Study of Particle Morphology in Polymer Emulsions and Their Minimum Film Formation Temperatures

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Synopsis

In the present paper, the emulsion polymerization of methyl methacrylate–butyl acrylate and styrene–ethyl acrylate were carried out. Polymer emulsions with latex particles of different morphology were prepared. The relationship between the minimum film formation temperature of the polymer latexes and the morphology of the latex particles were studied, and the film-forming mechanism of the polymer latexes with varied particle morphology was also discussed.

INTRODUCTION

The minimum film formation temperature (MFT) of a polymer emulsion is the lowest temperature at which the latex particles in the emulsions will coalesce mutually and form a continuous film when the water evaporates. It is an important technical index for polymer latexes. When this temperature is lower than environment temperature, the emulsions cannot be converted into film. When polymer emulsions are used directly as emulsion paints, adhesives, textile finishes, paper impregnants, leather coatings, and cement additives, etc., their operating temperature must be higher than the MFT values of the emulsions. Polymer emulsion is a complicated system; there are many factors which can affect the MFTs of emulsions. First, the MFTs relate to the chemical compositions and molecular structure of the emulsion polymers.[1,2] Second, they relate to the viscosity, surface tension, and pH of emulsions, and to the type and the amount of the emulsifiers, protective colloids, and other additives used.[3,4] Furthermore, they bear a relationship with environment temperature, humidity, and the nature of film-forming substrates.[4,5] Meanwhile, the size, the size distribution,[6] and the morphology of the latex particles can also considerably affect the MFTs of emulsions.[2,7–9] If other conditions are all constant, there may be a great difference in MFTs when the morphology of the latex particles is different. Therefore, we can produce polymer emulsions with a variety of particle morphologies by using different synthetic technology. The polymer latexes with lower MFT values may be obtained under the constant ingredient conditions. Thus, the processability of the polymer emulsions will be markedly improved. In addition, changing the morphology of the latex particles can impart

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to emulsion polymers excellent physical properties and some specific characteristics.[10–16]

In the current work, polymer emulsions having latex particles of distinct morphology are prepared. Their film-forming mechanism is studied, and the relationship between the MFTs of the polymer emulsions and the morphology of latex particles is also discussed.

EXPERIMENTAL

In these experiments, the monomers used were all industrial grade. They were vacuum-distilled prior to use. The initiator ammonium persulfate (APS) and emulsifier sodium lauryl sulfate (SDS) of analytically pure grade were used without further purification. The emulsion polymerizations of several monomer systems, i.e., methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), ethyl acrylate (EA), methyl methacrylate–butyl acrylate (MMA–BA), and styrene–ethyl acrylate (St–EA) were carried out. The polymer emulsions with their respective latex particles of different morphology were prepared. The recipes for preparing the polymer emulsions mentioned above are listed in Table I.

The emulsion polymerization was carried out in a 250-mL four-neck flask equipped with stirrer, heat exchanger, thermometer, thermostat, and feed funnel. The reaction temperature was 70°C. In order to ensure stabilization of the emulsion systems, the technology for supplementing emulsifier was adopted. The amount of the emulsifier supplemented at intervals of time was predicted by means of computer in accordance with the mathematical model programmed for this purpose.

MFTs of the polymer latexes were measured by use of QMB instrument for determining minimum film formation temperature. The morphology of latex particles was observed by Philips EM-400ST transmission electron microscope.

RESULTS AND DISCUSSION

MMA–BA System

In order to illustrate the effect of the particle morphology on the MFTs, the polymer emulsions with homopolymer, homogeneous copolymer, and core-shell

TABLE I
Recipes for Preparing the Polymer Emulsions

Ingredients	Ratio (part by weight)					
	PMMA	PBA	PSt	PEA	MMA–BA system	St–EA system
MMA	100	—	—	—	x	—
BA	—	100	—	—	100-x	—
St	—	—	100	—	—	x
EA	—	—	—	100	—	100-x
SDS	3.44	3.44	3.44	3.44	3.44	3.44
APS	0.4	0.4	0.4	0.4	0.4	0.4
Distilled water	150	150	150	150	150	150

latex particles were prepared for the MMA–BA system. The two-stage polymerization method was used for preparation of the emulsions with core-shell particles, namely, BA was added in the first stage and MMA in the second stage (IBA/IIMMA). The MFTs were measured for the emulsions (mentioned above) and for the blend emulsions; the latter were produced by mixing MMA and BA homopolymer emulsions in definite ratios. The results measured are shown in Figure 1.

It can be seen from Figure 1 that the MFTs of the emulsions of homogeneous copolymer increase gradually (curve 3) while increasing in the amount of hard component MMA. This results from the gradual rising of the contributions of hard component to MFTs. The MFTs of the blend emulsions change dramatically in the range of 62–65% MMA. This is because when the amount of PMMA in the blend polymer is less than 62%, the soft component PBA becomes continuous phase in the film (curve 2). Therefore the MFTs are very low (< 0°C). But, when the amount of PMMA is greater than 65%, the hard component PMMA becomes continuous phase in the film. Thus, the MFTs are considerably high (> 100°C).

For IBA/IIMMA emulsions, the MFTs (curve 1, Fig. 1) are much higher than those of both the emulsions having homogeneous copolymer particles and the blend emulsions with the same compositions. This shows that the internally soft and externally hard core-shell latex particles are formed. This is also proved electron-microscopically (see Fig. 2). Figure 2(a) shows the photo of the PMMA homopolymer latex particles. Because PMMA is a hard component, such that the particles do not deform during the process of making the plates for microscopy, the images of the latex particles appear as more regularly spherical. Figure 2(b) shows the photo of the PBA homopolymer latex particles. Because PBA is a soft component, such that the particles deform during the process of making the plates for microscopy, the images of the latex particles appear much more irregular in form. Figure 2(c) is the photo of IBA/IIMMA latex particles. The images appear as regular spheres. This shows that the core of the particles

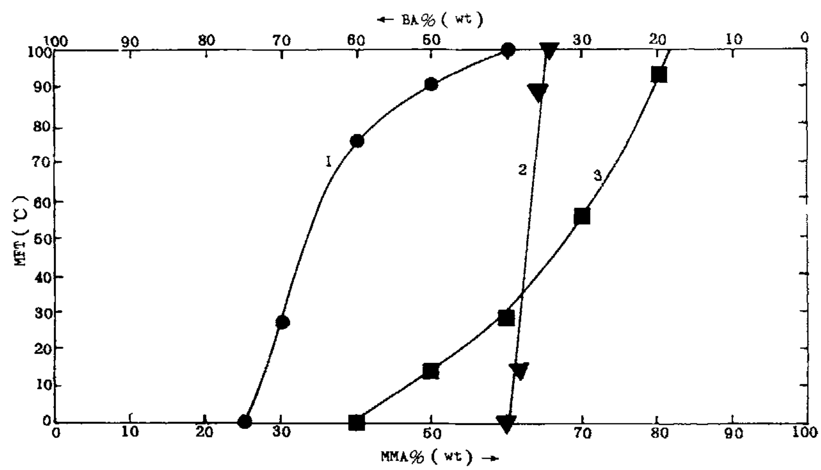
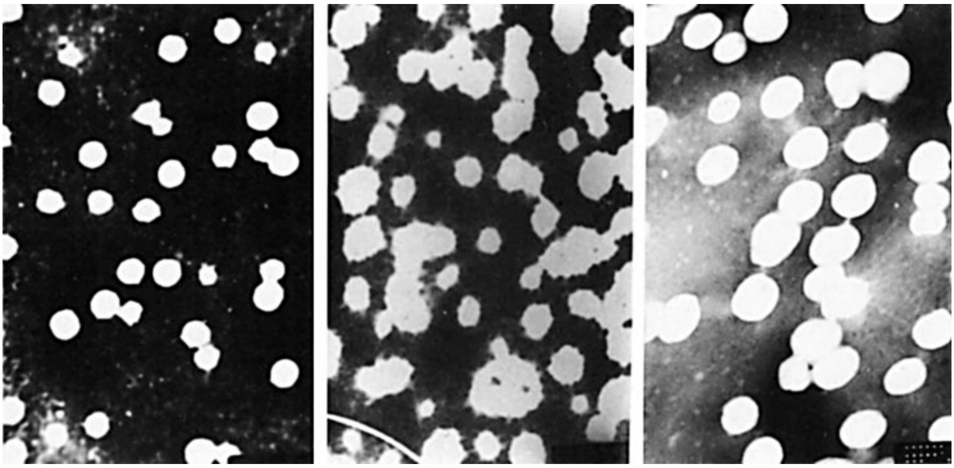


Fig. 1. Curves of polymer compositions in different morphology particles *vs.* MFTs of emulsions for the MMA–BA system: (●) IBA/IIMMA; (▼) blend; (■) copolymer.



(a) (b) (c)

Fig. 2. Electron microscope images of latex particles for the MMA–BA system: (a) PMMA homopolymer latex particles; (b) PBA homopolymer latex particles; (c) IBA/IIMMA latex particles (PMMA : PBA = 50 : 50 wt).

is the soft component PBA, while the hard component PMMA surrounds the PBA core to form a hard shell. In this case, the particles cannot deform during preparation of the plates for microscopy. As a result, the images have distinct edges and more regular form. In order to form film for the polymer emulsions with core-shell latex particles, it is necessary to increase temperature so that the polymer constructing the shell of the particles deforms, allowing them to permeate and penetrate each other. Because the shell of IBA/IIMMA particles is PMMA, which is of rather high glass transition temperature (T_g = 105°C), it requires a higher temperature to form film. Therefore the MFTs of IBA/IIMMA emulsions are much higher than those of the copolymer emulsions and blend emulsions with the same compositions as shown in Figure 1.

In addition, the polymer emulsions with gradient structure particles, which transit gradually both from internally soft to externally hard and from internally hard to externally soft, were prepared by gradually changing the feed compositions according to the fixed program. The MFTs measured are shown in Figure 3. Because the outer layer of the latex particles in transition from internally soft to externally hard is enriched with hard component so that the latter contributes more to film formation, their MFTs are higher than those of the homogeneous copolymer emulsions with the same ingredients as shown by curve 3. in Figure 3. On the contrary, for polymer emulsions with latex particles in transition from internally hard to externally soft, the MFTs are lower than those of the homogeneous copolymer emulsions with the same ingredients as shown by curves 2 and 3 in Figure 3.

St–EA System

The polymer emulsions with homopolymer and homogeneous copolymer latex particles were prepared for the St–EA system. The following two types of lattices

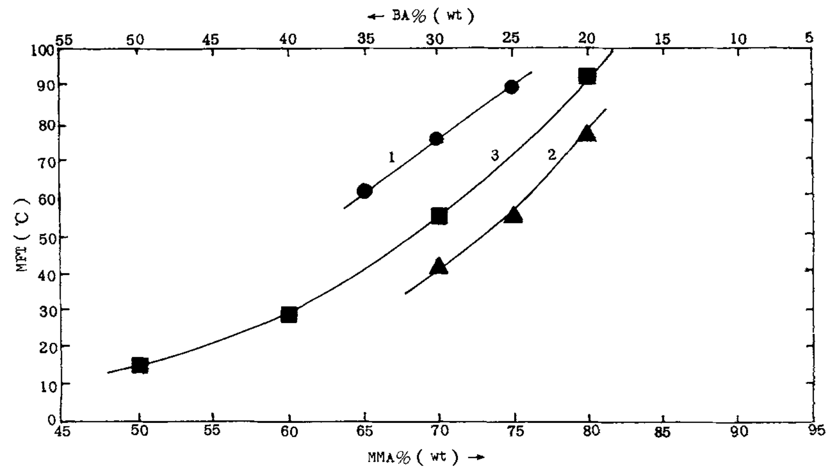


Fig. 3. Curves of polymer compositions in gradient latex particles *vs.* MFTs of emulsions for the MMA–BA system: (●) from internally soft to externally hard; (▲) from internally hard to externally soft; (■) homogeneous copolymer latexes.

were also produced by use of two-stage polymerization technique. With the first, EA is added in the first stage; after reacting completely St is charged in the second stage. These emulsions can be abbreviated to IEA/IISt. The second lattice is produced as follows: St is added in the first stage, and after reacting completely, EA is charged in the second stage. These emulsions can be abbreviated to ISt/IIEA. The experimental data for the MFTs of the emulsions versus the compositions are shown in Figure 4.

It can be seen from Figure 4 that, in common with MMA–BA system, the MFTs of blend emulsions change dramatically with the compositions for St–EA system (curve 1), while the MFTs of the homogeneous copolymer emulsions increase smoothly as increasing the hard component St (curve 2).

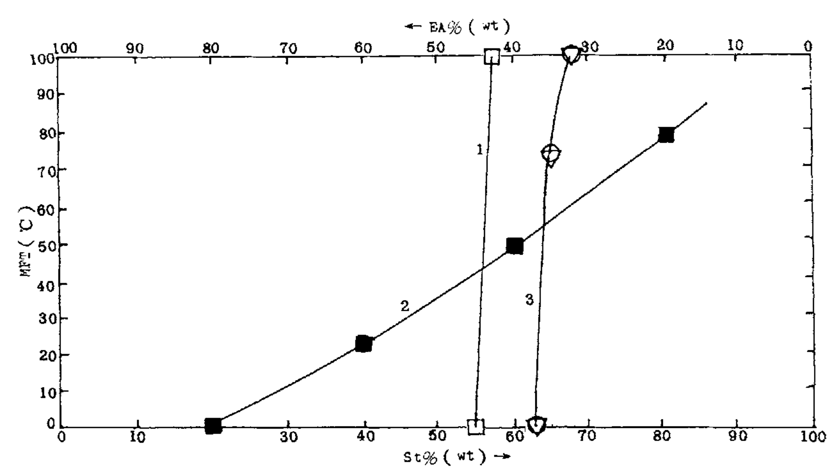


Fig. 4. Curves of polymer compositions in different morphology particles *vs.* MFTs of emulsions for the St–EA system: (□) blend; (■) copolymer; (▽) IEA/IISt; (○) ISt/IIEA.

Our experiments have shown that the composition–MFT curves of both IEA/IISt and ISt/IIEA coincide with each other almost completely (Fig. 4, curve 3). In other words, when the emulsion polymerizations in two stages are carried out for styrene–ethyl acrylate system, in spite of the fact that styrene is added in the first stage (ethyl acrylate in the second stage) or ethyl acrylate is added in the first stage (styrene in the second stage), the MFTs measured are almost all the same under the constant composition conditions. The data for this are listed in Table II.

It can be also seen from Figure 4 that in a wide composition range (St% = 20–62.5%), the MFTs of both IEA/IISt and ISt/IIEA emulsions are remarkably lower than those of the homogeneous copolymer emulsion (Fig. 4, curves 2 and 3). Figure 4 thus shows that the outer layer of the latex particles in both IEA/IISt and ISt/IIEA emulsions is enriched with the soft composition (PEA). Namely, in these two cases, the latex particles with internally hard and externally soft core-shell structure are both formed. This is demonstrated in the photos obtained by electron microscope for these two types of polymer emulsion, as shown in Figure 5.

Figure 5(a) shows the photo of the St homopolymer latex particles. It appears as black on the image. Figure 5(b) shows the photo of EA homopolymer latex particles. It appears as white on the image. Figures 5(c) and 5(d) show the photos of ISt/IIEA and IEA/IISt latex particles by using two-stage emulsion polymerization. It is found that in the latter two photos the interior region of the particle images appears black, while the exterior region appears white. Moreover, there is a more distinct separation between the shell and core. This suggests that the core of the latex particles is polystyrene, but that the shell is polyethyl acrylate. In other words, when the two-stage emulsion polymerization is carried out for St–EA system, regardless of the charging sequence, the latex particles are all of internally hard and externally soft structure.

Because the hydrophobicity of styrene is much greater than that of ethyl acrylate (the solubility of styrene in water at 25°C is 0.027%, while that of ethyl acrylate 1.5%), styrene tends to permeate into the interior region of the latex particles. It is polymerized as far from aqueous phase as possible. Besides, styrene is also able to polymerize on the surface of the latex particles to form polystyrene at first, and then phase separation occurs. Namely, the polystyrene formed diffuses into the interior of the latex particles. This may be called "inverting phenomenon".[17,18] Thus when the polymerizations are carried out in two stages for St–EA system, regardless of charging sequence, polystyrene is always located in the interior of the latex particles to become the core of the particles, while polyethyl acrylate is always situated in the outer layer of the

TABLE II
The MFT's of the Emulsions Under Different Composition Conditions in the Case of Two-Stage Reactions

Compositions St/EA (wt)		45/55	50/50	55/45	60/40	62.5/37.5	65/35	67.5/32.5	70/30
MFT	ISt/IIEA	< 0	< 0	< 0	< 0	< 0	73.1	> 100	> 100
(°C)	IEA/IISt	< 0	< 0	< 0	< 0	< 0	72.3	> 100	> 100

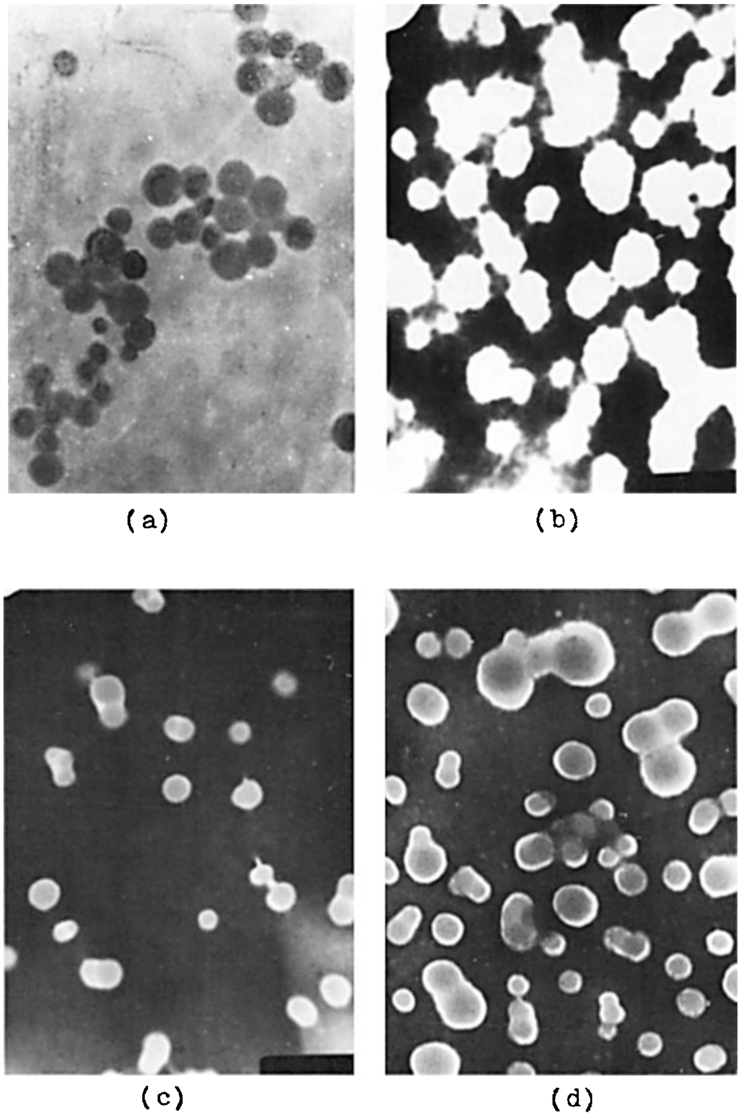


Fig. 5. Electron microscope images of latex particles for the St–EA system: (a) PSt homopolymer latex particles; (b) PBA homopolymer latex particles; (c) ISt/IIEA latex particles; (d) IEA/IISt latex particles.

particles to form the shell of the particles. As a result, both ISt/IIEA and IEA/IISt form the polymer emulsions with internally hard and externally soft core-shell latex particles.

CONCLUSION

The morphology of the latex particles seriously affects the MFTs of the emulsions. In the case of the emulsions with homogeneous copolymer latex particles, the MFTs increase smoothly as increasing in hard compositions. While for the blend emulsions prepared by mixing two homopolymer emulsions, the MFTs change dramatically in a very narrow range of compositions. When the outer layer of core-shell latex particles is made up of a hard component or when the outer layer of the gradient latex particles is enriched with hard component, the MFTs are much greater than those of the homogeneous copolymer emulsions with the same compositions, and vice versa.

Our experiments have shown that, according to the measured MFTs and electron microscopy, both ISt/IIEA and IEA/IISt emulsions have internally hard and externally soft core-shell latex particles. This is a result of the inverting phenomenon.

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