

Theoretical aspects of developing latex particle morphology

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Abstract - Seeded emulsion polymerization was used to prepare composite latex particle for particle morphology studies. The polymerizations were carried out at 70°C using monodisperse polystyrene latex particles as seed and methyl methacrylate as the second stage monomer. The morphologies of the composite latex particles were investigated using transmission electron microscopy.

A thermodynamic analysis based on three interfacial tensions was used to describe the free energy changes corresponding to various possible morphologies. Based on experimentally measured interfacial tensions, the relative stabilities of particle morphologies were calculated based on minimization of the free energy changes. Differences between observed and predicted particle morphology were found to be due to kinetic effects, mainly due to restricted chain mobility because of the high internal viscosity during the final stage of polymerization or solvent removal.

INTRODUCTION

Latex systems with well designed particle morphology are necessary for advanced engineering plastics with high impact strength, improved toughening, for optimum peel strength of adhesives, and many other high value-added products in other application areas such as membrane separations and biotechnology. Composite latex particles of different morphological features are usually prepared by seeded emulsion polymerization techniques where a second stage monomer is polymerized in the presence of seed latex particles. Elucidation of the morphology of two-stage latex particles and the factors controlling it were the goals of many papers published in recent years; notably those of Sundberg et al.¹, Dimonie et al.², Cho and Lee³ and Okubo et al.⁴. These factors fall into two broad categories: thermodynamics and kinetics. The thermodynamic factors determine the equilibrium morphology of the final composite latex particle, and the kinetic factors determine the ease with which such thermodynamically favored morphology can be achieved. In this context, several such influences and their interactions in the development of composite latex will be discussed.

THERMODYNAMIC APPROACH AND MODEL PREDICTION

The thermodynamic analysis which will be considered for determining the latex particle morphology is based on the approach presented 20 years ago by Torza and Mason⁵. They pioneered the interfacial behavior of systems containing three mutually immiscible liquids. In this case the thermodynamics of the system were influential in determining the final morphology since the liquid phase was highly mobile. They examined the conditions necessary for a coacervate droplet (liquid 3) to engulf an initial droplet (liquid 1) when both are immersed in a continuous phase (liquid 2) by the spreading coefficient, S , which is defined as:

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad (1)$$

By assuming that the interfacial tension of liquid 1 against liquid 2 (γ_{12}) is greater than that of liquid 3 against liquid 2 (γ_{23}), only three possible sets of values for S exist. These correspond to the three

different equilibrium configurations: complete engulfing (core-shell), partial engulfing (hemisphere), and nonengulfing (individual particle). Complete engulfing occurs only if $S_3 > 0$, $S_2 < 0$, and $S_1 < 0$. On the other hand, when $S_2 < 0$, $S_3 < 0$, and $S_1 < 0$ the partial engulfing was preferred. Torza and Mason demonstrated the general validity of their approach by making a number of interfacial tension measurements, calculating values of S , and then observing what occurred in actual three-phase system. In most cases, prediction of engulfing based on S were satisfactory. This approach should be broadly applied in determining when the engulfing will occur in various encapsulation systems. Recently, Sundberg et al.¹ by applying Torza and Mason's approach presented a thermodynamic analysis of the morphology of a system comprising a polymer encapsulating a relatively large-size oil droplet in the μm range. Their analysis revealed that the interfacial tension of each phase is the key factor governing the type of microcapsules formed. Dimonie et al.² supported experimentally the hypothesis that in addition to the viscosity of the polymerization locus (related to the chain mobility), the interfacial tension of the polymer phases is one of the main parameters controlling the particle morphology in a composite polymer latex system.

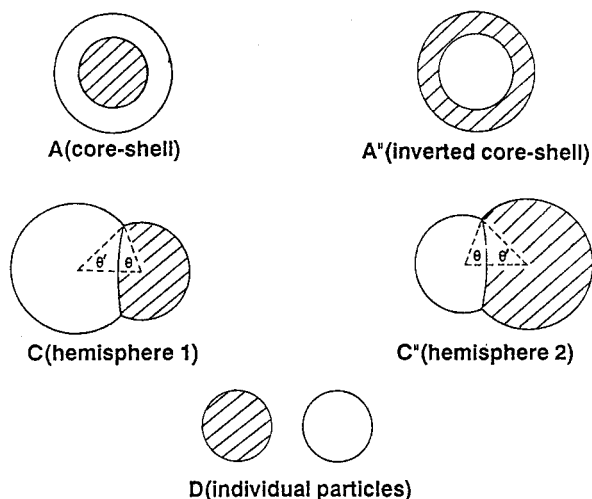


Fig. 1. Various morphological structures of particles dispersed in water.

(hatched area : polymer 1,
open area : polymer 2)

Our thermodynamic analysis is similar to that presented by Sundberg et al.¹ and a mathematical model were derived to describe the free energy changes corresponding to various composite latex particle morphologies (shown in Figure 1). The model was applied and verified for predicting the final morphology for particles in the submicron size range. The methodology involves consideration of the free energy changes for the following hypothetical pathways. The initial state was considered to consist of a polymer phase 1 (seed particles of polymer 1 swollen by the second stage monomer, i.e. monomer 2) suspended in water containing surfactant. The final state is one of the morphologies shown in Figure 1. The only contribution to the free energy change for this pathway is the creation of new interfaces and changes in the corresponding interfacial tensions. For latex particles dispersed in a continuous water phase, those interfaces include polymer phase 1/water, polymer phase 2/water, and polymer phase 1/polymer phase 2. Polymer phase 2 is polymer 2 (formed as a result of the polymerization of monomer 2 in the presence of polymer 1) swollen by its own monomer. The total concentration of monomer 2 is dependent on the conversion. The monomer distribution between polymer 1 and polymer 2 is assumed to be proportional to the volume fraction of each polymer. The total free energy change for all types of configurations shown in Figure 1 can be expressed as

$$\Delta G = \sum \gamma_{ij} A_{ij} - \gamma_0 A_0 \quad (2)$$

where γ_{ij} is the interfacial tension between i and j and A_{ij} the corresponding interfacial area, γ_0 is the interfacial tension of original polymer phase 1 (i.e. seed particles of polymer 1 swollen by monomer 2) suspended in water phase and A_0 is its interfacial area. The equations describing the free energy change for each case shown in Figure 1 were derived⁶. Calculation of the free energy change for each case involves a trial and error solution method. A FORTRAN77 computer program was prepared for this purpose. The thermodynamically preferred morphology will be the one which has the minimum interfacial free energy change. This approach is feasible if all of the interfacial tensions of various phases, γ_{1w} (polymer phase 1 and water), γ_{2w} (polymer phase 2 and water) and γ_{12} (between two polymer phases), can be measured independently.

Table 1 shows the calculated morphologies using a number of hypothetical conditions corresponding to various values of γ_{ij} and V_r (where V_r is the volume ratio of polymer phase 2/polymer phase 1). A comparison of the data in group 1 and 2 shows that one expects a higher chance of obtaining the desired core-shell morphology (case A) if the interfacial tensions between the seed polymer and water is higher than that between the second stage polymer and water (i.e. $\gamma_{1w} > \gamma_{2w}$). On the other hand, one only has to allow γ_{2w} to be greater than γ_{1w} in order to invert the particle morphology (case A"). Analyzing the data in groups 1 and 3, one finds that as the polymer phase 1/polymer phase 2 interfacial tension (γ_{12}) increases while maintaining the γ_{1w} , γ_{2w} and V_r constant, the equilibrium particle morphology changes from case A (or A") to case C (or C"), and finally to case D (individual particles). This phenomenon of the increase in the phase separation as γ_{12} is increased indicates that the γ_{12} is a parameter which decides the interfacial area between the two polymer phases. The data in group 4 show how the volume ratio of the second stage polymer to the seed polymer affects the particle morphology. If γ_{1w} is greater than γ_{2w} , the tendency of decreasing phase separation can be enhanced by increasing the volume ratio, as indicated by the increase in θ (86° - 129°) while V_r is increased from 0.5 to 5.5. On the contrary, if γ_{2w} is greater than γ_{1w} , increasing of volume ratio V_r in the range of 0.5 to 5.8 should result in an increase in tendency of phase separation as indicated by the decrease in θ from 114° to 65° .

TABLE 1. Various morphological structures of latex particles dispersed in water under hypothetical conditions

Group	γ_{1w}	γ_{2w}	γ_{12}	V_r	Case Predicted
1	9	5	3	1	A
	5	9	3	1	A"
2	7	5	3	1	C $\theta = 86^\circ$
	5	7	3	1	C" $\theta = 86^\circ$
3	9	5	4.1	1	C $\theta = 134^\circ$
	9	5	6	1	C $\theta = 70^\circ$
	9	5	10	1	C $\theta = 40^\circ$
	9	5	15	1	D
	5	9	4.2	1	C" $\theta = 119^\circ$
	5	9	7	1	C" $\theta = 61^\circ$
	5	9	9	1	C" $\theta = 46^\circ$
	5	9	15	1	D
4	9	5	4.5	0.5	C $\theta = 86^\circ$
	9	5	4.5	1.5	C $\theta = 109^\circ$
	9	5	4.5	3.5	C $\theta = 124^\circ$
	9	5	4.5	5.5	C $\theta = 129^\circ$
	5	9	4.5	0.5	C" $\theta = 114^\circ$
	5	9	4.5	1.5	C" $\theta = 93^\circ$
	5	9	4.5	2.5	C" $\theta = 81^\circ$
	5	9	4.5	5.8	C" $\theta = 65^\circ$

TABLE 2. Recipe of seeded emulsion polymerization for PS190/PMMA-AIBN and PS-190/PMMA-KS

Ingredients	PS190/PMMA-AIBN (g)	PS190/PMMA-KS (g)
PS Seed Particle	1.0	1.0
Igepal Co-990 ^a	0.08	0.08
MMA monomer	variable ^b	2.35
DDI water	11.0	12.6
AIBN	variable ^c	---
K ₂ S ₂ O ₈	---	0.0118

a. nonylphenol polyethylene oxide, 100 mole ethylene oxide, GAF Co.

b. seed/monomer wt. ratio = 30/70, 50/50 or 65/35.

c. AIBN/monomer wt. ratio = 2.143×10^{-3}

TABLE 3. Configurations of PS190/PMMA-AIBN system at 30/70, 50/50 and 65/35 polymer weight ratio.

wt. ratio	γ_{1w}^a	γ_{2w}^a	γ_{12}^b	final configuration	
				case predicted	observed
30/70	4.46	5.66	1.50	C" $\theta = 92^\circ$	C"
50/50	4.46	5.66	1.55	C" $\theta = 109^\circ$	C"
65/35	4.46	5.66	1.63	C" $\theta = 116^\circ$	C"

a. see reference 8.

b. see reference 6.

EXPERIMENTAL

The composite latexes were prepared by batch seeded emulsion polymerization using Dow LS1102A (denoted as PS190), monodisperse polystyrene latex as the seed particles. Methyl methacrylate monomer was used in the second stage polymerization. The seed particles were first swollen by MMA monomer for one hour, then the second stage polymerization was carried out at 70°C in batch using magnetically stirred polymerization bottles. Table 2 gives the standard recipes used in the preparation of the latex samples, PS190/PMMA-AIBN and PS190/PMMA-KS at different seed/monomer weight ratios. The particle morphology was observed by TEM after preferential staining of the polystyrene domains with RuO₄ vapor and negative staining with phosphotungstic acid (PTA) to better delineate the particle edges, especially for the methacrylate-rich domains, which are unstained by RuO₄⁷.

RESULTS AND DISCUSSION

Effect of volume ratio

Based on the methodology outlined above and the interfacial tensions reported in our previous work^{6,8}, the composite particle configurations of the PS190/PMMA-AIBN system at weight ratios of 30/70, 50/50 and 65/35 were predicted using the thermodynamic model⁶. The predicted composite particle morphology is the one which has the lowest free energy change. The required interfacial tensions between polymer phases 1, 2 and water were determined experimentally using the drop-volume method⁸. The interfacial tensions between polymer 1 and polymer 2, each dissolved in MMA monomer, were estimated based on the work of Broseta et. al.^{8,9}. The last two columns of Table 3 show the predicted morphology based on thermodynamic calculations and the observed morphology based on TEM examination of the composite particles. For the PS190/PMMA-AIBN system at 30/70 weight ratio, the predicted morphology was case C" (see Figure 1) with θ angle 92° . The predicted morphology can be observed in Figure 2. The electron micrograph given in Figure 2A shows that the second stage polymer PMMA (lighter region TEM picture) is partially engulfed by the seed polystyrene (darker regions). This is even more evident in the micrograph in Figure 2B where as a result of the beam damage in the TEM the PMMA domains shrunk and the cap shape of polystyrene domains is easier to be observed.

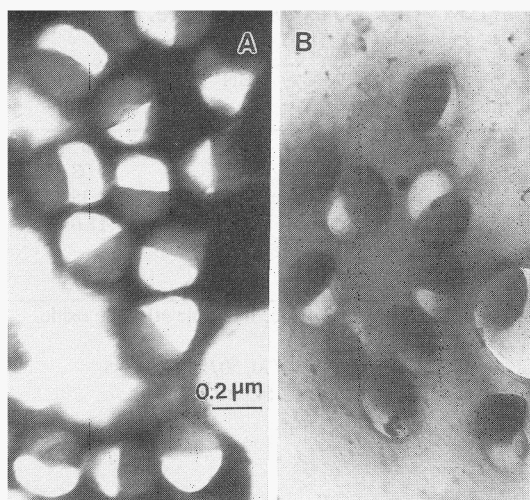


Fig. 2. (A) TEM of seed PS190/PMMA-AIBN composite latex with 30/70 weight ratio. (B) As PMMA was damaged by electron beam, the cap shape of PS190 was observed. Dark regions are PS domains stained with RuO₄ and lighter regions are PMMA domains outlined using phosphotungstic acid stain.

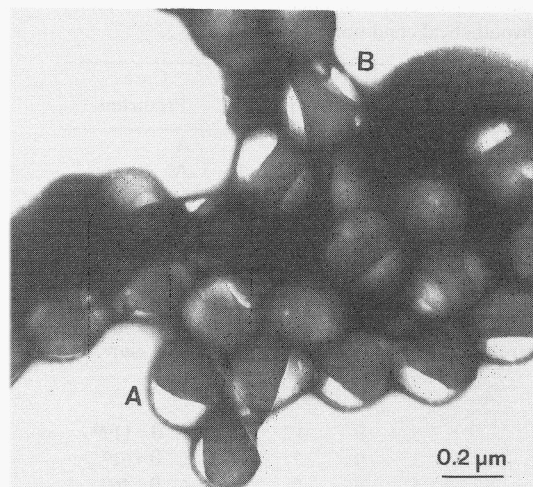


Fig. 3. TEM of seed PS190/PMMA-AIBN composite latex with 50/50 weight ratio. Dark regions are PS domains stained with RuO₄ and lighter regions are PMMA domains outlined using phosphotungstic acid stain.

For the PS190/PMMA-AIBN system at 50/50 weight ratio, the predicted morphology was case C" (see Figure 1) with θ angle 109° . The electron micrograph given in Figure 3 shows that some particles have a case C" type morphology where the polystyrene darker regions are partially covering the PMMA lighter regions (see particle A). This kind of morphology agrees with the theoretical predictions. On the other hand, the electron micrograph also shows that some other particles have a sandwich-like structure (see particle B). Based on the thermodynamic analysis⁶, this type of morphology is due to restricted chain mobility related to high internal viscosity during the final stage of polymerization, thus preventing the thermodynamically predicted configuration from being attained. After swelling of this final latex with toluene to enhance polymer chain mobility, the particle morphology showed a tendency towards a thermodynamically more favorable morphology (case C").

A comparison of the particle morphologies shown in Figures 2A and 3 (both are case C"), demonstrates that the composite latex particles prepared at 30/70 seed/monomer weight ratio (volume ratio of polymer 2 to polymer 1, $V_r=2.061$) have a higher degree of phase separation (lower θ angle, see Table 3) than particles prepared at 50/50 polymer weight ratio ($V_r=0.883$). Further

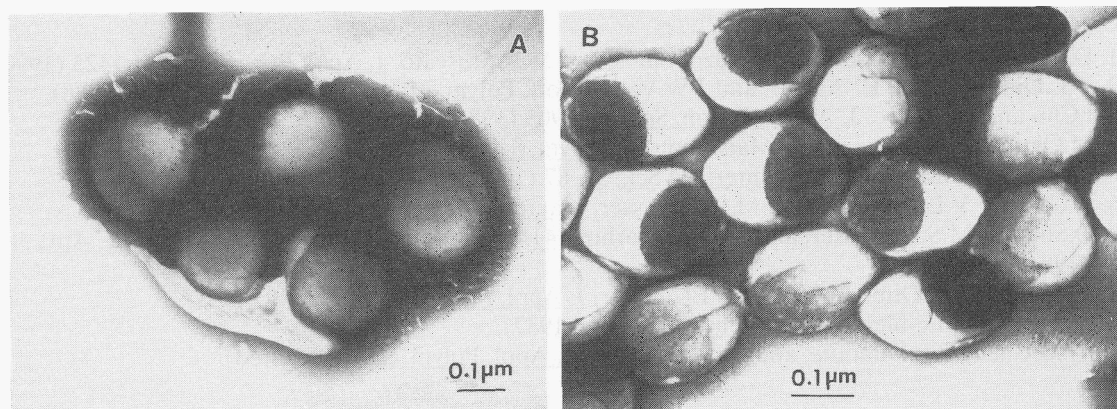


Fig. 4. (A) TEM of PS190/PMMA/Pluronic composite latex with 30/70 weight ratio (B) TEM of PS190/PMMA/Igepal composite latex with 30/70 weight ratio. Dark regions are PS domains stained with RuO_4 and lighter regions are PMMA domains outlined using phosphotungstic acid stain.

decrease in the volume ratio of polymer 2 to polymer 1 ($V_r = 0.476$) for the system of PS seed/MMA monomer weight ratio 65/35 causes further decrease in the degree of phase separation as demonstrated by the highest θ angle of 116° in Table 3. The tendency of increasing phase separation with volume ratio (V_r) of polymer 2 to polymer 1, when $\gamma_{1w} < \gamma_{2w}$, has been predicted in Table 1 based on thermodynamic analysis. The results given in Table 3 and Figures 2 and 3 demonstrate experimentally the predicted tendency of increased phase separation with increased volume ratio of the second stage polymer to seed polymer particle.

Role of surfactant

Two systems of composite latexes were prepared using the same recipe (Table 2 for PS190/PMMA-KS), but two different types of nonionic surfactants. Their morphologies are shown in Figure 4. In the first system, when Pluronic F-108 (polyethylene oxide-propylene oxide, 80% polyoxyethylene, BASF/Wyanadotte)) was used, the final particle morphology showed the PMMA domains to be partially covered by polystyrene. However, in the second system, when Igepal Co-990 (nonylphenol polyethylene oxide) was used under the same polymerization condition of the first system, one observed a reversed type of encapsulation (i.e. PS is partially engulfed by PMMA). The interfacial tension of the polymer phase against water containing surfactant measured by drop-volume method, was in good agreement with the observed particle morphologies¹⁰. The phase with higher polymer phase/water interfacial tension is engulfed by the phase with lower polymer phase/water interfacial tension. The existence of surfactant at the interface between the polymer phase and aqueous phase can affect the polymer phase/water interfacial tension and therefore, the particle morphology.

Effect of initiator

Composite latexes, PS190/PMMA-AIBN and PS190/PMMA-KS, with 30/70 seed/monomer weight ratio were prepared using different initiators. When the AIBN initiator was used, the second stage polymer (PMMA) containing CN chain end groups from the initiator, showed a higher polymer phase/water interfacial tension than the seed polystyrene polymer phase. The final particle morphology showed that the PMMA (core) was partially covered by polystyrene. However, when the $\text{K}_2\text{S}_2\text{O}_8$ initiator was used, the composite particle showed reverse type of encapsulation (i.e. PS core is partially engulfed by PMMA). The second stage PMMA polymer with SO_4 chain end groups from initiator exhibited a lower polymer phase/water interfacial tension than PS seed polymer. These results indicate that the initiator used can modify the particle surface polarity⁸, change the polymer phase/water interfacial tension, then, composite particle morphology.

CONCLUSIONS

The development of composite particle morphology is determined by the interaction of thermodynamics and kinetics. Based on the minimum surface free energy change principle, polymer phase/water and polymer phase/polymer phase interfacial tensions have been proved as key parameters in deciding the thermodynamically preferred morphology. The surfactant and initiator can affect the polymer phase/water interfacial tension, therefore, particle morphology.

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