Preparation of Epoxy Resin/Acrylic Composite Latexes by Miniemulsion Polymerization Method

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ABSTRACT: Epoxy resin/acrylic composite latexes were prepared by miniemulsion polymerization. Epoxy resins have a functional epoxy group in them and excellent characteristics, such as heat resistance and good adhesion. Acrylic latexes have weather and water resistance. Combining the epoxy resin and the acrylic latex was an attempt to actualize these advantages. The miniemulsion polymerization method was effective in obtaining the composite latex. A less than 500-nm droplet size for the monomer preemulsion was necessary to obtain the latex in a stable manner. Dimethylaminoethylmethacrylate and methacrylic acid as the reactive functional monomer with an epoxy group were introduced to the latexes. The effect of the polymerization method of these functional groups on the properties of latexes and their films was investigated. The latex prepared by the two-stage polymerization method had good polymerization stability, storage stability, and solvent resistance. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 128–133, 2001

Key words: miniemulsion; homogenize; droplet size; epoxy resin; acrylic latex; particle morphology

INTRODUCTION

Acrylic or acrylic-styrene latexes are widely used for paints, coatings, textiles, nonwoven fabrics, adhesives, polishes, waxes, graphic arts, paper, sealants, cement additives, and other applications. Acrylic latexes have hydrolytic, light, and oxidative stability.[1] Epoxy resins have functional epoxy groups in them and have subsequent excellent characteristics, such as heat resistance and good adhesion.[2]

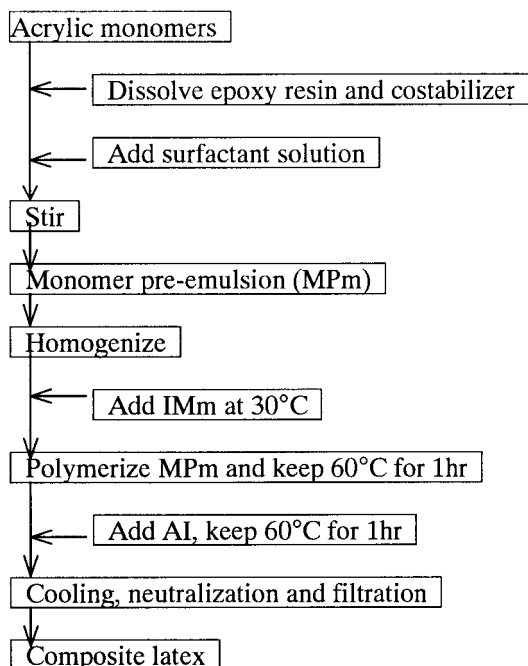We combined epoxy resin with acrylic latexes to try to actualize these advantages. However, in emulsion polymerization it was difficult to polymerize the acrylic monomer in the presence of the epoxy resin. As is well known, the monomer must have solubility in water; however, epoxy resins are quite insoluble.[3–6] Thus, the miniemulsion polymerization method was used to prepare the composite latexes.[7–9]

Emulsions can be classified into three categories based on their droplet size: macroemulsions, miniemulsions, and microemulsions. Macroemulsions contain droplets with average diameters greater than 1 μm. A typical preparation method for a macroemulsion is making a milky, opaque emulsion by the agitation mixture of a surfactant (ionic and/or nonionic), oil, and water. The emulsions separate rapidly after standing. The insta-

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Acrylic monomers

→ Dissolve epoxy resin and costabilizer

→ Add surfactant solution

Stir

Monomer pre-emulsion (MPm)

Homogenize

→ Add IMm at 30°C

Polymerize MPm and keep 60°C for 1hr

→ Add AI, keep 60°C for 1hr

Cooling, neutralization and filtration

Composite latex

Figure 1 A flowchart of miniemulsion polymerization.

bility of the emulsions is due to a reduction of the interfacial area by droplet degradation and the decrease of the free energy of the systems. The surfactant lowers the interfacial tension between the oil and water phases and also provides either steric or electrostatic stabilization for the oil droplets.

Microemulsions have droplets that are less than 50 nm in diameter. They are prepared with an ionic surfactant and a short chain alcohol. Usually, large amounts of surfactant are used in their preparation. They tend to appear clear and translucent because of their extremely small droplet size. Microemulsions are formed spontaneously and are thermodynamically stable.

Miniemulsions have droplet sizes between 50 and 500 nm and appear opaque and milky. Miniemulsions are typically formed by subjecting the oil/water/surfactant/costabilizer system to a high shear field created by devices. Typical costabilizers employed in miniemulsion systems are fatty alcohols or long chain alkanes.[10,11] Miniemulsions in which polymerizable monomers were included as oil droplets were polymerized by adding initiators. In miniemulsion polymerization, nucleation can take place in the monomer droplets. Therefore, a hydrophobic epoxy resin may relatively easily composite with acrylic latexes by miniemulsion polymerization.
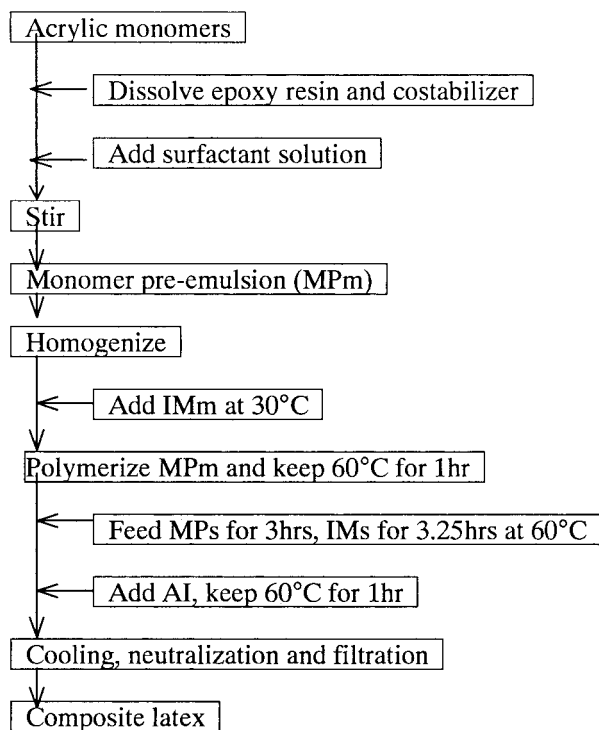
EXPERIMENTAL

Materials

Technical grade reagents were used. Epicron® 850 (Ep850, Dainippon Ink & Chemicals, Inc.) is one of the bisphenol A diglycidyl ethers, and its epoxy equivalent weight is about 190. n-Butylacrylate and methylmethacrylate (MMA) were used as the acrylic monomers. Methacrylic acid (MAA) and dimethylaminoethylmethacrylate (DMAEMA) were used as the functional acrylic monomers. Emulgen® 931 (polyoxyethylene alkylphenylether, HLB 17.2, Kao Corporation) was used as a nonionic surfactant. Levenol® WZ (polyoxyethylene alkylphenylether sulfate sodium salt, Kao Corporation) was used as an anionic surfactant. n-Hexadecane was used as a costabilizer. Sodium persulfate and t-butyl hydroperoxide were used as initiators. Iron(III) chloride 6-hydrate and sodium formaldehyde sulfoxylate were used as the initiation accelerators (Redox initiator system). An ammonia solution was used for the neutralization for the latex. Distilled and deionized water was used throughout all experiments arranged here.

Table I   Typical Experimental Recipe of Miniemulsion Polymerization

	Weight Ratio
Monomer Preemulsion (MPm)	
nBA	18.0
MMA	17.0
Ep850	3.0
nHD	1.4
Levenol WZ	1.4
Emulgen 931	1.4
DDI water	25.0
DDI water	90.0
Initiators (IMm)	
0.75% FeCl$_3$ 6H$_2$O solution	0.2
10% SFS solution	2.0
10% NaPS solution	2.0
Additional initiator	
10% TBHPO solution	0.5
Neutralizing agent	
10% Ammonia solution	Neutralize to pH 7.5–8.5

nBA, n-Butylacrylate; nHD, n-hexadecane; DDI, distilled and deionized water; SFS, sodium formaldehyde sulfoxylate; NaPS, sodium persulfate; TBHPO, t-butyl hydroperoxide.

Acrylic monomers

↓ ← Dissolve epoxy resin and costabilizer

↓ ← Add surfactant solution

Stir

↓

Monomer pre-emulsion (MPm)

↓

Homogenize

↓ ← Add IMm at 30°C

Polymerize MPm and keep 60°C for 1hr

↓ ← Feed MPs for 3hrs, IMs for 3.25hrs at 60°C

↓ ← Add AI, keep 60°C for 1hr

↓

Cooling, neutralization and filtration

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Composite latex

Figure 2   A flowchart of two-stage emulsion polymerization.

Preparation of Composite Latex by Miniemulsion Polymerization

All polymerizations were carried out with a redox initiator system in a stainless steel vessel equipped with a stirrer, reflux condenser, thermometer, and an inlet system for nitrogen, monomer preemulsion, and initiators.

A typical procedure for latex production is shown in Figure 1. The monomer preemulsion (MPm, used for the miniemulsion polymerization) was prepared by stirring the mixture of epoxy resin, acrylic monomers, surfactants, costabilizer, and water. The MPm was homogenized by a TK Homomixer® (type M, Tokushukika Kogyo Co., Ltd.). The polymerization was carried out by adding the initiators to the reactor (IMm, used for MPm) at 30°C in an atmosphere of nitrogen. Then, the temperature of the system was kept at 60°C for 1 h with a water bath. Additional initiator solution (AI) was added. One hour later the system was cooled and neutralized by an ammonia solution. The latex formed in the reactor was filtered by nylon mesh, and the amount of coagulum was weighed. A typical experimental recipe is shown in Table I.

Introduction of Functional Groups to Composite Latex: Batch Polymerization Method

MAA and/or DMAEMA were added to the MPm to introduce the functional groups to the composite latexes. Then the microemulsion polymerization was carried out (mentioned above). The polymerization stability, storage stability of the latex, and solvent resistance of their films were investigated. The stability in the polymerization was investigated by measuring the amount of coagulum after preparation of the latexes was finished. The storage stability of the latexes was investigated by the observation of the coagulation or viscosity of the latexes for 30 days at 50°C. The solvent resistance of the latex films was investigated by the xylene rubbing test. The test load

Table II   Typical Experimental Recipe of Two-Stage Emulsion Polymerization

	Weight Ratio
Monomer Preemulsion (MPm)	
nBA	18.0
MMA	17.0
Ep850	3.0
nHD	1.4
Levenol WZ	1.4
Emulgen 931	1.4
DDI water	25.0
DDI water	90.0
Initiators (IMm)	
0.75% FeCl$_3$ 6H$_2$O solution	0.2
10% SFS solution	2.0
10% NaPS solution	2.0
Monomer Preemulsion (MPs)	
nBA	33.0
MMA	30.5
MAA	1.5
DMAEMA	1.0
Levenol WZ	2.6
Emulgen 931	2.6
DDI water	30.0
Initiators (IMs)	
10% SFS solution	3.0
10% NaPS solution	3.0
Additional initiator	
10% TBHPO solution	0.5
Neutralizing agent	
10% ammonia solution	Neutralize to pH 7.5–8.5

nBA, n-Butylacrylate; nHD, n-hexadecane; DDI, distilled and deionized water; SFS, sodium formaldehyde sulfoxylate; NaPS, sodium persulfate; TBHPO, t-butyl hydroperoxide.
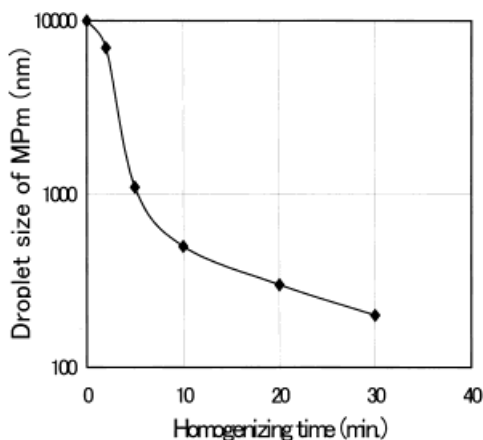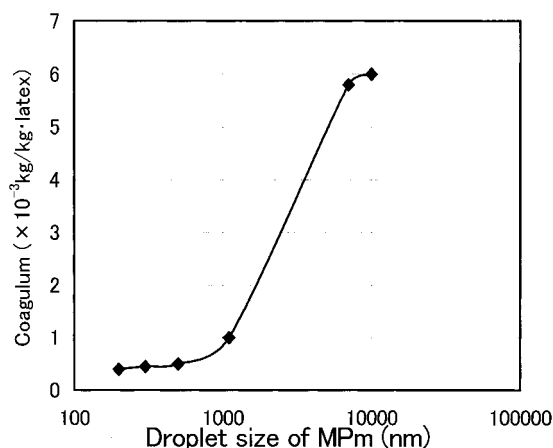
Figure 3   The relationship between the homogenizing time and the droplet size of MPm.

Figure 4   The effect of the droplet size of MPm on the stability of polymerization.

was 1 kg. The films were rubbed 100 times and evaluated. The films were made by a 0.254-mm applicator on a glass plate and drying at 20–25°C (55–65% relative humidity) for 24 h.

Introduction of Functional Groups to Composite Latex: Two-Stage Polymerization Method

The two-stage polymerization method was used. In the first stage of polymerization, miniemulsion polymerization (mentioned above) was used to obtain the seed particle. Semicontinuous polymerization was carried out in the second stage. The monomer preemulsion (MP, used for semicontinuous polymerization and prepared by stirring a mixture of acrylic monomers, surfactants, and water) and initiator solution (IMs, used for MPs) were added into the seed latex for 3 and 3.25 h, respectively. A flowchart of two-stage polymerization is shown in Figure 2.

The functional monomers were introduced to the MPm or MPs. The typical experimental recipe is shown in Table II. In Table II, MAA and DMAEMA are introduced to MPs as the functional monomers. The latexes were investigated for polymerization stability, storage stability, and

solvent resistance of their films (mentioned above).

RESULTS AND DISCUSSION

Effect of Droplet Size of MPm on Polymerization Stability

The droplet size of the MPm was controlled by varying the homogenization time (12,000 rpm rotation speed). The effect of the homogenization time on the droplet size of the MPm is shown in Figure 3. The droplet size of the MPm ($>1~\mu$m) was measured using optical microscopy. The droplet size of the MPm ($<1~\mu$m) and the particle sizes of the latexes were measured by a Microtrac® particle size analyzer (model UPA150, Honeywell, Inc.) at room temperature.

The effects of the droplet size of the MPm on the polymerization stability and particle size of the latex are shown in Figure 4 and Table III, respectively. The droplet of the MPm that were more than 1 μm obstructed the preparation of the latexes. In this case, particle initiation did not

Table III   Relationship between Droplet Size of MPm and Particle Size of Latexes

	Homogenization Condition	
	4,000/rpm 30/min	12,000/rpm 30/min
Average droplet size of MPm (nm)	2913	326
Particle size of latex (nm)	86 (76%), 1945 (24%) (bimodal)	289 (90%), 1635 (10%) (bimodal)

Table IV   Effect of Functional Groups on Properties of Latexes and Their Films with Batch Polymerization Method

Functional Groups	Polymerization Stability	Storage Stability	Solvent Resistance
Epoxy	Good	Good	Poor
Epoxy/DMAEMA	Good	Coagulation	Good
Epoxy/MAA	Good	Coagulation	Poor
Epoxy/MAA/DMAEMA	Coagulation	—	—

occur in the monomer droplet and the epoxy resin was not hybridized and was coagulated. The MPm droplet of less than 500 nm was useful to obtain the latex in a stable manner. In Table III the latex prepared by polymerization of a fine miniemulsion has a larger particle than that of a coarse miniemulsion. Particle initiation partially occurred in the fine monomer droplet, and the epoxy resin was effectively combined with the acrylic polymer particle.

Effect of Functional Groups on Properties of Latexes and Their Films for Batch Polymerization Method

The effect of the functional groups on the properties of the latexes and their films is shown in Table IV. Not all of the properties of the latexes or their films were good (Table IV). It was expected that the epoxy groups would react with the amino or acid groups during storage or polymerization.

Effect of Functional Groups on Properties of Latexes and Their Films for Two-Stage Polymerization Method

The effect of the location of the functional groups in the latex particle on the properties of the latexes and their films is shown in Table V. The location of the functional groups was controlled by

introducing the functional monomers to the MPm or MPs. Because the MPm and MPs contained the epoxy resin, and MAA and DMAEMA, respectively, the latex prepared by the two-stage polymerization method had good polymerization stability, storage stability, and solvent resistance. The epoxy resin was a hydrophobic material, and carboxylic acid and amino groups supplied with MAA and DMAEMA were hydrophilic groups. In the latex the epoxy group did not actively interact with MAA or DMAEMA, so the storage stability became good. Good solvent resistance was obtained, because the epoxy groups reacted with carboxylic acid or amino groups in the film formation. A schematic diagram of the crosslinking reaction of the latex at film formation is shown in Figure 5. It was interesting that the properties of the latexes and their films were changed by the location of the functional groups. A one-packed ambient curing coating system has few prospects for the preparation of a high performance latex.

CONCLUSION

1. A MPm droplet size of less than 500 nm was necessary to obtain the latex in a stable manner.
2. Particle initiation partially occurred in the fine monomer droplet (<500 nm), and the

Table V   Effect of Functional Groups on Properties of Latexes and Their Films with Two-Stage Polymerization Method

Functional Groups		Polymerization Stability	Storage Stability	Solvent Resistance
MPm	MPs			
Epoxy	MAA/DMAEMA	Good	Good	Good
Epoxy/DMAEMA	MAA	Good	Good	Fair
Epoxy/MAA	MAA/DMAEMA	Good	Coagulation	Good
Epoxy/MAA/DMAEMA	None	Coagulation	—	—
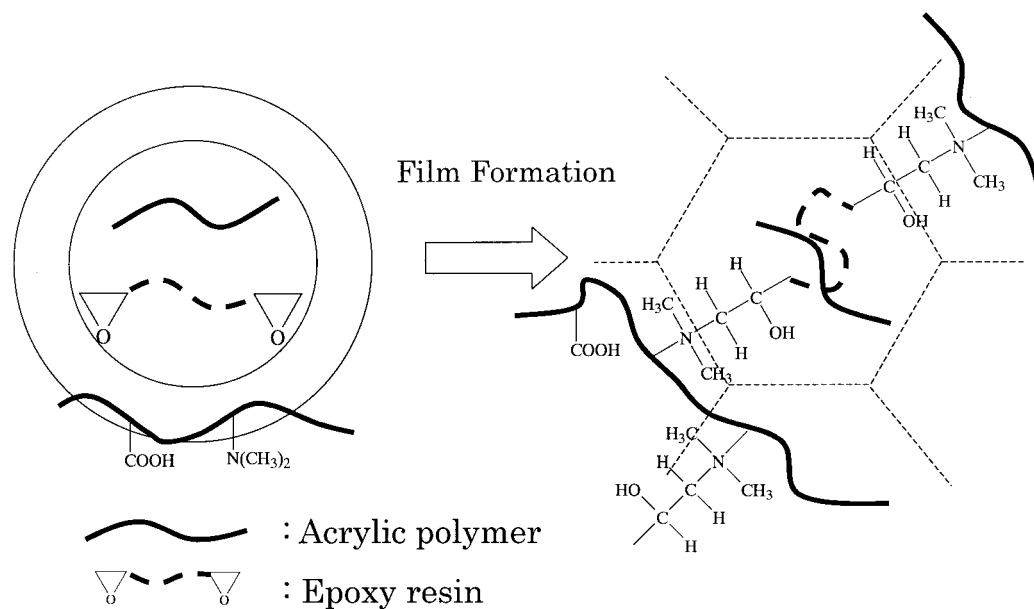
Figure 5   A schematic diagram of the crosslinking reaction.

epoxy resin was effectively combined with an acrylic polymer particle.

3. The latex prepared by the two-stage polymerization method with intentionally introduced functional groups had good polymerization stability, storage stability, and solvent resistance.

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