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Effect of initiator on morphology in poly(vinyl acetate)/ polystyrene and poly(butyl acrylate)/polystyrene composite latexes

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Summary

A simple method of related sensitivity range to predict thermodynamic equilibrium morphology of a core-shell latex particle (J Appl Polym Sci. 2004, 92, 3144), is recently explored. The article proposed that it is necessary to classify core-shell latex systems as sensitivity and no-sensitivity by their equilibrium morphology sensitivity to initiator and emulsifier. As for the sensitivity system, the final morphology may change by adjusting initiator and emulsifier, whereas, for the no-sensitivity system, it is hard to change its final morphology in this way. Equilibrium morphologies in system poly(vinyl acetate) (PVAc)/polystyrene (PSt) and poly(butyl acrylate) (PBA)/ PSt composite latexes particles were observed by changing initiator. Composite latexes of the two systems were synthesized by two-stage semi-continuous emulsion polymerization. The types or/and concentration of initiator changed in two stages in which the oil-soluble initiator 2,2-azobis(isobutyronitrile) (AIBN) and the water-soluble initiator potassium persulfate (KPS) were used respectively, the concentration of which was 0.5% or 2% based on the weight of monomer. The results showed that the two systems had different characteristics. At different experiment conditions designed, the same equilibrium morphologies with PSt as core and PVAc as shell were obtained in system PVAc/PSt, whereas, three different equilibrium morphologies, core-shell, inverted core-shell and hemisphere, were obtained in system PBA/PSt. The equilibrium morphology in system PVAc/PSt is no-sensitive to initiator, and the equilibrium morphology in system PBA/PSt is sensitive to initiator.

Introduction

The two-stage emulsion polymerization is the typical method of synthesizing composite latex. The performance of polymers formed by the composite emulsion is strongly dependent on the morphology of the latex particles. Profound and extensive studies on the influencing factors in morphology were carried out. Sundberg et al. [1,2] initially proposed that there are only four kinds of thermodynamic equilibrium morphology [core-shell(CSOP), inverted core-shell(CSPO), hemisphere(HS) and individual particles(IP)].The thermodynamic preferred morphology of composite latex is the one that has the minimum interfacial free energy change. Later they [3] extended their earlier thermodynamic equilibrum approach for the prediction of ‘final’ equilibrium composite polymer particle morphologies, which allows the prediction of intermediate equilibrium morphologies along the reaction patheway during the polymerization of monomer-swollen seed particle. As initiator and emulsifier have great effect on interface tensions, which also has a great effect on morphology, it is important to study the effect of initiator and emulsifier on the thermodynamic equilibrium morphology of composite latex. Chen et al. [4–8] studied and proved that composite latex particles had different equilibrium morphologies (core-shell, inverted core-shell and hemisphere), if initiator and emulsifier were changed in system PSt/PMMA. However, the equilibrium morphology studied by different researchers [9–13] in system PBA/PVAc was almost the same, with all PBA as core and PVAc as shell. So we propose that there may exist two kinds of systems, the sensitivity system and the no-sensitivity system to initiator and emulsifier. As for the sensitivity system, the final morphology may change by adjusting initiator and emulsifier, whereas, for the no-sensitivity system, it is hard to change its final morphology in this way. If this is proved, it will be the original study in this area.

The most important thing is how to judge the sensitivity. Recently, Zhao and coworkers [14] propose a simple method to calculate the sensitivity range, the method will be introduced briefly later. According to their calculation, the equilibrium morphology in system PVAc/PSt is no-sensitivity to initiator, and the equilibrium morphology in system PBA/PSt is sensitivity to initiator, so that we choice system PVAc/PSt and PBA/PSt to study. The aim of this article is experimental proved that the equilibrium morphology of system PVAc/PSt and PBA/PSt are sensitive or no-sensitive to initiator.

Simple method of calculation the sensitivity range

The total interfacial free energy change (ΔG) for all the different types of possible equilibrium morphologies can be expressed as follows [2]:

$$\Delta G = \sum_i (\sigma_{ij} . A_{ij}) - \sigma_{1w} A_0 \qquad \mathbf{(1)}$$

Where σ_{ij} is the interfacial tension of *i*th and *j*th interface and A_{ij} is the corresponding interfacial area of *i*th and *j*th interface, σ_{1w} is the interfacial tension of seed polymer phase 1 suspended in water phase (with an emulsifier, if present), and A_0 is its interfacial area. Therefore, the reduced interfacial free energy change per unit of surface area of the original polymer 1 particle ($\Delta\gamma$) is obtained by the division of the expression for ΔG by A_0:

$$\Delta\gamma = \Delta G / A_0 = \sum_i (\sigma_{ij} . A_{ij}) / A_0 - \sigma_{1w} \qquad \mathbf{(2)}$$

Based on Sundberg et al.’s [2] theory, the important factor in predicting the equilibrium morphology of composite latex particle is that the three kinds of interfacial tension must be known before the prediction. However, the related three interfacial tensions are very difficult to obtain under the reaction conditions.

Huo and coworkers [15,16] used a simple calculation method to get the three interfacial tensions to predict the equilibrium morphology of composite latex. The surface tension γ and the polarity χ^p of polymers and water (with an emulsifier, if present) can be determined from the literature [17] or by experiment. The three interfacial tensions can be calculated by harmonic mean method.

$$\sigma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \qquad (\mathbf{3})$$

Where γ^d and γ^p ($\chi^p = \gamma^p/\gamma$) are the dispersive and polar components of the surface tension, respectively.

Under real reaction conditions, the three interfacial tensions can be the same or different from the ones calculated with equation (3) with the date in literature [17], if they are different, the difference between the calculation and experiment may exert an effect on the prediction. However, the reliability of the prediction is different for different composite latexes, some systems of the possible equilibrium morphology of a core-shell latex are sensitive to the three interfacial tensions, and others are not. We can use the method to predict the possible equilibrium morphology of a core-shell latex before the related experiment, when the possible equilibrium morphology is not sensitive to the three interfacial tensions. However, the method could be a failure in predicting the possible equilibrium morphology of a core-shell latex before the related experiment, when the possible equilibrium morphology is sensitive to the three interfacial tensions. The most important thing is to judge the sensitivity, which involves the relationship between the possible equilibrium morphology of a core-shell latex and the three interfacial tensions.

Based on equation (3), γ and γ^p can have an important effects on the three interfacial tensions. The nature of the polymers, emulsifier and initiator can influence γ and γ^p, so possible changes in γ and γ^p can reveal the nature of polymers, emulsifier and initiator, and have important effects on the three interfacial tensions and, therefore, on the equilibrium morphology. The article [14] discussed the problem of how changing the range of γ and γ^p influences the possible equilibrium morphology. Based on the basic thermodynamic data in literature [17], γ and χ^p are related with the nature of polymer and water, but, the effects of the emulsifier and initiator are not taken into account. KS and KX are used to represent the possible changing range of γ and χ^p of water and polymer with the effects of the emulsifier and initiator, KS is the percentage of change of γ, KX is the percentage of change of χ^p. KS=1 and KX=1 mean γ and χ^p are not changed.

When the core-shell equilibrium morphology is unchanged in the more greatly changing ranges of KS and KX, the equilibrium morphology is not sensitive to the effects of the emulsifier and initiator. When the equilibrium morphology is unchanged in the less changing ranges of KS and KX, the equilibrium morphology is sensitive to the effects of the emulsifier and initiator. The changing ranges of KS and KX, in which the equilibrium morphology of a core-shell latex is kept unchangeable, represent the sensitivity range for the effects of the emulsifier and initiator. The sensitivity range is defined as the minimum range in the entire minimum interfacial free energy change curve crosslink range.

As an example, a sensitivity analysis of the prediction of the equilibrium morphology on PVAc/PSt and PBA/PSt has been calculated [14]. The calculation results show that the initiator can have great effect on $\Delta\gamma$. The sensitivity range of PVAc/PSt and PBA/PSt can be found in Figures1–4 ($\Delta\gamma$–KS and $\Delta\gamma$–KX curves), which is calculated by effects of the initiator on $\Delta\gamma$.

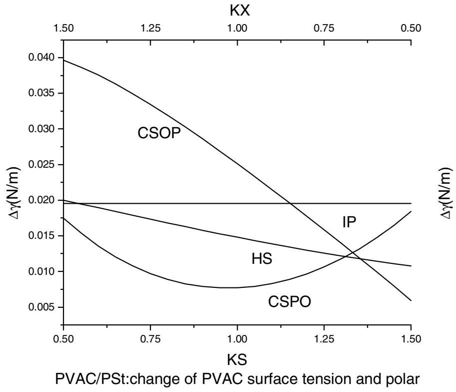


Figure 1. The surface tension and polarity of PVAc changing ±50%

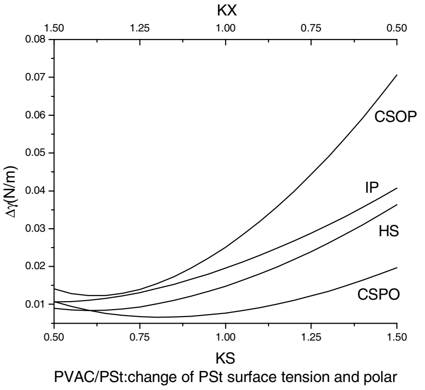


Figure 2. The surface tension and polarity of PSt changing ±50%

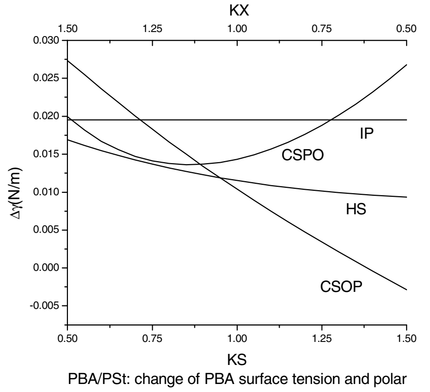


Figure 3. The surface tension and polarity of PBA changing ±50%

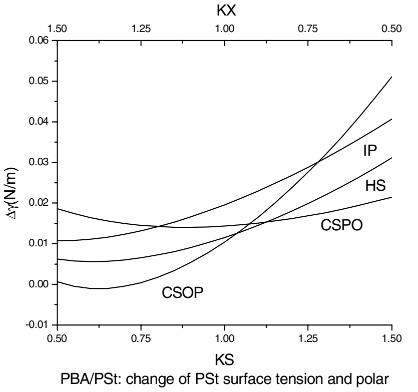


Figure 4. The surface tension and polarity of PSt changing ±50%

Based on the calculation [14], the sensitivity range of PVAc/PSt is (−45%, 30%), which can be easily obtained from Figures 1 and 2, we call it no−sensitivity system, the equilibrium morphology of the latex is not easily changed, inverted core-shell can be gotten, that is PVAc as shell and PSt as core. The sensitivity range of PBA/PSt is (−4%, 10%), which can be easily obtained from Figures 3 and 4, we call it sensitivity system, the equilibrium morphology of the latex is sensitive to initiator, different equilibrium morphologies may be gotten. The experiments on system PVAc/PSt and PBA/PSt are as follows.

Experiment

Materials

Butyl acrylate (BA), styrene (St) was vacuum distilled before use. Vinyl acetate (VAc) was distilled before use. 2,2-azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. All the other chemicals were of analytical grade and used as supplied. Distilled and deionized water(DDIH_2O) was used.

Synthesis of PVAc/PSt and PBA/PSt composite latexes

Eight composite latexes of PVAc/PSt and PBA/PSt were synthesized by two-stage semi-continuous polymerization, the recipe was summarized in Table I. The first stage monomer 1 is VAc or BA, the second stage monomer 2 is St. The types or/and concentration of initiator changed in two stages in which the oil-soluble initiator AIBN and the water-soluble initiator KPS were used respectively, the concentration of which was 0.5% or 2% based on the weight of monomer. All reactions were carried out in a five-necked jacket glass reactor equipped with a stirrer, a reflux condenser, thermocouples, feed inlet, and a nitrogen gas inlet system. Polymerization of the first stage: all ingredients except monomer 1 and initiator were poured into the glass reactor and nitrogen gas was inlet for 10 min to eliminate the residual air. The reaction temperature was raised to 70°C. When KPS used as initiator, added KPS and 5g monomer 1 and reacted for 0.5 hr. Added the rest of the monomer 1 at a certain rate (finished in one hour) and continuously reacted for 2 hours. Then the temperature was raised to 90°C and reacted for 1 hour, resulting in consuming all of the initiator. When AIBN used as initiator, added 5g monomer 1 and pre-emulsified for 0.5 hr. Added the monomer 1 dissolved AIBN at a certain rate (finished in one hour) and then continuously reacted for 2 hours. Then the temperature was raised to 90°C and reacted for 1 hour, resulting in consuming all of the initiator. Polymerization of the second stage: When KPS used as initiator, added KPS to the first stage product at 70°C. Then added monomer 2 at a certain rate (finished in one hour) and continuously reacted for 2 hours. Then temperature was raised to 90°C and reacted for 1 hour, resulting in consuming all of the initiator. When AIBN used as initiator, added 5g monomer 2 to the first stage product at 70°C and pre-emulsified for 0.5 hr. Then added the rest of monomer 2 dissolved AIBN at a certain rate (finished in one hour) and continuously reacted for 2 hours. Then temperature was raised to 90°C and reacted for 1 hour, resulting in consuming all of the initiator.

Table I. Recipe for Synthesis of PVAc/PSt and PBA/PSt composite latexes

	The first stage				The second stage			Other ingredients	
No	Monomer 1 (g)	KPS (g)	AIBN (g)	SDS (g)	Monomer 2 (g)	KPS (g)	AIBN (g)	$NaHCO_3$ (g)	DDIH_2O (g)
1	VAc, 25	0.125		0.5	St, 25		0.125	0.125	150
2	VAc, 25		0.125	0.5	St, 25	0.125		0.125	150
3	VAc, 25	0.5		0.5	St, 25		0.5	0.5	150
4	VAc, 25		0.5	0.5	St, 25	0.5		0.5	150
5	BA, 25	0.125		0.5	St, 25		0.125	0.125	150
6	BA, 25		0.125	0.5	St, 25		0.125	0.125	150
7	BA, 25		0.5	0.5	St, 25	0.5		0.5	150
8	BA, 25	0.5		0.5	St, 25		0.5	0.5	150

The concentration of initiator used in the two stages (based on the weight of monomer) was summarized in Table II.

Table II. The Concentration of Initiator in the Composite Latexes of PVAc/PSt and PBA/PSt

No	The concentration of initiator	No	The concentration of initiator
1	PVAc (0.5%KPS) / PSt (0.5%AIBN)	5	PBA (0.5%KPS) / PSt (0.5%AIBN)
2	PVAc (0.5%AIBN) / PSt (0.5%KPS)	6	PBA (0.5%AIBN) / PSt (0.5%AIBN)
3	PVAc (2%KPS) / PSt (2%AIBN)	7	PBA (2%AIBN) / PSt (2%KPS)
4	PVAc (2%AIBN)/PSt (2%KPS)	8	PBA (2%KPS) / PSt (2%AIBN)

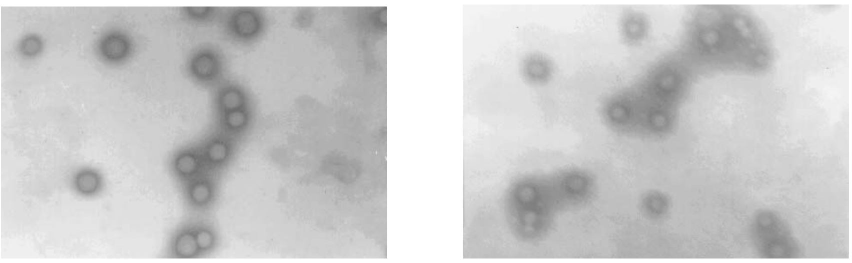
In Table II, PVAc (0.5%KPS) / PSt (0.5%AIBN) in sample No1 represents that the first stage monomer is VAc and the initiator is KPS with a concentration of 0.5% ; the second stage monomer is St and the initiator is AIBN with a concentration of 0.5%. The rest in Table 2 follows the same rule.

After the reaction was finished, the emulsion sample is taken out to investigate the morphology of latex. The particle morphology is observed by TEM of JEM-100CX made in Japan, work voltage 100kV, amplification factor 5,000.

Results and discussion

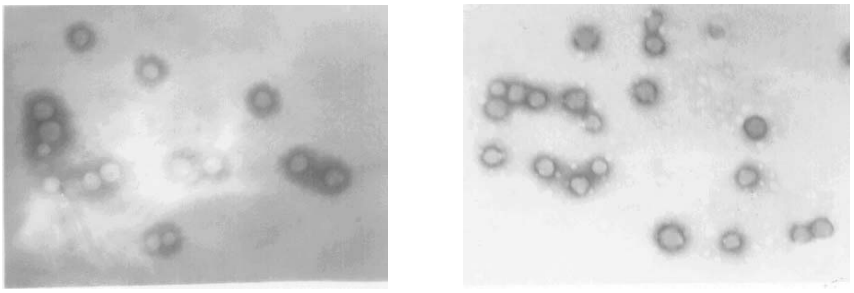
TEM photos of composite latexes particles

In order to obtain the equilibrium morphology, all samples were swelled with toluene at room temperature for 1 week [6]. Swelling of the final composite particle with a solvent should decrease the internal viscosity and allow chain mobility, then the equilibrium particle porphology with the lowest free energy change can be obtained.The photos of TEM in Figure 5 correspond to latexes from samples 1–4.



5-1 TEM photo of particles from sample 1
PVAc (0.5%KPS) / PSt (0.5%AIBN)

5-2 TEM photo of particles from sample 2
PVAc (0.5%AIBN) / PSt (0.5%KPS)



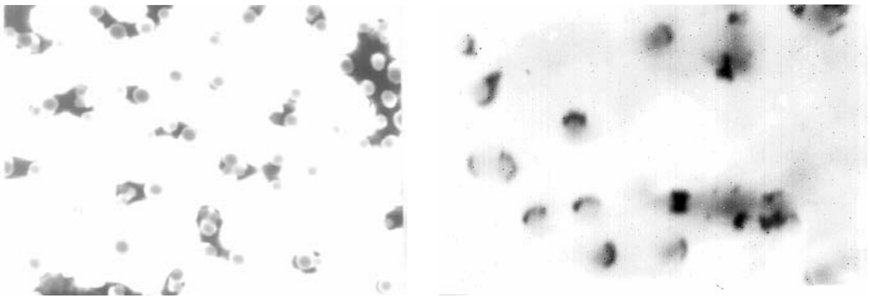
5-3 TEM photo of particles from sample 3
PVAc (2%KPS) / PSt (2%AIBN)

5-4 TEM photo of particles from sample 4
PVAc (2%AIBN)/PSt (2%KPS)

Figure 5. TEM photos of particles in different conditions in PVAc/PSt
Darker Regions are PVAc and Lighter Regions are PSt

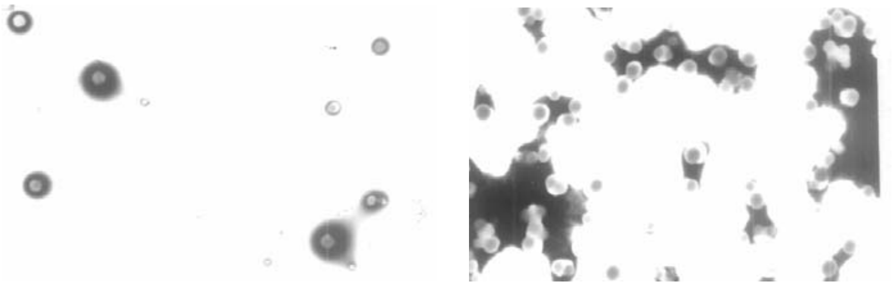
In Figure 5, samples 1–4 was stained by Phosphotungstic acid(PTA). PTA is easily combined with hydrophilic substance, but difficult with hydrophobic substance. The dissolvability of PTA in water is different from in ester [18]. When the concentration of PTA dissolved in water is 1–1.5%, the acidity of the PTA solution is pH=2.0, the dissolvability of PTA in ester is higher than in water, ester is stained by PTA and appears black. Samples 1–4 was stained with PTA 1.5% and pH=2.0, PVAc is stained by PTA and appears black. PSt is unstained by PTA and appears white. From these photos, it was found that the morphologies in system PVAc/PSt did not change even if the initiator changed. The morphologies shown in TEM were all PVAc as shell and PSt as core. So we deduce that this system belonged to no-sensitivity system. The experimental results of literatures [19–21] were consistent with that in this article, the final morphologies were all PVAc as shell and PSt as core.

The photos of TEM in Figure 6 correspond to latexes from samples 5–8.



6-1 TEM photo of particles from sample 5
PBA (0.5%KPS) / PSt (0.5%AIBN)

6-2 TEM photo of particles from sample 6
PBA (0.5%AIBN) / PSt (0.5%AIBN)



6-3 TEM photo of particles from sample 7
PBA (2%AIBN) / PSt (2%KPS)

6-4 TEM photo of particles from sample 8
PBA (2%KPS) / PSt (2%AIBN)

Figure 6 TEM photos of particles in different conditions in PBA/PSt
Darker Regions are PSt and Lighter Regions are PBA

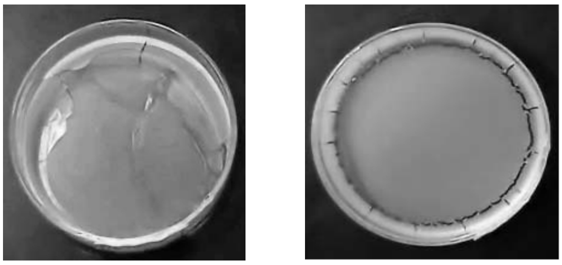
The mass thickness of PSt is greater than that of PBA, if the latex particles of PBA/PSt were non-stained, PSt appears darker, and PBA appears lighter, the color of background is similar as PBA. Figures 6-2 and 6-3 are the photos of Non-stained latex particles of sample 6 and 7 respectively. It can be seen that the morphologies of sample 5 is hemisphere in which darker region is PSt, and the morphologies of sample 6 is core-shell which is PBA as core and PSt as shell.

In Figures 6-1 and 6-4, samples 5 and 8 were stained by PTA. When the concentration of PTA dissolved in water is 1~1.5%, pH of the PTA solution is adjusted by sodium hydroxide(NaOH) to pH=6.4, PTA is presented as sodium phosphotungstate, the dissolvability of sodium phosphotungstate in water is higher than in ester [18], the background is stained by sodium phosphotungstate and appears black. Samples 5 and 8 were stained by PTA, PTA 1.5% and pH=6.4, the morphologies of samples 5 and 8 can be shown in Figures 6-1 and 6-4, which are inverted core-shell, The background is stained and appears black, PSt and PBA unstained, PSt as core appears gray and PBA as shell appears white.

Three kinds of morphologies were prepared in a series of the designed recipes. It was proved that there was great effect on equilibrium morphology in system PBA/PSt by changing initiator. The morphologies reported in literatures [22–26] were more than one kind.

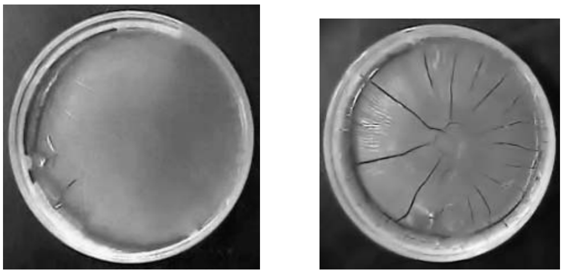
The photos of composite latexes film

The system PBA/PSt is soft-hard monomer pairs. The glass temperatures of the two monomers are quite different. PBA is –55°C and PSt is 100°C. The ability of their film formation is different at room temperature. The film can be easily formed if PBA is located in shell; but otherwise, it is hard. Therefore, the ability of their film formation can be used as an assistant proof to help us decide which monomer is located in core or shell. The appearance of the polymer films from these samples was observed, which was dried at room temperature and 70°C, respectively.



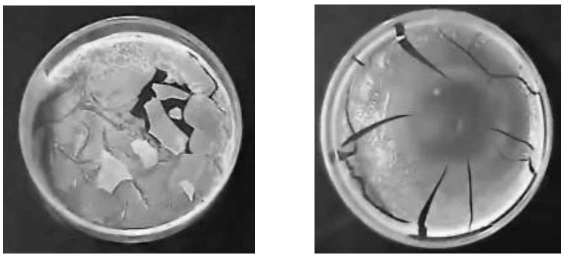
7-1 at 70°C 7-2 at room temperature

Figure 7. The photo of composite latex film drying from sample 5



8-1 at 70°C 8-2 at room temperature

Figure 8. The photo of composite latex film drying from sample 6



9-1 at 70°C 9-2 at room temperature

Figure 9. The photo of composite latex film drying from sample 7

10-1 at 70°C 10-2 at room temperature

Figure 10. The photo of composite latex film drying from sample 8

From these photos, we may deduce that the core of samples 5 and 8 is PSt and the shell is PBA because their films are excellent. The core of sample 7 is PBA and the shell is PSt because it's film could not be formed. Sample 6 may be hemisphere because it's ability of film formation was medium. The conclusion is consistent with the morphology shown in the photos of TEM.

From the calculation and the experiments, it can be seen that initiator has a great effect on interface tensions, and then has a great effect on the thermodynamic equilibrium morphology of composite latex. how does one know the effect of changing the type/or amount of the intiator on the interfacial tensions? The method proposed by Chen et al. [4] can be used. The method is as follows: (a) Preparation of homopolymer latexes by changing the type/or amount of the intiator. (b) Latex surface polarity measured by contact angle method. (c) The interfacial tension measurements of polymer/water interface can be done by drop-weight-voluem method.(d) The interfacial tension of polymer 1 / polymer 2 interface can be calculated by the method proposed by Broseta et al.[27].

Conclusions

When the experiment conditions varied in the systems of PVAc/PSt and PBA/PSt, the types or/and the concentration of initiator changed the same range in the two systems. The oil-soluble initiator 2,2-azobis(isobutyronitrile) (AIBN) and the water-soluble initiator potassium persulfate (KPS) were used in two stages, the concentration of which was 0.5% or 2% based on the weight of monomer, respectively. The equilibrium morphologies obtained in PVAc/PSt are all PVAc as shell and PSt as core, but the equilibrium morphologies obtained in PBA/PSt varies in different conditions, which are core-shell, inverted core-shell and hemisphere. Therefore, PVAc/PSt system belongs to no-sensitivity system and PBA/PSt belongs to sensitivity system. This classification of sensitivity and no-sensitivity system can bring convenience to experiment design for core–shell morphology. As for the sensitivity system, the final morphology may change by adjusting initiator and emulsifier, whereas, for the no-sensitivity system, it is hard to change its final morphology in this way.

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