

Effect of Amount of Emulsifier Added in the Second Stage on Morphology of Composite Latex Particles

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ABSTRACT: In this article, PBA/P(MMA-crosslinking agent)-composite particle latexes were prepared by semicontinuous seeded emulsion polymerization. To determine the seed emulsion's saturating capacity of an emulsifier, a mathematical model was built to simulate the changes of the seed PBA emulsion's surface tension with the amount of emulsifier added dropwise. The effects of the emulsifier amount added in the second stage and the addition method on the morphology of the composite particles were studied. The results were shown as follows: If the amount of emulsifier added in one batch to the seed emulsion in the second stage was less than or equal to the saturating capacity of emulsifier of the seed emulsion (C_s), the morphology of the particles was "core-shell"; otherwise, a few particles were of a core-shell structure. However, if shell materials were preemulsified and added dropwise at an appropriate rate, the latex particles were still of a core-shell structure, even when the amount of emulsifier added to the seed emulsion was greater than the C_s . © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 969–975, 1998

Key words: emulsifier; seeded emulsion polymerization; core-shell latex; saturating capacity of emulsifier; computer simulation

INTRODUCTION

Latex systems with well-designed morphologies are necessary for advanced engineering plastics with high impact strengths, for improved toughening, for optimum peel strength of adhesives, and for many other high value-added products in fields such as membrane separation and biotechnology. Currently, composite polymer latex with different components and, hence, different morphological features have been prepared via seeded emulsion polymerization and multistage emulsion polymerization.

The most advantageous aspect of composite polymer latexes is that they allow an optimal com-

ination of properties from both components. This largely depends on the morphological features of the latex particles; hence, the investigation of a particle's morphology and factors controlling it has been the goal of many scientists, notably Sundberg et al.,¹ Dimonie et al.,² Okubo et al.,^{3,4} and Cheng et al.⁵ Many parameters of the emulsion polymerization process are known to affect the particle's "core-shell" morphology, for example, reactivity ratios and water solubility of the monomers, mode and schedule of monomer addition, and type, amount, and mode of addition of other ingredients such as emulsifier, initiator, chain-transfer or crosslinking agent, and temperature. The amount of the emulsifier added in the second stage and modes of addition are the determining factors that control the composite particle's core-shell structure for a given polymerization system. The goal of the current work was to investigate

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Table I Standard Recipe for the Preparation of Seed PBA Latexes

Ingredients	Quantity
BA	80 g
AP	0.4 g
10% CE	30 mL
H ₂ O	140 mL

in detail the influence of the determining factors on the morphology of PBA/P(MMA-crosslinking agent) latex particles.

EXPERIMENTAL

Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) were distilled under reduced pressure and stored in a refrigerator. Analytical-grade ammonium persulfate (AP) was purified by recrystallization. Sodium dodecyl sulfate (SDS) and OS-15 were used without further purification. Deionized water was used in all polymerizations. A 10% composite emulsifier (CE) solution was made by dissolving a composition of $\frac{2}{3}$ SDS/OS-15 (by weight) in water. The crosslinking agents *N*-hydroxymethylacrylamide (HMAA) and methylene-bisacrylamide were reagent grade.

Preparation of Seed PBA Latexes

A 500-mL four-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a gas inlet tube were thoroughly purged with pure nitrogen gas. The chemicals in Table I in the indicated amounts were placed in the flask under a gentle stream of nitrogen. The mixture was stirred for 30 min at room temperature while nitrogen gas was gently bubbled through and was heated gradually in a water bath to a temperature of 70°C. After the peak time, the reaction system was heat-treated at 84°C for 2 h.

Synthesis of Composite Particle Latexes

In the reactor vessel where the seed PBA latex was prepared, shell material was added in two ways: The first way is that 10% CE was added in one batch; then the AP solution (made of 0.1 g AP dissolved in 40 mL water) was added dropwise

through a funnel, and the mixture of MMA and the crosslinking agent was added dropwise through another funnel. The second way is that prior to the shell addition reactions 10% CE, MMA, AP, the crosslinking agent, and water were mixed under stirring to form the preemulsion; then, the preemulsion was added dropwise at 2.0 mL/min. The recipe used is listed in Table II. With the dropwise addition complete, we kept the temperature at 84°C for 2 h and then cooled it with an ice-water bath to ambient temperature.

Titration

In our work, we determined the *C*s by changes of the surface tension of the PBA seed emulsion. We titrated the seed emulsion with 10% CE on a JZHY-180 DuNouy interfacial tensionmeter using the ring methods.

Particle Morphology

The morphology of the latex particles was studied by latex OsO₄-stained or phosphotungstic acid (PTA)-stained TEMS. In this article, the method of preparation of the core-shell latex was different from those reported in the literature. In the literature, the emulsifier must be removed by dialysis from the seed emulsion. However, in this system, a small amount of emulsifier was added into the seed emulsion at the second stage. If no emulsifier was added, the shell material had to be added dropwise very slowly and the amount of the crosslinking agent added should be very small—smaller than 1% of total monomer weight; otherwise, it was easy to gelate. The amount of emulsifier added in the second stage must be referenced to the *C*s of the emulsifier of the seed emulsion; therefore, it is very important to determine the *C*s.

Table II Recipe for Composite Latexes in the Second Stage

Ingredients	Quantity
MMA	20 g
10% CE	Variable
AP	0.1 g
Crosslinking agent	5 g
H ₂ O	40 mL

Table III Changes of 25.0 mL in the Seed Emulsion's Surface Tension with the Amount of Emulsifier Added Dropwise

Accumulated Amount of Emulsifier (mL)	Surface Tension (Averaged, mN/m)	Accumulated Amount of Emulsifier (mL)	Surface Tension (Average, mN/m)
0	48.90	2.8	43.10
1.0	47.40	3.0	42.77
1.5	46.43	3.6	42.27
2.0	44.90	4.0	42.20
2.4	43.97	5.0	42.10

$t = 17.0^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Determination of the C_s of Seed PBA Emulsion

Some physical properties of seed emulsion, such as surface tension, conductivity, and osmotic pressure, changed significantly when the amount of the emulsifier added into the seed emulsion reached its C_s . Tables III and IV indicate the changes of the seed emulsion's surface tension with the amount of emulsifier added dropwise.

Tables III and IV shows that the surface tension of the seed emulsion kept on decreasing with the addition of the emulsifier, although the decreases were small after the amount of the emulsifier reached a certain amount. In the case of the water solution being added dropwise with the emulsifier, the surface tension of the water solution stayed constant after the concentration of the simplex emulsifier reached a certain value, which is known as the CMC. It was not strange that the seed emulsion's behavior was different from that of the water solution. Because the seed emulsion itself was a complicated system, the composite emulsifier had blending micelle effects and the emulsifier's molecules attracted onto the surface of the seed emulsion had interactive effects.⁶⁻⁸ We

assumed that this phenomenon was activated by two parts: The first and main part was the emulsification, which abided the law of the water solution being added dropwise with the simplex emulsifier. The second and subsidiary part was caused by the composite emulsifier's blending of micelle effects and interactive effects, which acted together in a way of linearity. In accordance with the above analysis, we built up a mathematical model to separate the two parts and put forward a procedure to estimate the C_s .

Mathematical Model

As shown in Figure 1, there existed an X_0 , the changing point of the seed emulsion's surface tension. If the amount of the emulsifier added was larger than X_0 , the surface tension descended in a slight slope, whereas on the left side of X_0 , the surface tension descended sharply in a concave curve. X_0 was the position fixed as the estimation of the C_s in the following context by testing gradually the linearity of the experimental data set that lay on the right side of an arbitrary point.

In our experiment, while we added the emulsifier into the seed emulsion dropwise, we drew a

Table IV Changes of 21.0 mL in the Seed Emulsion's Surface Tension with the Amount of Emulsifier Added Dropwise

Accumulated Amount of Emulsifier (mL)	Surface Tension (Averaged, mN/m)	Accumulated Amount of Emulsifier (mL)	Surface Tension (Averaged, mN/m)
0	49.90	2.9	40.83
0.5	47.30	3.4	40.77
1.0	44.77	4.4	40.27
2.0	41.97	5.4	40.00
2.5	41.10	6.4	39.90
2.7	40.88		

$t = 7.8^{\circ}\text{C}$.

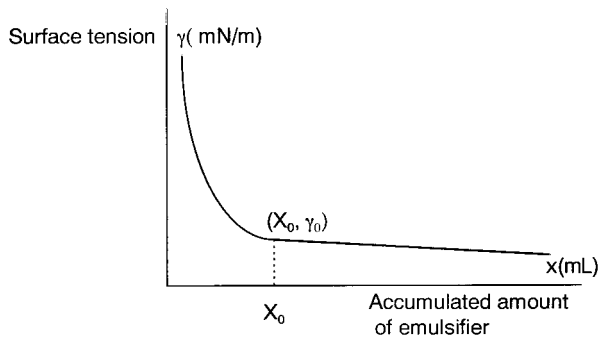


Figure 1 Change curve of seed emulsion surface tension with amount of emulsifier added dropwise.

sequence of data pairs, that is, sample points, $(x_1, \gamma_1), (x_2, \gamma_2) \dots (x_n, \gamma_n)$, where x_i stands for the amount of the emulsifier accumulated in the i th step, and γ_i , for the corresponding surface tension. Obviously, we had $x_i < x_j$ for $i < j$. If we at last added enough emulsifier to the seed emulsion, we could assert that X_0 lay between x_1 and x_n . Attention needs to be paid to the subsequence of those sample points after the i th point; for convenience, we denoted this subsequence by A_i . If x_i , the start point of A_i , satisfied $x_i \geq X_0$, those points in A_i would fall approximately on a slight slope. If $x_i < X_0$, otherwise, at some of those points in A_i , that is, the points where the emulsifier did not reach X_0 , the emulsifier’s emulsification function acted significantly. According to our assumption, those points in A_i , in essence, were not in a line. If we forced a line to fit those points, we would get a large fitting error. In this way, we might fit $n - 3$ lines to those point subsequences A_1, A_2, \dots, A_{n-3} and get $n - 3$ fitting errors. By comparing these errors, we picked out the subsequence with the smallest error and estimated X_0 by this start point or an appropriate value near it. Taking random errors into consideration, we applied a linear regression model to draw these fitting lines.⁹

The i th subsequence, A_i is expressed by a univariate regression model:

$$\gamma_j = a + bx_j + \varepsilon_j, \quad j = i, i + 1, \dots, n \quad (1)$$

in which ε_j is identically and independently distributed in a central normal distribution $N(0, \sigma^2)$ and a and b can be estimated by the least-squares (LS) method:

$$\tilde{b} = \frac{\sum_{j=i}^n (x_j - \bar{x}_i)\gamma_j - \bar{\gamma}_i \sum_{j=i}^n (x_j - \bar{x}_i)}{\sum_{j=i}^n (x_j - \bar{x}_i)^2} \quad (2)$$

$$\tilde{a} = \bar{\gamma}_i - \tilde{b}\bar{x}_i \quad (3)$$

where

$$\bar{x}_i = \sum_{j=i}^n x_j / (n - i + 1) \quad (4)$$

$$\bar{\gamma}_i = \sum_{j=i}^n \gamma_j / (n - i + 1) \quad (5)$$

The regression of the j th observation is

$$\tilde{\gamma}_j = \tilde{a} + \tilde{b}x_j \quad (6)$$

The fitting error of the i th subsequence A_i is

$$\text{err}_i = \sum_{j=i}^n (\tilde{\gamma}_j - \gamma_j)^2 \quad (7)$$

err_i stands for the closeness of the fitting line. If $x_i < X_0$, err_i tends to be large. Otherwise, err_i should be small. More sample points generally lead to a larger fitting error because more items are contained in eq. (1). To eliminate the distortion of the sample size, we noticed that

$$\text{err}_i / (n - i + 1) - 2 \sim \sigma^2 \chi^2(n - i - 1) \quad (8)$$

So, we deduced a new indicator index by the upper probability of the χ^2 distribution to measure the fitting result:

$$\begin{aligned} \text{Index} &= P[\chi^2(n - i - 1) \\ &> \text{err}_i / (n - i - 1) \sigma^2] \quad (9) \end{aligned}$$

Since the Index is a probability, it is between 0 and 1. By the theory of probability, a larger index stands for a better fitness.

In the expression of the Index, there is an unknown variable σ^2 . Here, we estimated it by repeated observations at each sample points, that is, for each x_i , we had m observations $(x_i, \gamma_{i1}), (x_i, \gamma_{i2}), \dots, (x_i, \gamma_{im})$. Let γ_i be mean of those m observations:

$$\gamma_i = \sum_{j=1}^m \gamma_{ij} / m \quad (10)$$

γ_i would be used in the regression model. The variance of all observations in all sample points would be the estimation of σ^2 , that is:

Table V Simulation Results of Table III

<i>i</i>	<i>x_i</i>	γ_{i1}	γ_{i2}	γ_{i3}	γ_i	<i>a</i>	<i>b</i>	err _{<i>i</i>}	<i>n</i> - <i>i</i> - 1	Index
1	0.0	49.0	48.9	48.8	48.90	48.312	-1.5451	5.590	8	≪0.001
2	1.0	47.4	47.3	47.5	47.40	47.881	-1.4149	4.991	7	≪0.001
3	1.5	46.4	46.5	46.4	46.43	47.122	-1.2035	3.608	6	<0.001
4	2.0	44.9	44.9	44.9	44.90	45.948	-0.8920	1.573	5	<0.001
5	2.4	44.0	44.0	43.9	43.97	44.986	-0.6497	0.680	4	<0.001
6	2.8	43.1	43.1	43.1	43.10	44.053	-0.4257	0.175	3	0.004
7	3.0	42.8	42.7	42.8	42.77	43.511	-0.3019	0.071	2	0.023
8	3.6	42.2	42.2	42.4	42.27	42.674	-0.1154	0.000	1	0.85
9	4.0	42.2	42.2	42.2	42.20					
10	5.0	42.1	42.1	42.1	42.10					

$\hat{\sigma}^2 = 0.004333$.

$$\hat{\sigma}^2 = \sum_{i=1}^n \sum_{j=1}^m (\gamma_{ij} - \gamma_i)^2 / n(m - 1) \quad (11)$$

The theory of mathematical statistics told us that $\hat{\sigma}^2$ was an accurate estimator of σ^2 . In our data processing, we just simply substituted σ^2 by $\hat{\sigma}^2$.

We simulated the data in Tables III and IV with a 386PC in the C programming language. The results are shown in Tables V and VI. In Table V, the Index of the eight point was the largest and its neighbors were much smaller. We, hence, took $X_0 = 3.6$ mL to estimate the *Cs* of 25.0 mL of the seed emulsion. In Table VI, the Indexes at the fifth and sixth points were the largest, that is, the saturating capacity was between 2.5 and 2.7 mL. We took $X_0 = 2.6$ mL, the mean of these two points, to estimate the *Cs* of 21.0 mL of the seed emulsion.

So, for every seed emulsion, we could get a small amount and titrate it with the emulsifier,

then simulate the experimental data in the computer and obtain its *Cs*. In the same way, if we determine the *Cs* of the seed emulsion by changes of the conductivity or osmotic pressure, we can also apply this mathematical model, for these physical properties of seed emulsion change in a way of linearity either before or after the emulsifier reaches its *Cs*.

Effect of Amount of Emulsifier Added in the Second Stage and Mode of Addition on Core-Shell Morphology of Composite Latex Particles

In our work, shell materials were added in two ways: The first way was that emulsifier was added in one batch to the seed emulsion and the others were added dropwise. The second way was that all shell materials were mixed and preemulsified for 30 min before being added dropwise into the seed emulsion at 2.0 mL/min. Figures 2-4 are

Table VI Simulation Results of Table IV

<i>i</i>	<i>x_i</i>	γ_{i1}	γ_{i2}	γ_{i3}	γ_i	<i>a</i>	<i>b</i>	err _{<i>i</i>}	<i>n</i> - <i>i</i> - 1	Index
1	0.0	49.9	50.0	49.8	49.90	46.457	-1.3897	34.743	9	0.001
2	0.5	47.4	47.2	47.3	47.30	45.028	-1.0421	17.969	8	0.001
3	1.0	44.8	44.7	44.7	44.77	43.526	-0.6926	6.459	7	<0.001
4	2.0	41.9	42.0	42.0	41.97	42.120	-0.3791	0.607	6	0.005
5	2.5	41.0	41.2	41.1	41.10	41.683	-0.2905	0.084	5	0.689
6	2.7	40.9	40.8	40.8	40.83	41.565	-0.2682	0.055	4	0.648
7	2.9	40.9	40.7	40.8	40.80	41.575	-0.2699	0.055	3	0.359
8	3.4	40.8	40.7	40.8	40.77	41.557	-0.2667	0.054	2	0.009
9	4.4	40.2	40.3	40.8	40.27	40.888	-0.1500	0.009	1	0.185
10	5.4	40.0	40.0	40.0	40.00					
11	6.4	39.9	40.0	40.0	39.97					

$\hat{\sigma}^2 = 0.005455$.

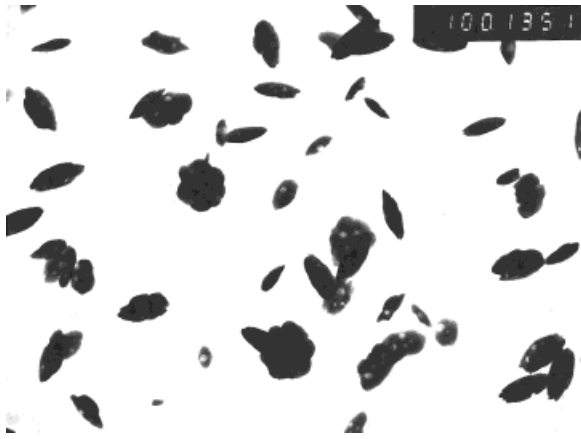


Figure 2 TEM photograph ($\times 100,000$) of composite particles when $A_e = 0$. A_e : = amount of emulsifier added in the second stage.

TEM photographs of the composite latex particles in which the shell materials were added the first way and the amounts of the emulsifier added in the second stage were 0, C_s , and $2C_s$, respectively. Figures 5–7 are TEM photographs of the composite latex particles in which the shell materials were added the second way and the amounts of the emulsifier added in the second stage were $0.7C_s$, C_s , and $3C_s$, respectively.

The particles in Figures 2 and 3 were clearly of a core–shell structure. In Figure 4, a few particles were of the core–shell structure, but most of them were of a non-core–shell structure. This indicated that if the amount of the emulsifier added in one batch into the seed emulsion was greater than the C_s , few particles were of the core–shell structure.

From Figures 5–7, we can see clearly that all the particles were of the core–shell structure.

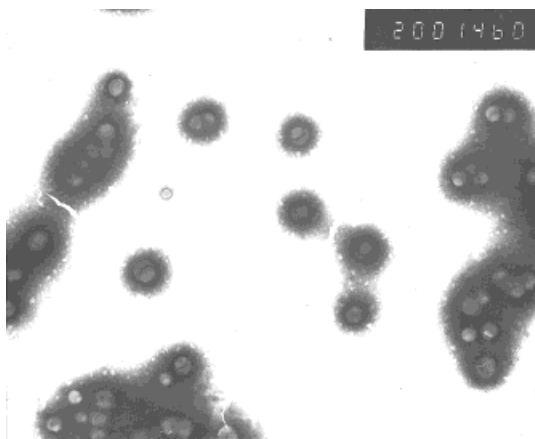


Figure 3 TEM photograph ($\times 200,000$) of composite particles when $A_e = C_s$.

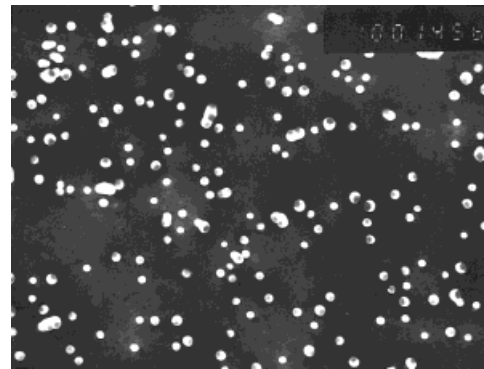


Figure 4 TEM photograph ($\times 200,000$) of composite particles when $A_e > C_s$.

This indicates that if the shell materials were pre-emulsified and added dropwise at an appropriate rate, the composite particles were all of the core–shell structure, no matter whether the emulsifier added in the second stage was less than, equal to, or greater than the C_s .

According to the theory of emulsion polymerization, after micelle generation, latex particles increase continuously along with the processing of polymerization and need to replenish the emulsifier to remain stable. When shell materials were preemulsified, even if the amount of the emulsifier added in the second stage was greater than the C_s of the seed emulsion, polymerization still proceeded in a starved condition, because the shell materials were dropped evenly and the concentration of the emulsifier in the emulsion was less than its saturating concentration at every moment. Therefore, no new particle was generated and the morphology of the particles was core–shell.

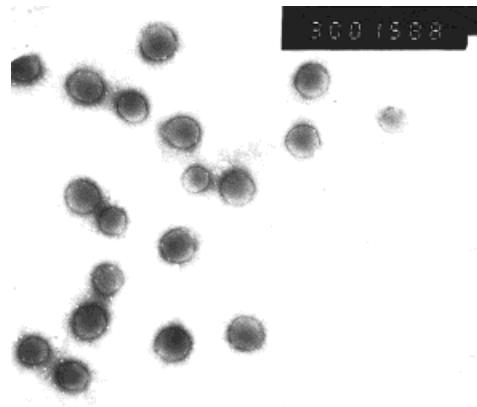


Figure 5 TEM photograph ($\times 300,000$) of composite particles when $A_e < C_s$ and shell materials were pre-emulsified.

CONCLUSIONS

Many of the emulsion polymerization process parameters are known to affect the particles core-shell morphology. The amount of the emulsifier added in the second stage and the mode of addition are the determining factors that control the composite particles' core-shell structure for a given polymerization regime. If the amount of the emulsifier added in one batch to the seed emulsion in the second stage is less than or equal to the saturating capacity of the seed emulsion, the morphology of the particles is core-shell; otherwise, only a few particles are of the core-shell structure. However, if the shell materials are preemulsified and added dropwise at an appropriate rate, all the particles are of the core-shell structure, no matter whether the amount of the emulsifier added in the second stage is less than, equal to, or greater than the C_s .

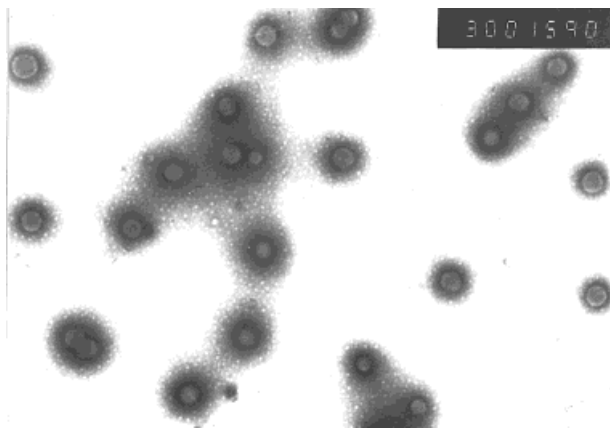


Figure 6 TEM photograph ($\times 300,000$) of composite particles when $A_e = C_s$ and shell materials were pre-emulsified.

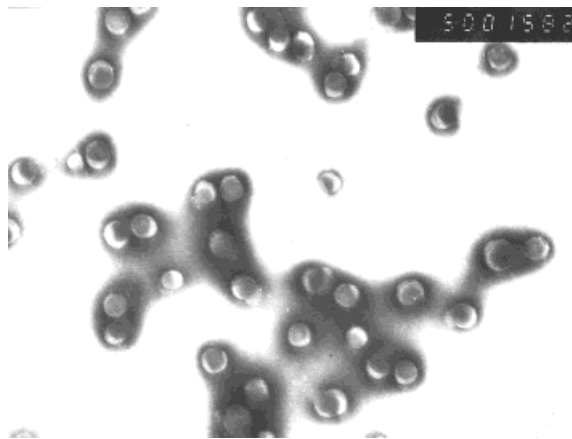


Figure 7 TEM photograph ($\times 300,000$) of composite particles when $A_e > C_s$ and shell materials were pre-emulsified.

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