

Influence of emulsifiers on particle size and particle size distribution of PVC latex synthesized by miniemulsion polymerization

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Abstract—We synthesized poly(vinyl chloride) (PVC) latexes via miniemulsion polymerization using a mixture of cetyl alcohol (CA) and sodium lauryl sulfate (SLS). A vinyl chloride miniemulsion is easily prepared by conventional mechanical stirring. Experimental design methods were applied to investigate the effects of composition and polymerization conditions on average particle size (APS) and particle size distribution (PSD) of the latexes produced. The APS of the latexes produced ranged from 0.4–0.7 μm . When the APS of the latex produced was above 0.7 μm , the resulting latex was highly unstable. The emulsifier ratio (CA/SLS) was the most prominent factor influencing APS and PSD.

Key words: Polyvinyl Chloride, Latex, Miniemulsion, Polymerization, Experimental Design

INTRODUCTION

Awareness of polyvinyl chloride (PVC) dates to the late 19th century, even though it was not commercially produced until the 1920s. PVC is the second most consumed plastic material worldwide, after polyethylene, with more than 29 million tons produced per year (data from 2003) due to its broad applications [1-3]. PVC latex represents 12% of total PVC production and is used to produce leather, flooring, wallpaper, under body coatings for automobiles, sealants and coated fabrics [4]. Although PVC latex plays a pivotal role in the PVC industry, little information about PVC latex synthesis is available in the literature [5-7].

Almost all commercial PVC latexes are synthesized by emulsion polymerization. However, PVC latex produced by emulsion polymerization has a sharp particle size distribution (PSD) with a maximum particle size of around 0.3 μm . Small monodispersed particle sizes result in a rapid increase of latex viscosity as solid content increases [8-10]. To decrease the viscosity of latex, it is necessary to increase particle size and the PSD. Seeded-emulsion polymerization is a useful technique to increase particle size and particle size distribution, but it entails a complicated multistage process. Microsuspension polymerization is another method used to produce latex that yields large particle sizes (1-20 μm) and broad PSDs. However, this method requires the use of a high intensity homogenizer during the preparation step, which results in high capital and energy costs [4].

During the last two decades, miniemulsion polymerization has emerged as a promising method for the synthesis of high solid content latex. The advantages of miniemulsion polymerization include the large particle sizes (0.3-1 μm) with multi-dispersed particles that are produced, and the versatility of the main particle formation mechanism, which is droplet nucleation. Droplet nucleation allows each droplet to be regarded as an individual batch reactor, and polymer-

ization proceeds as in a hypothetical bulk state resulting in polymer particles that are one-to-one copies of monomer droplets [11]. Therefore, miniemulsion polymerization can be applied not only for homogeneous polymerization but also other purposes, such as catalytic polymerization in aqueous media, encapsulation of an inorganic solid, preparation of hybrid polymer particles, implementation of anionic and step polymerization in aqueous dispersed media and process intensification by using continuous reactors [12]. A miniemulsion is usually created by using a high intensity homogenizer, high pressure homogenizer (microfluidizer) or sonifier [13-15], but miniemulsion can also be achieved by a conventional stirrer when using a mixture of ionic surfactants and fatty alcohols [16-19]. According to El-Aasser [19], when a fatty alcohol and an ionic surfactant mixture are dissolved in water, a rod-like crystalline structure is formed and the miniemulsification process follows as the result of three steps: (i) the solubilization of the monomer in the rod-like particles, yielding a very small number of relatively large droplets of 500 nm in diameter; (ii) a breakdown of these large droplets to a much greater number of very small droplets of about 130 nm in diameter; and (iii) the growth of droplet sizes to approximately 350 nm in diameter, primarily by diffusion. The preparation of miniemulsions with conventional stirrers is suitable for industrial applications. However, one disadvantage of this method that it is difficult to adjust the droplet size of the miniemulsion.

In the present report, the PVC latex was synthesized via miniemulsion polymerization by using a mixture including an anionic surfactant and fatty alcohol. The purpose of this study is to examine the effects of miniemulsion polymerization conditions on polymer particle sizes and distributions for a better understanding of how to obtain desirable particle sizes and PSDs during production of PVC latex.

EXPERIMENTAL

1. Materials

Polymer grade vinyl chloride monomer (VCM), azobisisobuty-

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ronitrile (AIBN) and azobisisovaleronitrile (ABVN) were provided by Hanwha Chemical. Sodium lauryl sulfate (SLS) and cetyl alcohol (CA) were purchased from Sigma-Aldrich. All reagents were used as received without further purification.

2. Polymerization Procedure and the Characterization of Polymer

PVC miniemulsion polymerization was carried out in a 1-liter stainless steel reactor with a four-blade mechanical stirrer. The water jacket was designed to adjust temperature (± 0.5 °C) within the reactor through water circulation. The temperature, pressure and agitation speed of the stirrer were monitored and controlled by a computer program. SLS and CA were dissolved in 147 ml of water and aged at 80 °C over 45 minutes. A predetermined amount of emulsifier solution and initiators (AIBN and ABVN with 2 : 1 in weight ratio) were subsequently charged into the reactor. The reactor was vacuumed for 10 minutes to completely remove all oxygen from the reactor. The agitation speed was set at 350 rpm and 120 g of VCM was slowly added into the reactor and stirred for 6 minutes. Then the agitation speed was reduced to 150 rpm and the temperature was increased to 58.5 °C to commence polymerization. The polymerization was continued for 4-6 hrs and stopped when the pressure of the reactor began to decrease.

The particle morphologies of the PVC produced were observed with field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500FR). The average particle size (APS) and particle size distribution (PSD) of the PVC latexes were measured by the dynamic light scattering (DLS) method (Mastersizer 2000, Malvern). The particle size (PS) and particle size distribution (PSD) in this work are defined as follows:

$$PS = D(4, 3)$$

$$PSD = \text{SPAN} = (D(v, 0.9) - D(v, 0.1)) / D(v, 0.5)$$

Where: $D(4, 3)$ is the volume mean diameter—the mean of the diameters of the spheres having the same volume as real particles.

$D(v, 0.1)$ is the ten percent cut-off point as ten percent of the dis-

tribution is below this point.

$D(v, 0.5)$ is the volume median diameter. Fifty percent of the distribution is above and fifty percent is below this value - it divides the distribution exactly in half.

$D(v, 0.9)$ is the ninety percent cut-off point as ninety percent of the distribution is below this point.

RESULTS AND DISCUSSION

1. Morphology of PVC Particles

Fig. 1 shows an FE-SEM image of PVC particles after drying the produced latex. The APS of the PVC particles in the figure was 0.79 μm and the PSD was 1.09 (Table 1, Run 15). Spherical PVC particles were observed and their sizes were distributed from tens of nm to more than 1 μm . In general, larger particle sizes and broader

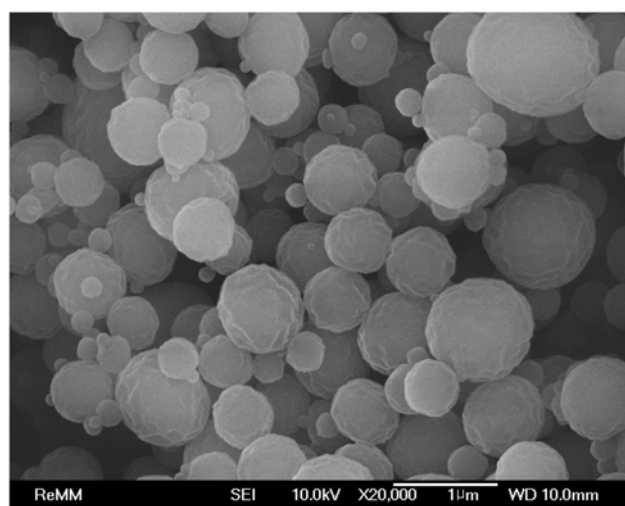


Fig. 1. FE-SEM image of PVC particles (SLS: 0.45 wt%, CA: 0.7 wt%, Initiators: 0.054 wt%, APS: 1.11 μm , PSD: 1.64).

Table 1. Box-Behnken experimental design for three factors: SLS, CA and initiators*

No.	Coded factors			Actual factors (wt%)			Responses	
	X_1	X_2	X_3	SLS	CA	Initiators	APS (μm)	PSD
1	-1	-1	0	0.45	0.7	0.054	1.11	1.64
2	1	-1	0	1.05	0.7	0.054	0.67	1.03
3	-1	1	0	0.45	1.3	0.054	0.81	1.56
4	1	1	0	1.05	1.3	0.054	0.60	1.11
5	-1	0	-1	0.45	1.0	0.034	1.15	2.19
6	1	0	-1	1.05	1.0	0.034	0.85	1.84
7	-1	0	1	0.45	1.0	0.074	0.85	1.78
8	1	0	1	1.05	1.0	0.074	0.65	1.09
9	0	-1	-1	0.75	0.7	0.034	1.01	1.98
10	0	1	-1	0.75	1.3	0.034	0.71	0.99
11	0	-1	1	0.75	0.7	0.074	0.77	1.32
12	0	1	1	0.75	1.3	0.074	0.61	1.12
13	0	0	0	0.75	1.0	0.054	0.78	1.05
14	0	0	0	0.75	1.0	0.054	0.76	1.33
15	0	0	0	0.75	1.0	0.054	0.74	1.09

*Concentrations of SLS, CA and initiators are based on vinyl chloride monomer

PSDs create latex with lower viscosity, even when the latex produced has a higher solid content [9].

2. Effects of Emulsifiers and Initiator Concentrations on APS and PSD

A Box-Behnken experimental design for three factors was applied to investigate the influences of SLS, CA and initiator concentration on the APS and PSD of PVC latex [20]. The mathematical models that correlate the concentration of SLS, CA and initiators with the particle size and PSD were built from the data in Table 1. As shown in Eqs. (1)-(4), their relationships were determined as the following second-order polynomial equations.

In terms of the coded factors for APS and PSD:

$$\text{APS} = 0.74 - 0.14X_1 - 0.10X_2 - 0.11X_3 + 0.058X_1X_2 + 0.071X_1^2 + 0.049X_2^2 \quad (1)$$

$$\text{PSD} = 1.10 - 0.26X_1 - 0.15X_2 - 0.21X_3 + 0.20X_2X_3 + 0.28X_1^2 + 0.3X_2^2 \quad (2)$$

In terms of the actual factors for APS and PSD:

$$\text{APS} = 3.01 - 2.30[\text{SLS}] - 0.825[\text{CA}] - 18.39[\text{initiators}] + 0.639[\text{SLS}][\text{CA}] + 0.791[\text{SLS}]^2 + 121.63[\text{initiators}]^2 \quad (3)$$

$$\text{PSD} = 8.55 - 5.59[\text{SLS}] - 2.28[\text{CA}] - 124.1[\text{initiators}] + 32.96[\text{initiators}] + 3.141[\text{SLS}]^2 + 745.5[\text{initiators}]^2 \quad (4)$$

The regression coefficient (R^2) of Eq. (1) or (3) for APS was 0.953, indicating that the equation was acceptable to express the experimental data. On the other hand, the R^2 value of Eq. (3) or (4) for the PSD was 0.842, implying that the PSDs were more sensitive to the experimental conditions. As shown in Table 1, PSDs at the center point fluctuated in comparison with the particle sizes (Run 13-15). According to Eq. (1), the APS at the center point was $0.74 \mu\text{m}$ ($X_1 = X_2 = 0$). Based on the experimental design, particle sizes of the latex are in the range of 0.6 - $1.15 \mu\text{m}$, whereas the region 0.05 - $0.5 \mu\text{m}$ is observed for droplet sizes of miniemulsions [11,17]. As droplet nucleation is the main particle formation mechanism [11,12], the APS of latex is significantly larger than the droplet sizes of the miniemulsion, demonstrating the degradation of miniemulsion during polymerization. Thus, the particle size of latex ultimately depends on the stability of the miniemulsion.

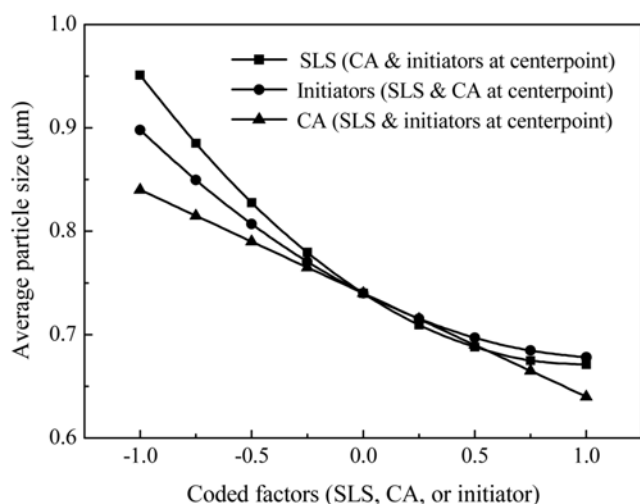


Fig. 2. The effects of SLS, CA and initiator on the APS of PVC latex produced.

The effect of SLS, CA and initiator concentration on APS is shown in Fig. 2, which was built from Eq. (1). The APS was inversely proportional to the concentration of SLS; CA and initiators and SLS showed the strongest influence on particle size. However, the effect of SLS was slightly higher than that of CA and the initiators, especially at high concentration. If the concentration of SLS and CA was increased, APS decreased due to the formation of small VCM droplets. Increasing the concentration of initiators (AIBN and ABVN) also decreased APS by shortening the reaction time. The experiments with $0.034 \text{ wt}\%$ of initiators proceeded for 6 hours, but when the concentration of initiators was raised to $0.074 \text{ wt}\%$, the reaction was finished within 4 hours. Because of the thermodynamic instability of the miniemulsion, like other kinds of emulsions, it becomes degraded with time, especially at high temperature. It is known that the degradation occurs through the coagulation of two or more droplets to form bigger polymer particles, leading to an incremental increase of APS [21].

APS can be increased by reducing each the SLS, CA, or initiator concentration, respectively, or by simultaneous reductions of all three factors. Decreasing the concentration of the initiator will increase reaction time, leading to increases in cost. Therefore, it is desirable to maintain initiators at a high concentration. Alternatively, decreases in SLS and CA concentrations will result in weakened latex stability because SLS and CA play roles not only as emulsifiers but also as latex stabilizers. Therefore, the determination of the optimum ratio of SLS and CA is very important.

The effects of SLS, CA and initiators on PSD were examined as shown in Fig. 3. The results were derived from Eq. (2) and similar to APS, PSDs were also inversely proportional to the concentration of SLS, CA and initiators. Typically, SLS and the initiators had almost the same effect on the PSD, as the SLS led to stronger effects at low concentrations while the initiators exerted stronger effects at high concentrations. However, the difference between SLS and initiators is not significant.

3. Effects of the CA/SLS Molar Ratio and the Total SLS and CA Concentration on APS and PSD

According to El-Aasser [19], CA/SLS plays an important role

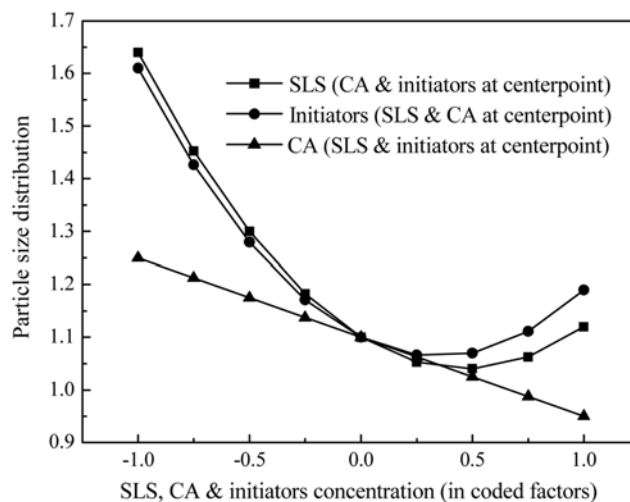


Fig. 3. The effects of SLS, CA and initiator on the PSD of PVC latex produced.

Table 2. Central composite design for two factors with three center points

Standard order	Run order	Coded factors		Actual factors		Response	
		X_1^*	X_2^*	CA/SLS molar ratio	CA+SLS concentration	APS (μm)	PSD
1	5	-1	-1	1.29	1.65	0.62	1.025
2	3	1	-1	2.71	1.65	0.83	1.512
3	10	-1	1	1.29	2.36	0.52	0.8887
4	9	1	1	2.71	2.36	0.64	1.216
5	6	-1.41	0	1.00	2.00	0.55	0.932
6	11	1.41	0	3.00	2.00	0.75	1.526
7	4	0	-1.41	2.00	1.50	0.81	1.062
8	8	0	1.41	2.00	2.50	0.58	1.04
9	1	0	0	2.00	2.00	0.62	1.021
10	2	0	0	2.00	2.00	0.65	1.092
11	7	0	0	2.00	2.00	0.61	0.9981

* X_1 : CA/SLS molar ratio; X_2 : total SLS and CA concentration (wt%, based on VCM loading)

in the formation and stabilization of miniemulsion. The effects of CA/SLS on the stability of styrene miniemulsions at room temperature were investigated by the shelf-life and centrifugation method. El-Aasser found that the most stable miniemulsions are prepared with CA/SLS in a molar ratio of 3 : 1 and 2 : 1, and the stability of styrene miniemulsions decreases in the following order: 3 : 1 > 2 : 1 > 1 : 1 > 0.5 : 1 > 0 : 1 (fixed SLS concentration and varying CA concentration). The decrease of miniemulsion stability leads to an increase of droplet size and droplet size distribution and results in an increase of the particle size and the PSD of the latex.

To investigate the effects of the CA/SLS molar ratio (emulsifier ratio) and total CA and SLS concentration (emulsifier concentration) on the APS and the PSD of PVC latex, the central composite design (CCD) for two factors with three center-points is applied [20]. The experimental design and responses are shown in Table 2. The relationships between the two factors are expressed in terms of the following second-order polynomial equations:

$$\text{In terms of the coded factors for APS and PSD:} \\ \text{PS} = 0.63 + 0.077X_1 - 0.077X_2 - 0.022X_1X_2 + 0.0271X_2^2 \quad (5)$$

$$\text{PSD} = 1.05 + 0.21X_1 - 0.058X_2 + 0.098X_1^2 \quad (6)$$

$$\text{In terms of the actual factors for APS and PSD:} \\ \text{PS} = 1.36 + 0.286 * \text{emulsifier ratio} - 0.902 * \text{emulsifier conc.} \\ - 0.089 * \text{emulsifier ratio} * \text{emulsifier conc.} \\ + 0.216 * \text{emulsifier conc.}^2 \quad (7)$$

$$\text{PSD} = 1.57 - 0.483 * \text{emulsifier ratio} - 0.163 * \text{emulsifier conc.} \\ + 0.193 * \text{emulsifier ratio}^2 \quad (8)$$

Regression coefficients (R^2) were calculated to be about 0.98 and 0.93 for APS and PSD, respectively, which implies that the equations reasonably represented the experimental data. From the Eq. (5), one may clearly observe that the APS or particle size at the center-point is 0.63 μm . As shown in Fig. 4, the APS increased linearly with respect to the CA/SLS emulsifier ratio. The effect of the emulsifier ratio was stronger at lower SLS concentration and diminished when the SLS concentration was increased. When the CA/SLS molar ratio was 1 : 1, the difference of APSs between 2 wt% and 2.5 wt% of SLS concentration was insignificant. To determine the emulsi-

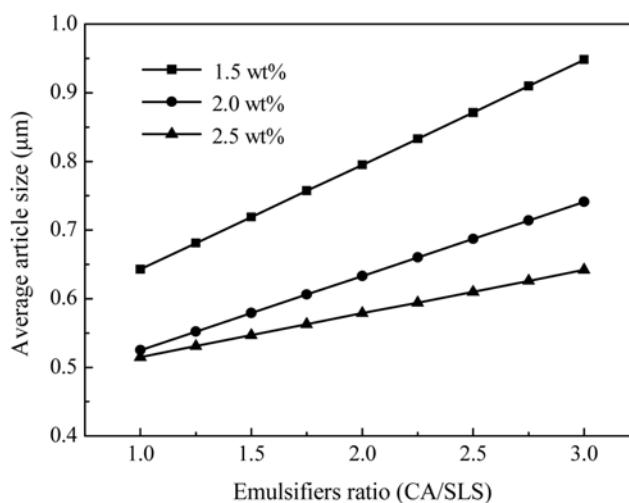


Fig. 4. The effect of the emulsifier ratio on the APS of PVC latex produced.

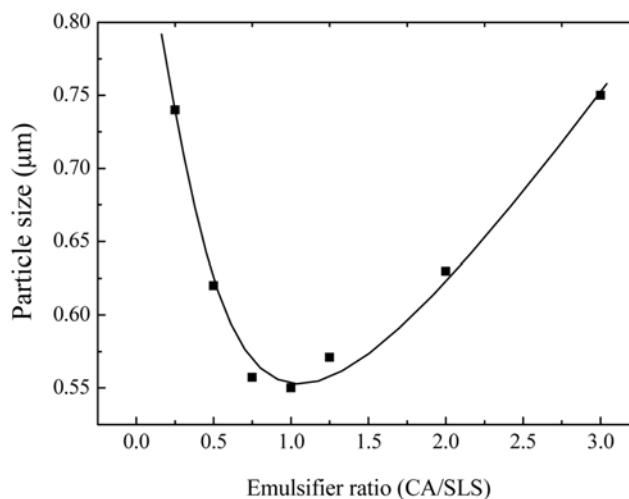


Fig. 5. The influence of the emulsifier ratio on the latex particle size (emulsifier concentration = 2 wt%).

fier ratio at which APS is minimized, the changes in particle size relating to the emulsifier ratios were further investigated. In Fig. 5, the minimum particle size was about $0.55\ \mu\text{m}$ when the CA/SLS ratio was in the range of 0.75-1.25, indicating that the latex was the most stable in this region. If the CA/SLS ratio was lower than 0.75, the particle size increased remarkably and the latexes became unstable. When the CA/SLS ratio was 0.25, the particle size increased to $0.74\ \mu\text{m}$ and the PSD reached 1.635, but the latex was very unstable as most of PVC particles were agglomerated and precipitated within 2 days.

As shown in Table 2, the PSD was remarkably influenced by CA/SLS. When the CA/SLS ratio was above 2.5, the PSDs of the produced latexes were over 1.2. One example of the broad PSD of PVC latex is shown in Fig. 6 (Table 2, Run 2). The particle size of latex was distributed continuously from $0.1\ \mu\text{m}$ to $2.2\ \mu\text{m}$. However, a few millimeter sizes of agglomerated PVC particles deposited on the bottom of the reactor and the PVC particles were coagulated during storage.

The results in Fig. 7 built from Eq. (4) demonstrated changes of

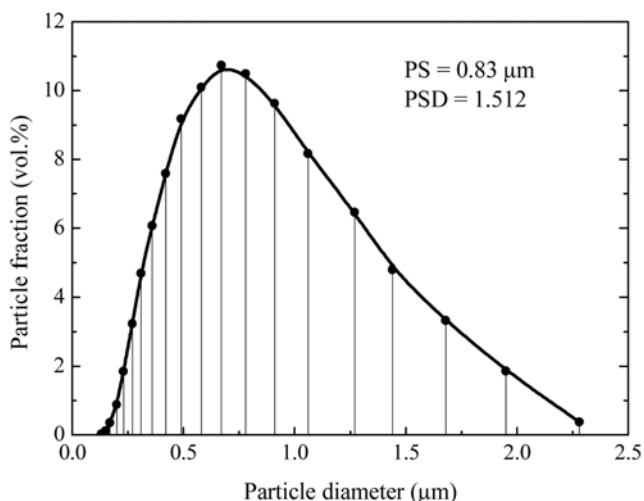


Fig. 6. The PSD of latex produced (CA/SLS=2.71, CA+SLS concentration=1.65 wt%).

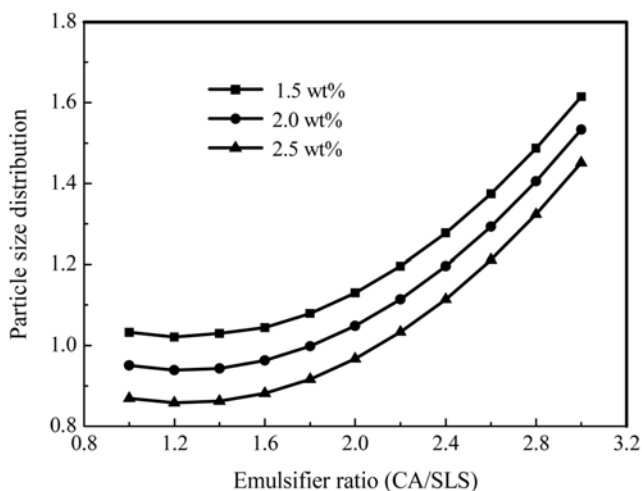


Fig. 7. The effect of the emulsifier ratio on PSD.

PSD according to the emulsifier ratio. Total CA and SLS concentration were varied from 1.5 wt% to 2.5 wt%. The CA/SLS ratio had strong influence on PSD, whereas emulsifier concentration only had slight effect. The PSD had a minimum value at a low emulsifier ratio between 1 and 1.5. Subsequently, the PSD strongly increased with respect to the emulsifier ratio up to a ratio of three. This can be explained by the degradation of the miniemulsion during polymerization as mentioned above. A low emulsifier ratio indicates a low CA concentration, which is not enough to inhibit the Ostwald ripening phenomenon [21], resulting in miniemulsion droplets approaching a uniform size. Otherwise, at a high emulsifier ratio, the high CA concentration gives effective protection against Ostwald ripening, while a low SLS concentration is not enough to stabilize the coalescence, leading to a broad droplet size distribution or broad PSD.

In summary, the APS and PSD of the latex depended on the degradation rate of the miniemulsion during polymerization. Particle size and PSD can be controlled by changing the CA/SLS ratio to increase or decrease stability of the VCM miniemulsion.

CONCLUSIONS

PVC latex synthesized by miniemulsion polymerization had an APS in the range of $0.4\text{--}0.7\ \mu\text{m}$, which is much larger than that prepared by conventional emulsion polymerization, while the PSD was multidispersed. Either APS or PSD was inversely proportional to the concentration of SLS, CA and initiators. The CA/SLS molar ratio also had a strong effect on the APS and PSD. The smallest average particle was attained at a CA/SLS molar ratio of 1 : 1, and it was increased with CA/SLS molar ratios. The best CA/SLS molar ratio was observed in the range of 1-2. The total SLS and CA concentration in range of 1.5-2 wt% was thought to be enough to stabilize the latex which possesses an APS smaller than $0.7\ \mu\text{m}$ and PSD less than 1.2.

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