

Production of Polymer Particles with Ethyleneurea Groups by Emulsifier-Free Emulsion Polymerization and the Wet Adhesion Property of the Emulsion Film

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ABSTRACT: A film was prepared from an *n*-butyl methacrylate/methacrylamide ethylethyleneurea (EU) copolymer [P(BMA–EU)] emulsion produced by an emulsifier-free emulsion copolymerization. The wet adhesion of the emulsion film on an alkyd resin was significantly improved by copolymerization with a small amount of EU (0.5–1.0 mol %). A sodium dodecyl sulfate emulsifier, postadded to the emulsifier-free emulsion, reduced the wet adhesion. The wet adhesion of a film prepared from a poly(*n*-butyl methacrylate) (PBMA)/P(BMA–EU) composite emulsion produced

by an emulsifier-free seeded emulsion copolymerization with PBMA seed particles was higher than that of a P(BMA–EU) film with the same EU content. The localization of EU and the cleanliness at the particle surface were also key factors in the improvement of the wet adhesion of the polymer emulsion film. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1825–1829, 2003

Key words: adhesion; emulsion polymerization; films; core-shell polymers

INTRODUCTION

Large amounts of volatile organic compounds are used to prepare oil-based paints. Waterborne paints have been used in place of oil-based paints, which have an adverse influence on the environment. However, waterborne paints display low adhesion under wet conditions because of hydrophilic components. Wet adhesion can significantly be improved with certain monomers called *wet adhesion monomers*,¹ such as monomers with ethyleneurea groups, including methacrylamide ethylethyleneurea (EU).^{2–4} In fact, the wet adhesion of emulsion films can be improved by the introduction of EU to polymer particles by emulsion polymerization.^{5,6}

In a general emulsion polymerization, an emulsifier is used to provide polymerization loci and to stabilize growing particles. However, the existence of an emulsifier at the particle surfaces reduces the wet adhesion because the emulsifier reduces the water resistance of the emulsion film.^{7,8} Therefore, it is expected that the wet adhesion of an emulsion

film can be improved with an emulsifier-free emulsion polymerization.

In this article, we show that films cast from polymer emulsions, produced by an emulsifier-free emulsion polymerization with the EU component localized predominantly at the particle surfaces,⁷ show a high degree of wet adhesion.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA) was purified by distillation under reduced pressure. EU was purified from Sipomer Wam-II (Rhodia Nicca, Tokyo, Japan), which has been commercialized as a mixture of EU (50%), methacrylic acid (20%), and water (30%), as follows. Calcium chloride and water were added to Sipomer Wam-II, and the mixture was kept in a refrigerator for 1 day; then, the precipitate in the mixture was removed by filtration. After the water was removed, EU was recrystallized from acetone as a white powder (mp = 114.5–117°C). The EU powder was dissolved in water, and the residues were filtered; a 40.3 wt % EU aqueous solution was prepared. Extrapure reagent potassium persulfate (KPS; Nacalai Tesque, Inc., Kyoto, Japan) was purified by recrystallization. Reagent-grade sodium dodecyl sulfate (SDS; Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used as received.

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TABLE I
Recipes for the Production of P(BMA–EU) Particles by Emulsifier-Free Emulsion Copolymerizations^a

Ingredient	EU content (mol %)		
	0.25	0.5	1.0
BMA (g)	14.95	14.90	14.80
EU ^b (g)	0.05	0.10	0.20
KPS (g)	0.30	0.30	0.30
Water (g)	285	285	285
D_h^c (nm)	423	514	562

^a In flask; N₂; 70°C; 12 h; stirring rate = 160 rpm.

^b Used as aqueous solution (40.3 wt %).

^c Hydrodynamic diameter measured by dynamic light scattering.

BMA–EU copolymer [P(BMA–EU)] particles

P(BMA–EU) particles were produced by an emulsifier-free emulsion copolymerization under the conditions listed in Table I. In the following experiments, the P(BMA–EU) emulsion, which was centrifugally washed three times with distilled water, was used.

Poly(*n*-butyl methacrylate) (PBMA)/P(BMA–EU) composite particles

First, PBMA seed particles were produced by an emulsifier-free emulsion polymerization under the conditions listed in Table II. PBMA/P(BMA–EU) composite particles were produced by an emulsifier-free seeded emulsion copolymerization of BMA and EU with the PBMA seed particles under the conditions listed in Table II as follows. BMA and a 40.3 wt % EU aqueous solution were added to the PBMA seed emulsion, and then the emulsion was stirred at 70°C for 30 min before a KPS aqueous solution was added to a 500-mL, four-necked flask. In the following experiments, the PBMA/P(BMA–EU) composite emulsion, which was centrifugally washed three times at 10°C with distilled water, was used.

Particle diameter

The hydrodynamic diameter of the particles was measured by dynamic light scattering (DLS-700, Otsuka Electronics, Kyoto, Japan) at a light-scattering angle of 90° at room temperature, after the emulsion was diluted to 10 ppm with distilled water.

Wet adhesion

First, each emulsion was cast at 60°C for 24 h on a plate coated with an alkyd resin. The thickness of each dry film was about 100 μm. Cross-cut adhesion tests for the emulsion films were conducted according to JIS K5400. Each emulsion film on the plate, which was coated with an alkyd resin, was dipped into distilled

water at 25°C for 1 day. The emulsion film was taken out of the water, wiped up with filter paper, and cut into 25 squares (5 × 5), with a 2-mm interval between each line. A pressure-sensitive adhesive tape was put on the film surface with a 2-kg roller (one round trip) and peeled off rapidly. The number of films remaining in the 25 squares on the plate was counted. This procedure was repeated several times, and an average percentage was obtained.

EU content in each particle

The EU content in each particle was determined from the nitrogen contents in the particles with an elemental analyzer (Sumigraph model NCH-21, Shimadzu, Kyoto, Japan).

ζ potential

Each emulsion was diluted to 1 × 10⁻⁴ wt % (solid content) with a 10 mM KCl aqueous solution, and the pH value of each emulsion was adjusted to pH 2, 4, or 6 with HCl or KOH aqueous solutions; then, the ionic strength of each sample was adjusted to the same value by the addition of a KCl aqueous solution. The ζ potential of each emulsion was measured with an electrophoresis light scattering instrument (LEZA-600, Otsuka Electronics, Osaka, Japan).

Minimum film-forming temperature (MFT)

The MFT of each emulsion was measured with an MFT measurement instrument (MFT-1, Yoshimitsu, Tokyo, Japan) on a stainless steel plate with a temper-

TABLE II
Recipes for the Production of PBMA Seed^a and PBMA/P(BMA–EU) Composite Particles^b

Ingredient	PBMA seed	PBMA/P(BMA–EU)		
		EU content in the monomers (mol %)		
		0.25	0.5	1.0
PBMA particles (g)	—	3.49	3.48	3.45
BMA (g)	80	17.4	17.4	17.2
EU (g)	—	0.06	0.13	0.27
KPS (g)	0.8	0.26 ^c	0.26 ^c	0.26 ^c
Water (g)	720	330	330	330
D_h^d (nm)	390	720	724	870

^a By emulsifier-free emulsion polymerization at 70°C for 10 h at a stirring rate of 120 rpm.

^b By emulsifier-free seeded emulsion copolymerization at 70°C for 24 h at a stirring rate of 160 rpm.

^c First, KPS of 0.175 g was added, and after 18 h, the remains (0.085 g) were added as aqueous solution.

^d Hydrodynamic diameter measured by dynamic light scattering.

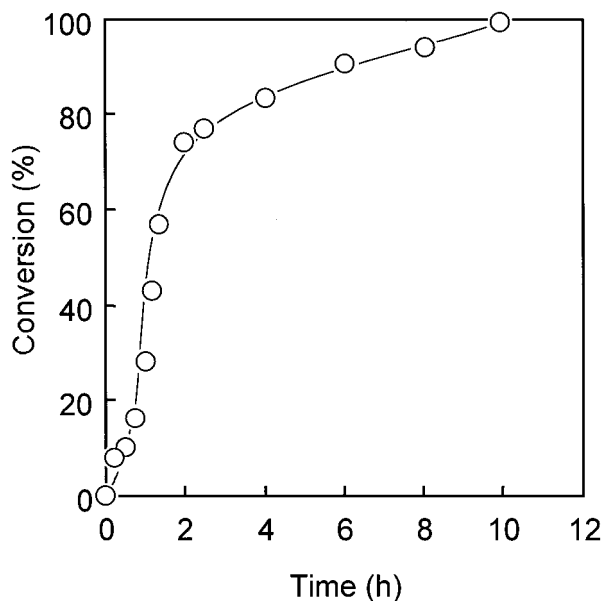


Figure 1 Time-conversion curve for the emulsifier-free emulsion copolymerization of BMA and EU (EU content = 1.0 mol %) at a monomer concentration of 5 wt %

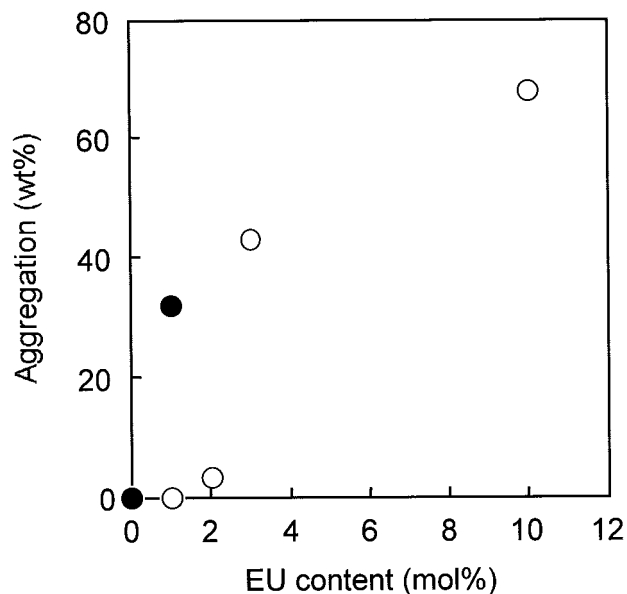


Figure 2 Relationships between the EU content and aggregation during the emulsifier-free emulsion copolymerization of BMA and EU at different monomer concentrations: (O) 5 and (●) 10 wt %.

ature slope (0.92–1.0°C/cm) at a relative humidity of 0% with silica gel.

RESULTS AND DISCUSSION

Figure 1 shows a time-conversion curve of an emulsifier-free emulsion copolymerization of BMA and EU (1 mol % EU) at a monomer concentration of 5 wt %. The emulsion copolymerization proceeded smoothly, and the conversion reached almost 100% after 10 h. In the other copolymerizations, the conversions were also almost 100% according to gravimetric measurements.

Figure 2 shows the relationship between the EU content and the amount of aggregate yielded during the emulsifier-free emulsion copolymerizations at monomer concentrations of 5 and 10 wt %. At 5 wt %, the emulsion was stable at an EU content of less than 2 mol %. However, the amount of the aggregate markedly increased with an increase in the EU content above that value. At 10 wt %, the emulsion was not so stable even at an EU content of 1 mol %. The water-soluble polymer increased with increasing EU content and monomer concentration. In the following experiments, the emulsion copolymerizations were carried out at EU contents of less than 2 mol % and at a monomer concentration of 5 wt %.

Figure 3 shows the wet adhesion properties of films cast from an emulsifier-free P(BMA-EU) (1.0 mol % EU) emulsion and those in which different amounts of SDS were postadded. During the copolymerization, the monomers were collectively added. The wet adhesion was estimated by the cross-cut adhesion test.

The retention percentage of the emulsifier-free film was 100%. That is, the emulsifier-free P(BMA-EU) film had excellent wet adhesion. The percentage drastically decreased with an increase in the amount of SDS added. At an SDS concentration greater than 6 mmol/L, the wet adhesion disappeared. This result indicates an advantage of emulsifier-free polymer emulsions for the improvement of wet adhesion.

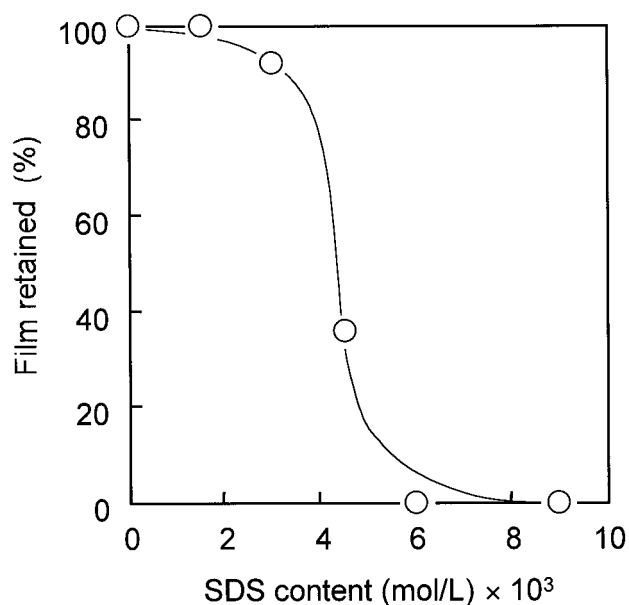


Figure 3 Wet adhesion of films prepared from an emulsifier-free P(BMA-EU) (EU content = 1.0 mol %) emulsion and those in which different amounts of SDS were postadded.

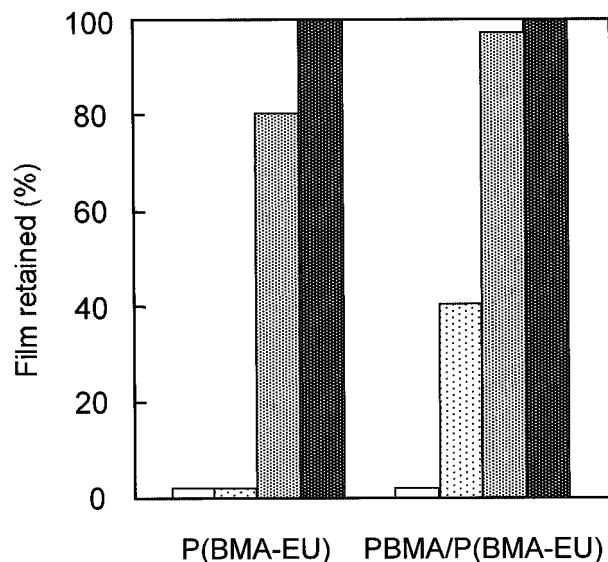


Figure 4 Film percentage retained after 50 cross-cut adhesion tests for films prepared from P(BMA-EU) emulsions and PBMA/P(BMA-EU) composite emulsions. The EU contents in the monomers (from left to right) were 0, 0.25, 0.5, and 1.0 mol %.

Figure 4 shows the wet adhesion properties of films prepared from the emulsifier-free P(BMA-EU) and PBMA/P(BMA-EU) composite emulsions. During the latter copolymerization, the monomers were collectively added to the emulsifier-free PBMA seed emulsion. The emulsifier-free PBMA emulsion films, which did not contain EU, were completely peeled off from the plate by the first cross-cut test. In the P(BMA-EU) emulsion film, the retention percentage after 50 cross-cut tests markedly increased with an increase in the EU content. As shown in Table III, EU incorporation was detected in the P(BMA-EU) and PBMA/P(BMA-EU) composite particles by elemental analysis. This indicated that the wet adhesion was significantly improved by copolymerization with EU. Although the amount of EU introduced into the PBMA/P(BMA-EU) composite particles was lower than that in the P(BMA-EU) particles, as shown in Table III, the wet adhesion of the PBMA/P(BMA-EU) composite emulsion films was higher than that of the P(BMA-EU)

TABLE III
EU Content in P(BMA-EU)^a and PBMA/P(BMA-EU)^b Composite Particles Measured by Elemental Analysis

EU content (mol %) in the monomers	EU content in the particles (mol %)	
	P(BMA-EU)	PBMA/P(BMA-EU)
0.25	0.1	0.05
0.5	0.2	0.2
1.0	0.4	0.3

^a Produced by emulsifier-free emulsion copolymerization.

^b Produced by emulsifier-free seeded emulsion copolymerization with PBMA seed particles.

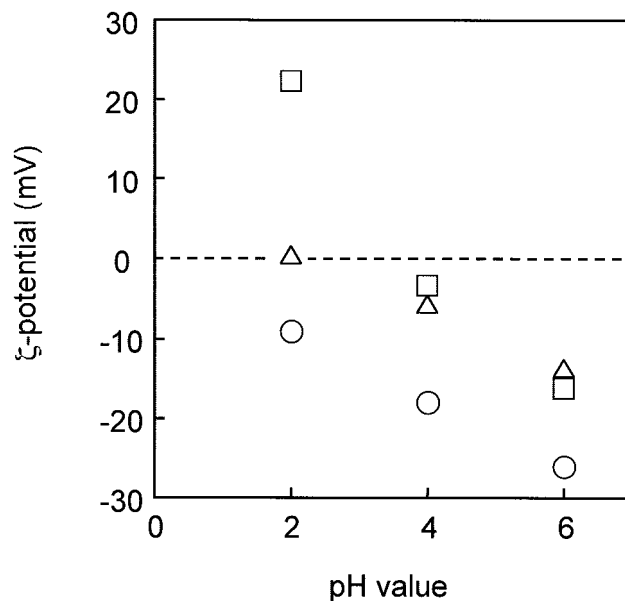


Figure 5 Relationship between the pH value and ζ potential of (○) PBMA, (△) P(BMA-EU), and (□) PBMA/P(BMA-EU) particles. The EU content in the monomers was 0.5 mol %.

emulsion film. This suggests that seeded emulsion copolymerization has the advantage of effectively introducing the EU component at the particle surface in comparison with emulsion copolymerization. The EU contents in both particles were always lower than that calculated from the polymer particle recipes. These results suggest that water-soluble polymers containing an EU component were prepared during the polymerizations. This problem needs to be addressed.

Figure 5 shows the ζ potentials of the PBMA particles, the P(BMA-EU) (0.5 mol % EU) particles, and the PBMA/P(BMA-EU) (0.5 mol % EU) composite particles at pH 2, 4, and 6. The ζ potentials of the PBMA particles were negative at any pH because of sulfuric end groups from the initiator. However, the ζ potentials of the P(BMA-EU) particles and PBMA/P(BMA-EU) composite particles were positive at pH 2. The positive ζ potentials seem to be due to the cationization of the ethyleneurea ring under acid conditions. The ζ potentials of the PBMA/P(BMA-EU) composite particles were more positive than those of the P(BMA-EU) particles, especially at pH 2. This result also supports the conclusion that the amount of EU localized at the surfaces of the polymer particles produced by the emulsifier-free seeded emulsion copolymerization was larger than that by the emulsifier-free emulsion copolymerization.

Figure 6 shows a photograph of PBMA, P(BMA-EU), and PBMA/P(BMA-EU) emulsions dried on a stainless steel plate with a temperature slope. The MFT of the PBMA emulsion was about 31°C. The MFTs of the P(BMA-EU) emulsions increased with an

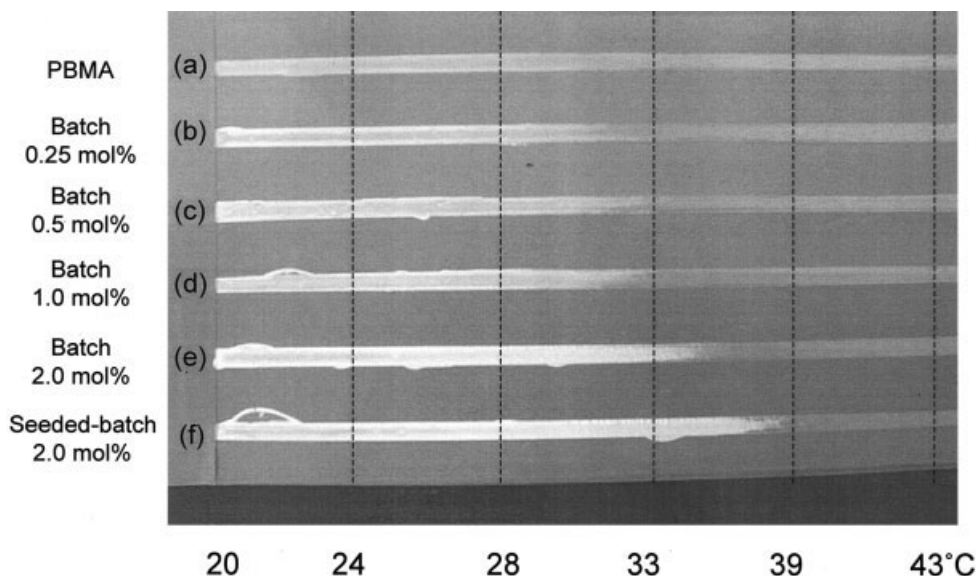


Figure 6 Photograph of emulsion films of (a) PBMA, (b–e) P(BMA–EU), and (f) PBMA/P(BMA–EU) on a stainless steel plate with a temperature slope. The EU contents in the monomers were (a) 0, (b) 0.25, (c) 0.5, (d) 1.0, and (e,f) 2.0 mol %.

increase in the EU content. It has been shown that MFTs can be correlated with the glass-transition temperature (T_g) of the polymer formed at the particle surface layer.^{9,10} If the distribution of EU in the particle is homogeneous, the theoretical T_g of P(BMA–EU) (2 mol % EU) calculated by Fox's equation is 31°C because T_g of PBMA is 30°C¹¹ and that of poly(methacrylamide ethylethyleneurea) is 87°C (according to a catalog). The measured MFT of the P(BMA–EU) (2 mol % EU) particles was 37°C, which is equivalent to that of P(BMA–EU) with an EU content of 13 mol %. The PBMA/P(BMA–EU) composite particles had higher MFTs than the P(BMA–EU) particles at the same EU content. This result also indicates that EU was considerably localized at the PBMA/P(BMA–EU) particle surface.

From these results, we can conclude that emulsifier-free polymer particles with a sufficient concentration of EU at their surfaces result in excellent wet adhesion. Emulsifier-free seeded emulsion copolymerization

with EU is a useful technique for the production of such polymer emulsions.

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