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Study on Acrylic Emulsion with Core-shell Structure Containing High Hydroxyl Content

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Using butyl acrylate, styrene, hydroxylethyl methacrylate and acrylic acid as comonomers, emulsions containing high hydroxyl content and having core-shell structure were synthesized from semi-continuous seed emulsion polymerization methods. Emulsifier types and levels, reaction temperature, core composite, weight percent of core on stability of the emulsion polymerizations were investigated. It was found that when mixed emulsifiers SDS/OP were used, at a level of 1%, and a ratio of SDS/OP of 4/6, the polymerization process had lower coagulum. Compared with emulsion without core-shell structure, when the hydrophilic monomer was not used in core composite, coagulum had decreased greatly and the amount of emulsifier may be reduced.

Keywords synthesis, acrylate emulsion, hydroxyl monomer, core-shell structure

Introduction

Core-shell polymers are structured composite particles consisting of two different polymers: one forms the core and the other the shell. These particles are very useful in a broad range of applications since they always exhibit improved physical and chemical properties. In recent years, core-shell emulsion has established its position in the adhesive and paint industry, the structure and morphology of core-shell emulsion has great influence on its property and application. Many studies focused on preparation (1–5), mechanism (6), properties (7–9), morphology (10, 11) and surfactants (12) of the emulsion with core-shell structure, but none has studied the core-shell emulsion with a high hydroxyl content. We have studied the emulsion containing high hydroxyl content without core-shell structure (13), since these emulsions may be used as hydroxyl component in a two-component waterborne coating as the replacement of traditional solvent-based hydroxyl component (14, 15). In order to make the hydroxyl groups distribute at the surface of the particle and not in the interior of the particles, it is necessary to add the hydroxyl monomer in the second polymerization stage, that means the prepared emulsion has different composite in core and shell. This paper deals with the emulsion containing high hydroxyl content with core-shell structure.

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Experimental

Materials

Styrene (ST) and butyl acrylate (BA) were distilled under reduced pressure before use. All the other materials were used as received, including hydroxylethyl methacrylate (HEMA) and acrylic acid (AA) monomers. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS) and sodium hydrogen carbonate ($NaHCO_3$) were used as initiator and buffer, respectively. Ammonia was used as the neutralization agent. The surfactants used were sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate (SDBS), nonylphenol polyethylene oxide ether (NP) and p-octyl polyethylene glycol phenyl ether (OP). Distilled water was used in all the experiments.

Emulsions Preparation

Polymerizations were carried out in a 250 mL glass reactor fitted with a reflux condenser, stainless-steel stirrer, nitrogen gas inlet, thermometer and funnels. The semi-continuous emulsion polymerizations were carried out using the recipes given in Table 1 (otherwise indicated). The glass transition temperature of the emulsion polymer was designed as 7°C (calculated according to the Fox equation) in all the experiments. The solids content of the emulsion was designed as 40% by wt and the initiator (APS) was kept at 5%, based on the total weight or amount of monomers used. Surfactant types, levels and ratio were variable.

The initial charge in the reactor was water, buffer and mixed surfactants. The feed was divided into three streams. The first was a solution of initiator, and the other two were a mixture of core monomers and shell monomers, respectively. When the first charge was heated to 75°C (otherwise indicated) and the reaction degassed with nitrogen gas for 20 min, the first stream was started by a dropwise addition and a core monomer mixture was added at the same time. After about 30 min, the system had an even bluish color, the shell monomer mixture was added dropwise in 2 h, and finished about the same time as the first stream. The system was kept at 75°C for an additional 2 h, after that, the temperature was reduced to 50°C, neutralized with $NH_3 \cdot H_2O$ to $pH = 7 \sim 8$, and

Table 1

Recipe used for the emulsion polymerization with core-shell structure

			Stream 2	
Reactants	Initial charge (g)	Stream 1 (g)	Core (g)	Shell (g)
Distilled water	80	9		
SDS/OP (1/1)	0.6			
$NaHCO_3$	0.2			
APS		0.3		
BA			1	25.2
ST			2	18.8
HEMA				12.0
AA				1.0

filtered with a 100 mesh filter. The procedure produced emulsions containing a high hydroxyl content with a core-shell structure, which means that the core and the shell had a different composite.

Characterization

The coagulum retained was collected together with that deposited on the reactor walls, agitator and thermometer. The dry weight of these coagulum related to the total monomer was defined as the coagulum percentage.

The particle size of the latex was measured by light scattering methods (16–18). The absorption valued emulsions diluted to 1.6×10^{-4} mol/L and 3.2×10^{-4} mol/L were measured at wavelengths of 370 nm, 430 nm, 500 nm, and 650 nm, using a U3400 spectrum (Hitachi, Japan) instrument, and subsequent calculation of the mean particle size was summarized as follows:

$$d_p = \alpha \frac{\lambda_m}{\pi} \tag{1}$$

$$\lambda_m = \frac{\lambda_0}{[1.7521 + (8.11 \times 10^{-11}/\lambda_0^2)]^{1/2}} \tag{2}$$

where λ_m was the wavelength of light in medium, λ_0 was the wavelength of light in vacuum which roughly equals to the wavelength of incident light, d_p was the particle size of emulsion, α was a parameter. When K is the scatter parameter, it has relationship with α as:

$$\frac{K}{\alpha = 0.4884\rho\lambda_m(E/C)C \rightarrow 0} \tag{3}$$

where E was absorption value of diluted emulsion at concentration C (g/cm^3), ρ was the density of emulsion particle. From Equation (3), the K/α may be obtained. After α was looked up in the book table (19), the d_p was calculated with Equation (1).

Glass transition temperature of the emulsion polymer was calculated from the Fox equation:

$$\frac{100}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + \cdots$$

where T_g was the glass transition temperature of emulsion copolymer, w_1, w_2, w_3 were the weight percent of each monomer, T_{g1}, T_{g2}, T_{g3} were T_g of each homo polymer with high molecular weight.

Viscosities were measured with a NDJ-8S digital viscometer (Shanghai Balance Factory, China), at 25°C, using a No. 2 rotor at a rotating velocity of 60 rpm.

Results and Discussion

Emulsifier

Emulsifiers are very important in emulsion polymerization, and it is very common to use mixed emulsifiers in industrial production, where anionic emulsifier provides chemical stability for emulsion particles and nonionic emulsifiers provides steric stability. As stated in our paper (13), we could not obtain a stable pre-emulsified solution, due to the hydrophilicity of HEMA and AA, in spite of emulsifier types and level or ratios of mixed anionic/nonionic surfactants used. The result of a mixed emulsifier on the influence of emulsion polymerization is shown in Figure 1.

Figure 1 shows that the mixed SDS/OP emulsifier system had a minimum coagulum content, whereas the coagulum content reached 2.8% for the SDBS/NP emulsifier system. The hydrophile-lypophile balance value (HLB) of the emulsifier also accounts for this. The HLB of the emulsifier SDS, SDBS, OP and NP were 40, 30, 13.3 and 12.8, respectively. According to weight percent of each emulsifier, the HLB of the mixed emulsifier SDS/OP, SDS/NP, SDBS/OP,SDBS/NP was 24.0, 23.7, 17, 16.7, respectively. The HLB of the mixed SDS/OP emulsifiers was higher than that of other mixed emulsifiers, close to the HLB needed for the emulsion polymerization. Thus, the SDS/OP emulsifier system was suitable for these systems, with a large amount of hydrophilic monomers.

Compared with a previous paper (13), it is very clear that the coagulum had decreased greatly. This is because the more hydrophilic monomer HEMA and AA were added in a later polymerization stage, that is in the shell polymerization stage and not in the core

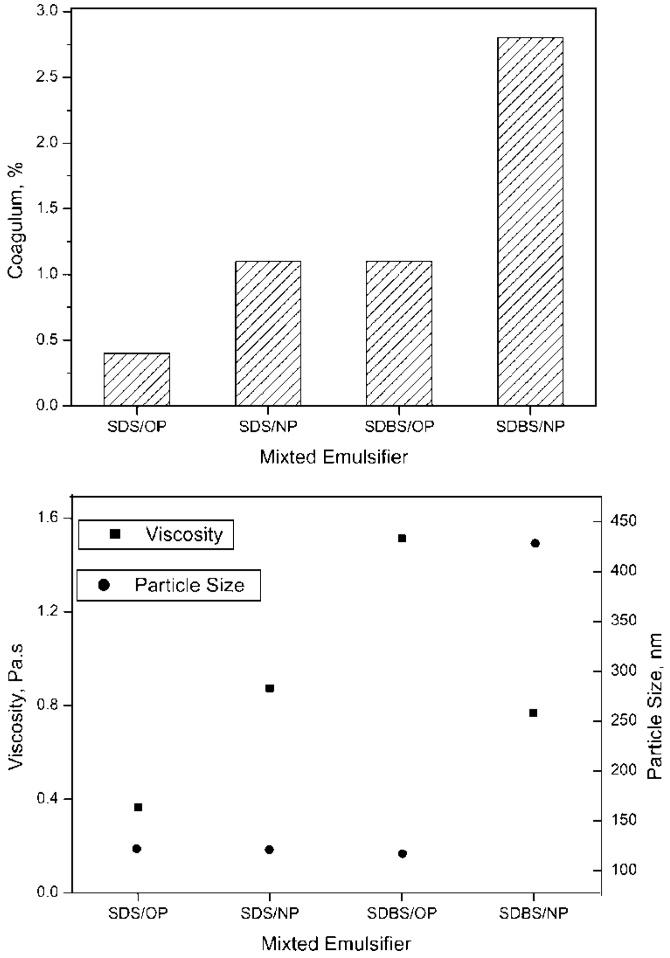

Figure 1. Effect of mixed emulsifier on the stability of polymerization (anionic/nonionic: 4/6. Emulsifier wt%: 2).

polymerization stage. It did not cause a coagulating in water phase in the early polymerization stage.

It is also shown that the emulsion prepared with SDBS/OP emulsifiers had the highest viscosity and the emulsion prepared with SDBS/NP emulsifiers had the largest particle size. From these works, we may believe that SDS/OP is more suitable to this system.

Emulsifier Level

Based on the above experiment, when the SDS and OP mixed emulsifier was used, the effect of levels of this mixed emulsifier on the polymerization process with core-shell structure was tested. The result is listed in Figure 2.

Figure 2 shows that as the level of mixed emulsifier is increased from 0.5% to 2%, the coagulum decreased from 3.4% to 0.4%. As known, more micelles were formed as the

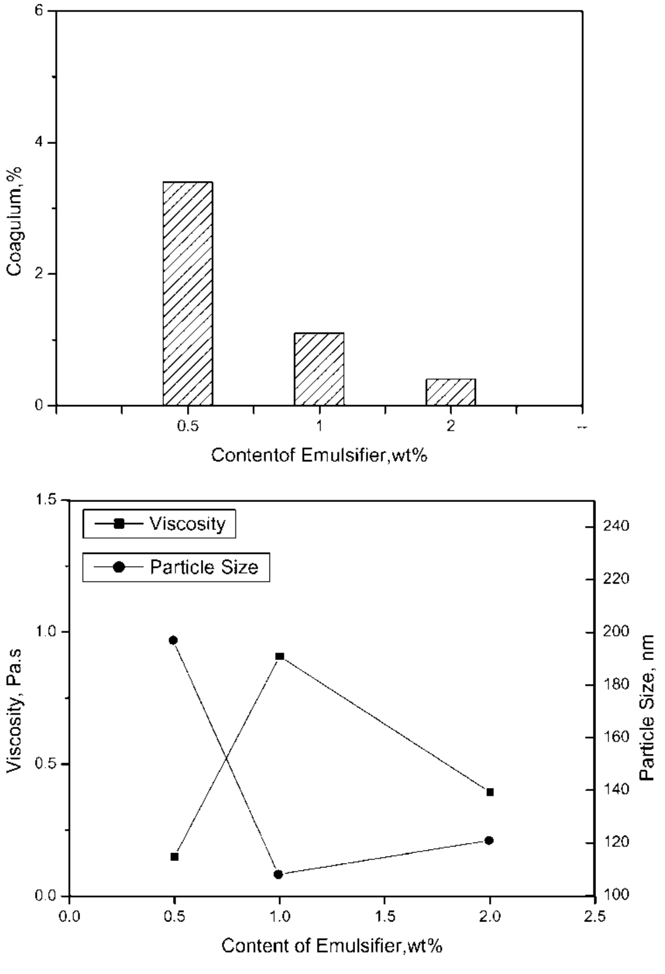

Figure 2. Effect of levels of emulsifiers on the stability of polymerization. (Emulsifier: SDS/OP, anionic/nonionic: 4/6,)

level of emulsifier increased, that is, more active centers were produced. The possibility of agglutination between particles was reduced greatly, so the coagulum decreased and the particle size also decreased, and that led to viscosity change. When the emulsifier level was 0.5%, more coagulum may be produced because the surface of the particle might not be completely covered with a emulsifier molecule. Compared with the emulsion without core-shell structure, the coagulum also decreased, and a small amount of emulsifier may be used in this system. From these experiments, the best level of emulsifier for this system was 1.0%.

Ratio of Anionic/Nonionic Emulsifier

When SDS/OP was used as mixed emulsifiers, and the level was kept at 2%, the weight ratio of SDS to OP had some influence on the polymerization process. Figure 3 showed

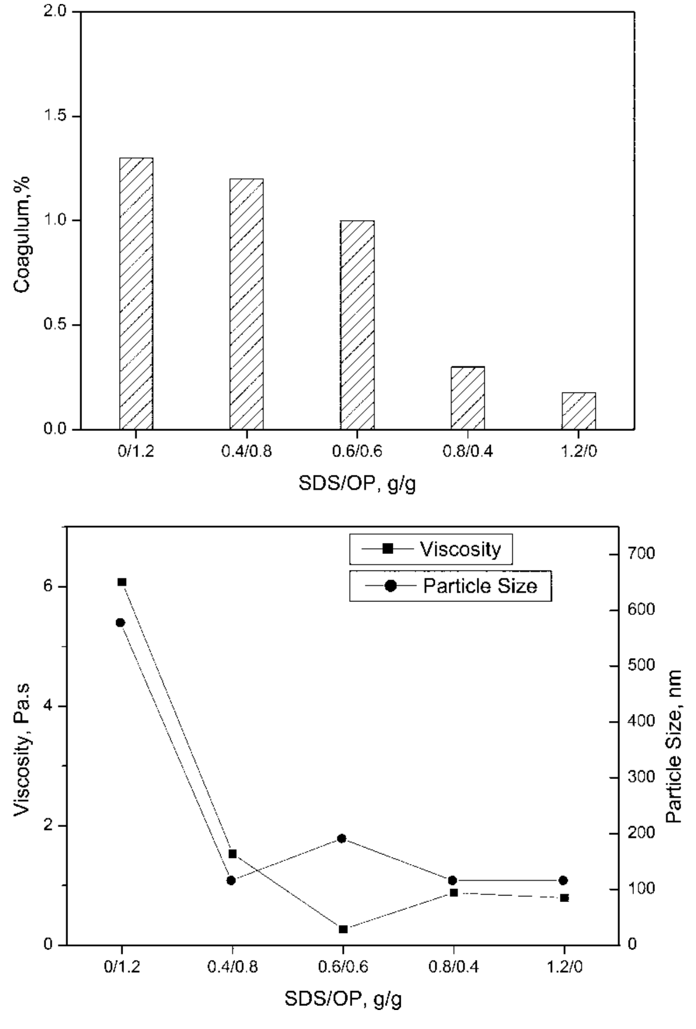

Figure 3. Effect of ratio of anionic/nonionic emulsifier on the stability of polymerization. (Emulsifier: SDS/OP.)

when the weight ratio of SLS/OP varied from 0/1.2 to 1.2/0, the coagulum decreased gradually. As the weight of SDS increased, the HLB of the system also increased, coming closer to the HLB needed in the emulsion polymerization process. Thus, the increased SDS/OP ratio had a better emulsifying result for emulsion particles. The OP emulsifier had a very poor emulsifying effect on emulsion polymerization when it was used solely. In this case, the emulsion had larger viscosity and particle size compared with that of mixed emulsifiers, which had almost the same viscosity and particle size.

Reaction Temperature

Figure 4 showed that as the reaction temperature rose from 65°C to 85°C, the amount of coagulum decreased slightly, which was contrary to the emulsion without core-shell structure. In this situation, the monomer conversion was complete and irrelevant to

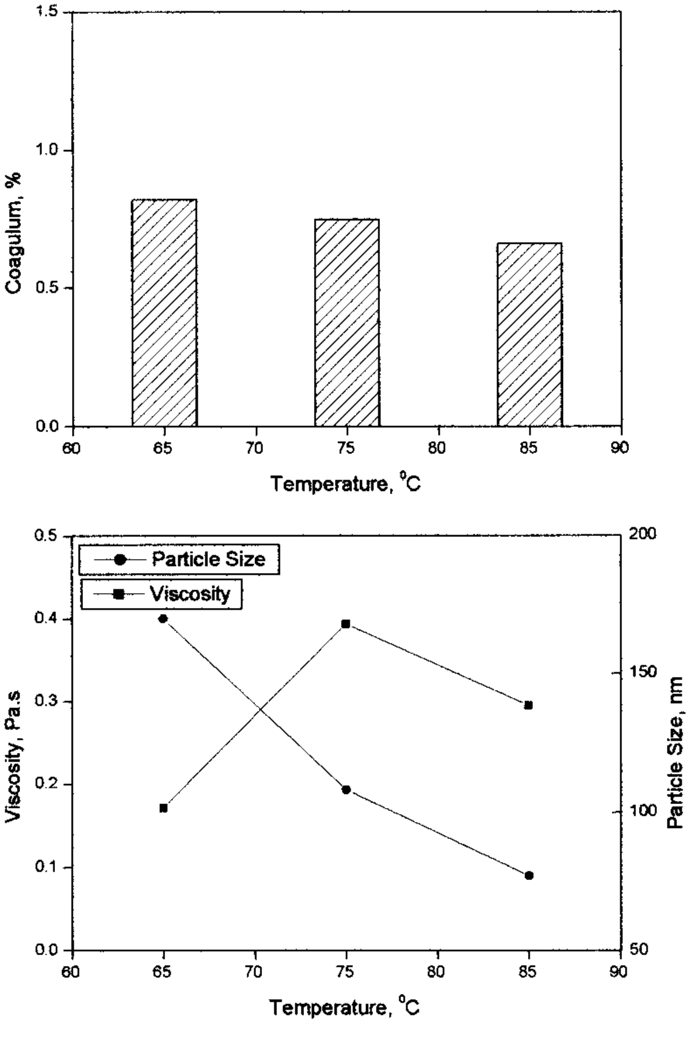

Figure 4. Effect of reaction temperature on the stability of polymerization. (Emulsifier: SDS/OP = 4/6.)

temperature. This may be due to the hydrophobic core, which was composed of ST and BA, and without AA and HEMA, it decreased the trend of coagulation as the reaction temperature rose. The thinned hydration layer at the particle surface at higher temperature accounted for the change of particle size as the reaction temperature increased.

Variation of Core Composite

When the total amount of ST and BA was kept at constant, respectively, and the core weight percent was kept at 5%, variation of core composite on the effect of emulsion polymerization is shown in Figure 5. It showed that the coagulum increased a little as the increase of weight ratio of BA/ST, the particle size of the emulsion had a very little increase when the amount of BA was below 2, and had a large increase when the amount of BA was 3. The reason is that BA monomer is more hydrophilic than ST

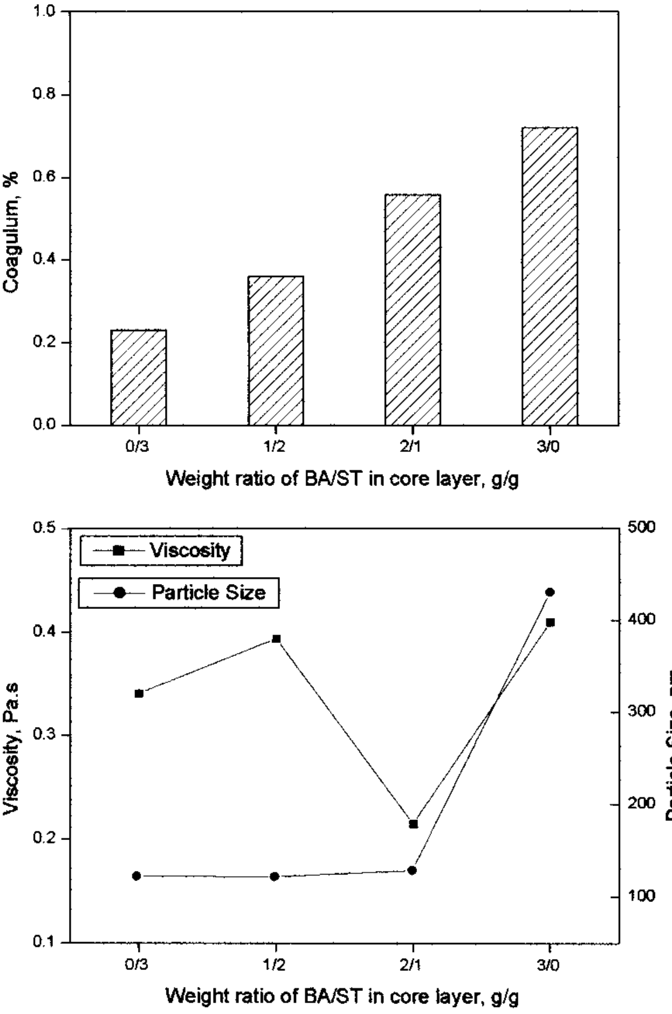

Figure 5. Effect of variation of core composite on the stability of polymerization. (Emulsifier: SDS/OP = 4/6.)

monomer, so a larger amount of BA was dissolved in water when the amount of BA was increased. The monomer dissolved in water polymerized in the water phase by free radical from APS, and formed a oligomer and finally partially settled down. This led to the increase of coagulum and particle size. Furthermore, thickening of the hydration layer on the particle surface also made the particle size increase. From this fact, we can assume that the emulsion with a soft core and hard shell structure has a larger particle size.

Core Weight Percent

When the total amount of ST and BA was kept at constant, respectively, and BA/ST weight ratio in core was kept at 2/1, a variation of core weight percent on the effect of emulsion polymerization was shown in Figure 6. It showed that when the amount of seed monomer (core layer) increased, the coagulum and particle size of the core-shell

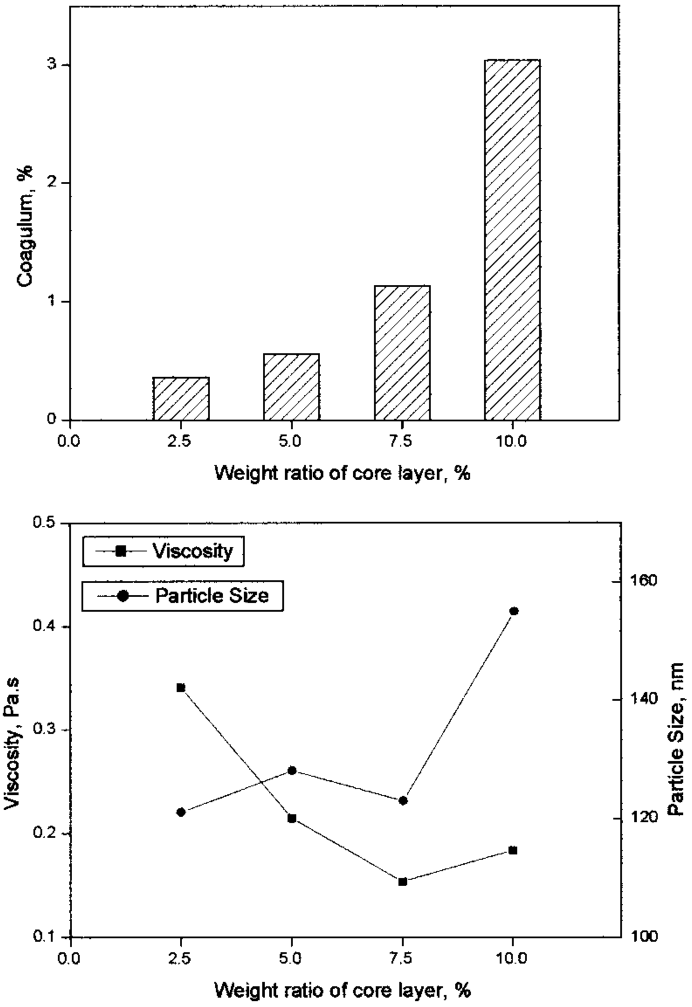

Figure 6. Effect of weight ratio of core on the stability of polymerization. (Emulsifier: SDS/OP = 4/6.)

emulsion increased, but the viscosity of the emulsion decreased. A higher level of seed monomer led to larger latex particle. The reason is that when the core amount was increased, as it was added all at once and not dropwise, much of the monomer was accumulated and formed monomer droplets which led to two results: on one hand, the possibility of monomer droplets forming a nucleus increased, which may produce a larger particle size and make the particle coagulate; on the other hand, more molecular emulsifier was absorbed at the surface of the particle in order to keep these droplets stable. These decreased the number of micelle and also the emulsion particle, thus increasing the particle size of the core-shell emulsion.

Conclusions

The emulsion with a core-shell structure containing high hydroxyl content was prepared and the polymerization process was investigated according to the emulsifier type, level and ratio, reaction temperature and core-shell composite. At same time, these were compared with the same composite, but without a core-shell structure. It showed that the coagulum, particle size, and viscosity had almost the same tendency as that without core-shell structure, but smaller coagulum. From these, we may prepare the emulsion containing a high hydroxyl content with a smaller level of emulsifier and without a hydrophilic monomer in core composite.

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