) is calculated by the formula:¹⁴

$$\omega = (M_2 - M_1) / M_0 \times 100\%$$

Where, M_0 is the weight of polyalkylsilsequioxane emulsion without drying; M_1 is the weight of reagent bottle; M_2 is the total weights of reagent bottle and latex dried.

2.4.2 Stability (σ) of the polymerization process

After the emulsion polymerization process was finished, the precipitate was collected and then washed with water, dried in a vacuum oven to stable weight. The stability of the polymerization process is calculated by the formula:¹⁵

$$\sigma = W_1 / W_0 \times 100\%$$

Where, W_1 and W_0 are the weight of the precipitate and monomers, respectively; σ is the gel ratio.

2.4.3 Size and morphology of the emulsion particles

Particle size measurement was carried out by dynamic laser scattering (DLS) using Malvern Zetasizer (Nano-ZS90). This apparatus gave the Z-average diameter and polydispersity index (PDI). PDI ranged from 0 to 1. The lower the PDI value is, the more uniform the particles are.

The morphology and structure of hybrid core-shell particles were observed by transmission electron microscopy (TEM, Tecnai G20) and scanning electron microscopy (SEM, JSM6510LV), field emission scanning electron microscopy (FESEM, JSM7100F). SEM samples were gold-coated before analysis. TEM 200 mesh-sized Cu grids were supplied by Beijing Xinxing Braim Technology Co., Ltd (China).

2.4.4 Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was carried out with DIAMOND TG/DTA at a heating rate of 10 °C min⁻¹ from 30 °C to 800 °C in a nitrogen and air atmospheres, respectively (gas flow = 80 ml min⁻¹).

2.4.5 X-ray powder diffraction analysis

XRD was collected on a D/MAX-IIIC X-ray diffractometer (Akishima-shi, Tokyo, Japan). XRD pattern was taken from 2 to 80° (2θ value) with Cu Kα radiation ($\lambda=1.5406\text{Å}$), operating at 35 kV and 25 mA) at a scanning speed of 10°min⁻¹.

2.4.6 FT-IR

The FTIR spectra images were collected by using FTIR spectrometer (Nicolet iS50, Thermofisher).

3. Results and discussion

3.1 Preparation of polyalkylsilsequioxane emulsion

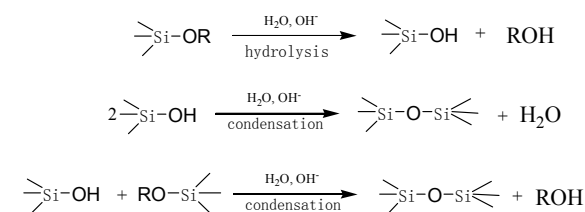


Fig. 1 The reaction mechanism of alkylalkoxysilane

The stable polyalkylsilsequioxane emulsion was prepared by batch method and semi-continuous method emulsion polymerization of methyl triethoxysilane (MTES) and n-propyltrimethoxysilane (PTMS). For these two methods, the initial reaction time was marked by starting adding monomers. The emulsion polymerization was alkaline because SDBS aqueous solution is alkaline.

The Fig. 2A is the particle size change curves of polyalkylsilsequioxane emulsion prepared by batch. It shows that under the condition of different reaction temperature,

particle size increased gradually, while PDI decreased as the extension of reaction time. After 120min, the particle size and PDI did not change significantly. The hydrolysis and condensation reactions could be happened between alkylalkoxysilane and water, alkylalkoxysilane and oligomers, even between alkylalkoxysilane themselves (Fig. 1).¹⁰⁻¹² and there was no specific reaction activity centre. As result, micellar nucleation, droplet nucleation and homogeneous nucleation were likely to exist. The Fig. 3A shows that the curve had two peaks when reaction time was 5min at 45°C, which one peak existed on the left side of the abscissa point 100nm, the other one existed on the right side of the abscissa point 1000nm. As the extension of reaction time, the peak existed on the right side of 1000nm was disappeared (reaction time 15min), the peak on the left side of the 100nm translated to the right. For the emulsion prepared by batch, a lot of oligomers were generated during the hydrolysis and condensation of alkylalkoxysilane in the initial reaction because of enough monomers in the system. Meanwhile, the latex particles were formed, and part of monomers were existed in the oil drops. The particle PDI was polydispersion in this stage. With the extension of reaction time, the polycondensation among oligomers in the system continued. Thus, the particle size increased and PDI gradually narrowed.

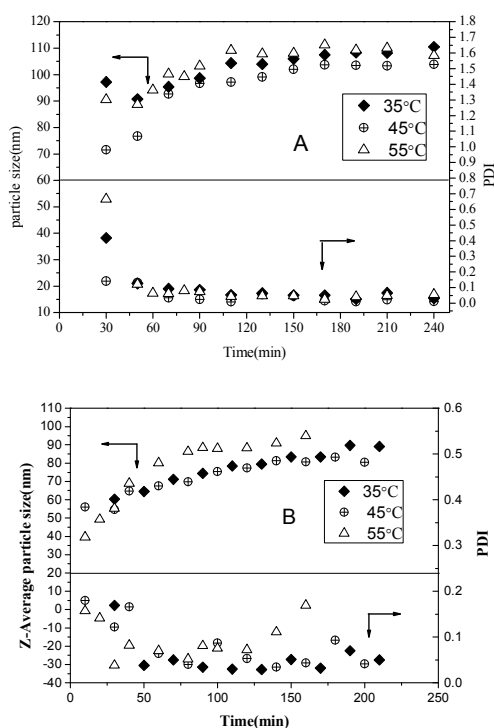


Fig. 2 Relationship between Z-Average particle size and time under different reaction temperature: (A) Batch method, (B) Semi-continuous method

The Fig. 2B is the particle size change curves of polyalkylsilsequioxane emulsion synthesized by semi-

continuous. Compared with polyalkylsilsequioxane emulsion synthesized by batch, particle size also increased gradually, and PDI decreased as the extension of reaction time, after 120min, the particle size and PDI did not change significantly. The difference between them is that the particle size was smaller and the PDI was larger. The Fig. 3B shows that the curve also had two peaks in the initial reaction at 45°C. Similar to the emulsion prepared by batch, in the semi-continuous emulsion polymerization, the peak on the right side of point 1000nm was gradually weak, the peak on the left side of point 100nm moved right, and the peak on the right side of point 1000nm was disappeared after 30min. Because the monomer was added using semi-continuous process (feed rate=2-3seconds per drop), the coexistence time of the two peak was longer than the former by batch. The monomer concentration in the initial stage of emulsion polymerization was low, and the latex particle size would be small. During the monomer dropping process, the particle size would increase. However, after all monomers added to the system, the change of latex particle size would be not apparent with the decrease of monomer concentration.

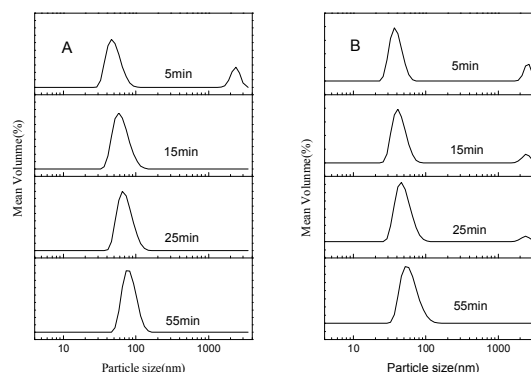


Fig. 3 Curves of particle size distribution with different reaction time: (A) Batch method, (B) Semi-continuous method

3.2 Stabilities of polyalkylsilsequioxane emulsion

In this paper, the mass fraction ratio of alkylsilsequioxane is 30%. However, the actual solid content of polyalkylsilsequioxane emulsion is lower because of volatile small molecule (H_2O , CH_3OH , CH_3CH_2OH) generated with alkylsilsequioxane hydrolysis condensation reaction. Table 1 shows that after the emulsion polymerization process was finished, the actual solid content of emulsion ω_1 was 15.6% (by batch) and 15.5% (by semi-continuous). After stored 12months, the ω_2 of polyalkylsilsequioxane emulsion (by batch) was 14.4%, while the ω_2 of polyalkylsilsequioxane emulsion (by semi-continuous) was 15.5%. Because latex particle size by batch was larger than that by semi-continuous, coagulation was more likely to happen. Thus, the actual solid content of emulsion by batch was smaller.

The gel ratio was 0.3% (by batch) and 0.2% (by semi-continuous). It suggests that the polymerization stabilities of polyalkylsilsequioxane emulsion prepared by batch and semi-

continuous were very good. On the other hand, the storage stability of emulsion was very good. After stored 6 months, the emulsion appearance had no obvious change, and there were a few physical crosslinking floccules at the bottom of the bottle. Nevertheless, the physical crosslinking floccules would be disappear after shaking.

Table 1 Stabilities of polyalkylsilsequioxane emulsion by different methods

Method	σ (%)	ω_1^a (%)	ω_2^b (%)	Storage stability
Batch	0.3	15.6	14.4	More than 6 months
Semi-continuous	0.2	15.5	15.5	More than 6 months

a: after agitation stopped

b: after stored 12 months

3.3 Morphology of the polyalkylsilsequioxane emulsion latex particles

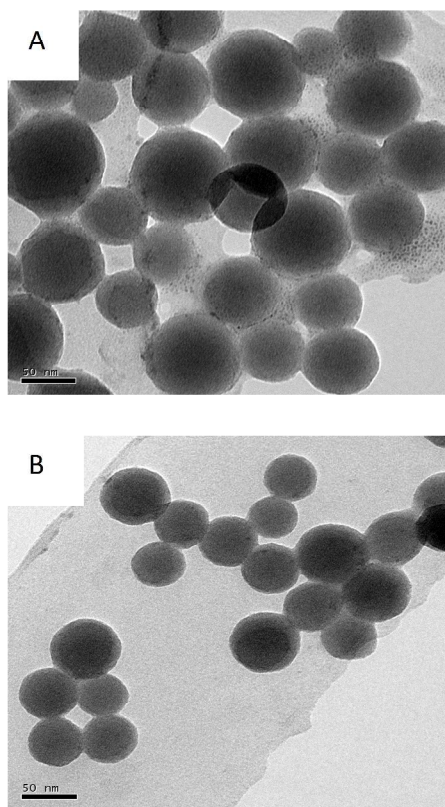


Fig. 4 TEM images of polyalkylsilsequioxane emulsion particles: (A) Batch method, (B) Semi-continuous method

Fig.4 shows the TEM photographs of polyalkylsilsequioxane emulsion particles with different feeding modes. It could be found that all latex particles were sphere shape, and there were core-shell structure particles.^[16] It was consistent with particle size measured with DLS that the latex particles sizes by batch

were larger. Besides, the polydispersibility of particle size by batch was more obvious. The SEM photographs of polyalkylsilsequioxane emulsion particles by semi-continuous provided further evidence that the latex particle morphology was spherical. (Fig.5)

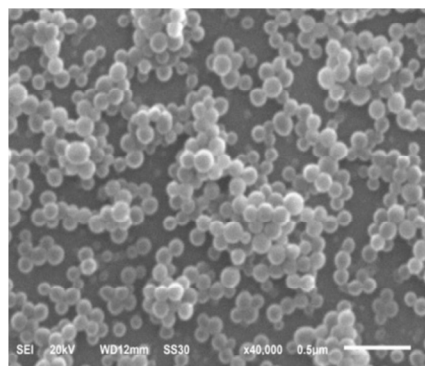


Fig. 5 SEM images of polyalkylsilsequioxane emulsion (Semi-continuous method)

3.4 XRD analysis

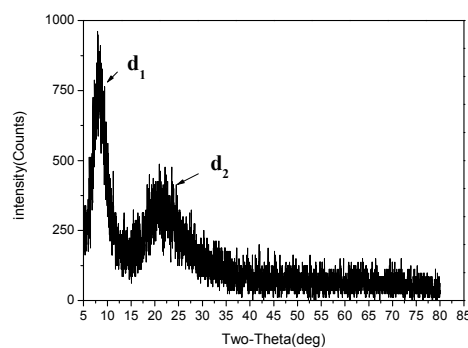


Fig. 6 XRD patterns of polyalkylsilsequioxane

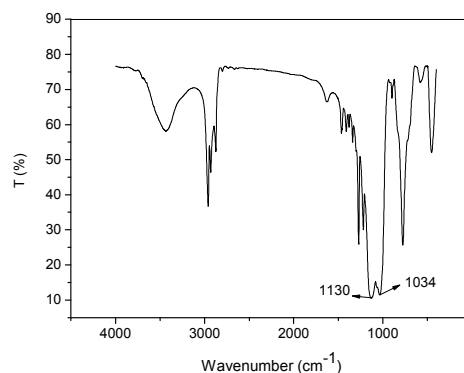


Fig. 7 FT-IR of polyalkylsilsequioxane

Based on the literature¹⁷⁻²⁰, Fig.6 shows the XRD pattern of polyalkylsilsequioxane, showing two distinct diffraction halos. The first halo (d_1), appearing at 8.123° , indicates an intramolecular chain-to-chain distance of approximately

1.088nm. The second diffuse halo (d_2), which covers a wider range of diffraction angles, appears at approximately 21.691° and indicates that average intermolecules was approximately 0.409nm. These peaks represent the ladder width and the ladder thickness.

FTIR spectra of polyalkylsilsequioxane are shown in Fig.7. Strong absorption bands attributed to asymmetric Si-O-Si stretching were observed at 1130 and 1034cm^{-1} . Hiroyasu Seki et al. [21] also reported two sharp Si-O-Si stretching absorption bands at 1130 and 1030cm^{-1} for ladder polymethylsilsequioxane (PMSQ).

These results indicate that the ordered and unordered polymer regions in the molecular chain of polyalkylsilsequioxane. Therefore, we deduced that there was the existence of some similar crystal structures in the molecular chain of polyalkylsilsequioxane prepared with alkyltrialkoxysilane.

3.5 TG analysis

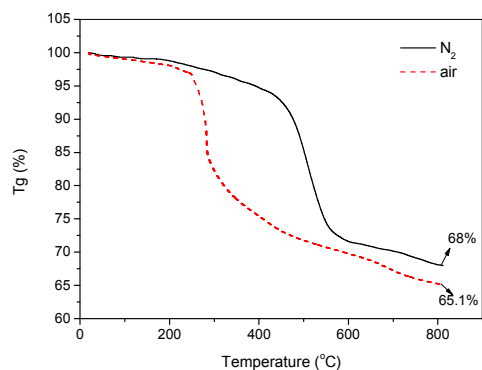


Fig. 8 TGA curves of polyalkylsilsequioxane

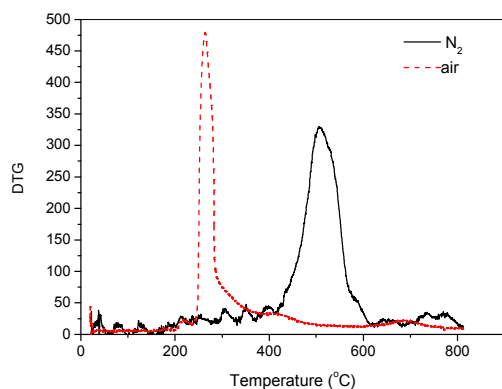


Fig. 9 DTG curves of polyalkylsilsequioxane

In polysiloxane polymer, the bond energy of four kinds of main covalent bonds Si-O, Si-C and C-C is 460.5KJ/mol , 304KJ/mol , 326KJ/mol , respectively.²²⁻²³ The degradation of the sample should start from initial cleavage of Si-C and C-C

bonds in the polymer. Fig.8 shows that there was one step loss mass process in the nitrogen atmosphere. Fig.9 shows that the weight loss rate was max at 515°C . It could be found that the loss mass step at 274°C was rapid in the air atmosphere (Fig.9). The residual mass in the nitrogen atmosphere (68%) was higher than the residual mass in the air atmosphere (65.1%). There was still carbon residue after thermal degradation of organic groups in the nitrogen atmosphere, while there was nothing in the air atmosphere. These results indicate that thermal properties of polysiloxane are good.

4. Conclusions

The stable polyalkylsilsequioxane emulsion was prepared using batch method and semi-continuous method emulsion polymerization respectively. Under the condition of different reaction temperature, particle size of polyalkylsilsequioxane emulsion of prepared by batch method and semi-continuous method increased gradually, and PDI decreased as the extension of reaction time. Finally, the particle size and PDI do not change significantly. The latex particle size by batch was larger than that by semi-continuous, while the PDI smaller. The actual solid content of emulsion ω_1 was 15.6% (by batch) and 15.5% (by semi-continuous). The polymerization stability and storage stability of emulsion prepared by both batch method and semi-continuous method are good. The morphologies of latex particle prepared by both methods were spherical and core-shell structure. The polyalkylsilsequioxane possessed an ordered structure. Thermal degradation weightlessness peaks of polymer in nitrogen atmosphere was at $450\text{-}600^\circ\text{C}$, while in air atmosphere was at $250\text{-}300^\circ\text{C}$ and the final residues were 68% in nitrogen, 65.1% in air atmosphere.

Notes and references

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