Colloid Polym Sci (2003) 282: 88–91
DOI 10.1007/s00396-003-0981-3

SHORT COMMUNICATION

Masayoshi Okubo
Yasuyuki Kagawa
Mitsuo Matsuda
Akinori Terada

Preparation of polymer particles having ethyleneurea groups at their surfaces by emulsifier-free seeded emulsion polymerization and wet adhesion of its emulsion film

Received: 21 April 2003
Accepted: 4 August 2003

Part CCXLIX of the series "Studies on suspension and emulsion"

M. Okubo (✉) · Y. Kagawa · M. Matsuda
A. Terada
Graduate School of Science
and Technology, Kobe University,
657–8501 Kobe, Japan
E-mail: okubo@cx.kobe-u.ac.jp
Tel.: +81-78-803-6161
Fax: +81-78-803-6161

Present address: M. Matsuda
R & D Application Laboratory,
Rhodia Nicca Ltd.,
910–8670 Fukui, Japan

Abstract Polymer emulsion having ethyleneurea groups at particle surfaces was produced by emulsifier-free seeded emulsion copolymerization of *n*-butyl methacrylate (BMA) and methacrylamide ethylethyleneurea (EU) with poly(BMA) seed particles utilizing the starved-fed monomer addition method. This emulsion film, prepared by casting the polymer emulsion on an alkyd resin plate, had a superior adhesion in water, as well as on stainless steel. Such superior wet adhesions seem to be based on a large amount of EU predominantly localized at the particle surfaces.

Keywords Ethyleneurea group · Emulsion film · Wet adhesion · Seeded emulsion polymerization · Particle

Introduction

Recently, waterborne paints have been used in place of oil-based paints, which have an adverse influence on the environment because of a large amount of volatile organic compounds. However, the water resistance of waterborne paint is lower than that of oil-based paint because of hydrophilic components, which lead to a decrease in the adhesion property on a substrate in water (generally called "wet adhesion" in coating technology). The wet adhesion property of an emulsion film is significantly improved by copolymerization with particular monomers, named "wet adhesion monomer" [1], for example, monomers having a ethyleneurea group such as methacrylamide ethylethyleneurea (EU) [2, 3, 4, 5, 6].

In a previous study [7], it was found that a film prepared from a *n*-butyl methacrylate (BMA)-EU copolymer [P(BMA-EU)] emulsion produced by emulsifier-free emulsion copolymerization had higher wet adhesion than its emulsifier-containing emulsion films. Furthermore, wet adhesion of an emulsion film from poly (BMA)/P(BMA-EU) [PBMA/P(BMA-EU)] composite emulsion produced by emulsifier-free seeded emulsion copolymerization with PBMA seed particles was higher than that of the P(BMA-EU) film at the same EU content in PBMA/P(BMA-EU) composite particles. These results suggest that localization of EU at the particle surfaces is a key factor for the improvement of wet adhesion of emulsion films.

In this study, on the basis of those ideas, in order to localize a large amount of EU at the particle surface layer, a PBMA/P(BMA-EU) composite emulsion was produced by emulsifier-free seeded emulsion copolymerization with slow monomer feeding to keep the monomer-starved state. The wet adhesion of this emulsion film for an alkyd resin was hoped to be superior to those prepared in the previous study [7].

Experimental

Materials

BMA was purified by distillation under reduced pressure. EU, which was purified, was provided by Rhodia Nicca (Tokyo, Japan) as a white powder (mp, 114.5–117 °C). EU was dissolved in water, and the residues were filtered off to obtain a 1.6 wt% EU aqueous solution. Extra pure reagent grade potassium persulfate (KPS) (Nacalai Tesque, Kyoto, Japan) was purified by recrystallization. Deionized water with a specific resistance of 5×10^6 Ω cm was distilled.

PBMA seed emulsion

PBMA seed particles were produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1. First, water and BMA were poured into a 1-L four-necked flask, and the temperature of the mixture was raised to 70 °C with stirring by an anchor-type stirrer. KPS aqueous solution was added after 30 min, and the polymerization was carried out at 70 °C for 24 h under a nitrogen atmosphere. The conversion was almost 100% by gravimetric measurement. Free ions in the medium were removed by ion-exchange treatment.

Table 1 Recipes for the productions of poly(*n*-butyl methacrylate) (PBMA) seed particles by emulsifier-free batch emulsion polymerization and PBMA/*n*-butyl methacrylate (BMA)-methacrylamide ethylethyleneurea (EU) copolymer [PBMA/P(BMA-EU)] composite particles by emulsifier-free seeded emulsion copolymerization[a] with the seeded-batch and starved-fed monomer addition methods

Ingredients	Seed particles	EU contents (mol%)		
		0.25	0.5	1.0
	(g)			
PBMA particles [b, c]	–	3.49	3.48	3.45
BMA[d]	80	17.4	17.4	17.2
EU[e]	–	0.06	0.13	0.27
Potassium persulfate (KPS)[f]	0.8	0.26	0.26	0.26
Water	720	330	330	330
Dh[g]	(nm)			
Batch	440	–	–	–
Seeded-batch	–	720	724	826
Starved-fed	–	741	759	769

[a] In flask: N_2; 70 °C; 24 h; stirring rate 160 rpm (batch and seeded-batch) or 220 rpm (starved-fed)

[b] Produced by emulsifier-free emulsion polymerization

[c] The hydrodynamic diameter measured by DLS was 440 nm

[d] In case of the starved-fed, the feeding rate was 2.5 g/h for 7 h

[e] In case of the starved-fed, the feeding rates of 1.60 wt% EU aqueous solution were 0.5 g/h, 1.1 g/h, and 2.4 g/h in the system of 0.25, 0.5, and 1.0 mol% of EU contents, respectively

[f] First, 0.175 g of KPS was added and after 18 h (seeded-batch) or 7 h (starved-fed) the remains (0.085 g) were added as aqueous solution

[g] Hydrodynamic diameter measured by dynamic light scattering

PBMA/P(BMA-EU) composite emulsion

PBMA/P(BMA-EU) composite particles were produced by emulsifier-free seeded emulsion copolymerization of BMA and EU with PBMA seed particles with two kinds of monomer addition methods under the conditions listed in Table 1.

Seeded-batch method

First, water and all second monomers were charged with one-batch to the PBMA seed emulsion in a 500-mL four-necked flask, and then the mixture was stirred at room temperature for 30 min to swell the PBMA seed particles by the second monomers. After the temperature of the mixture was raised to 70 °C, KPS aqueous solution was added to initiate the copolymerization. The copolymerization was carried out at 70 °C for 24 h under a nitrogen atmosphere. After the copolymerization, the emulsion was centrifugally washed three times with distilled water at 5 °C.

Starved-fed method

First, water and the PBMA seed emulsion were added into a 500-mL four-necked flask. After the temperature of the mixture was raised to 70 °C, KPS aqueous solution was charged, and then BMA and 1.6 wt% EU aqueous solution were added dropwise. The feeding rate of BMA was 2.5 g/h and those of the 1.60 wt% EU aqueous solution were 0.5, 1.1, and 2.4 g/h for 7 h in the systems of 0.25, 0.5, and 1.0 mol% EU content, respectively. The copolymerizations were carried out at 70 °C for 12 h under a nitrogen atmosphere. After the copolymerization, the emulsion was centrifugally washed three times with distilled water at 5 °C.

Particle diameter

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

Wet adhesion

Each emulsion was cast on an alkyd resin plate or a stainless steel plate and dried at 60 °C for 24 h. The thickness of each dried film was about 100 μm. Wet adhesion of each emulsion film was estimated by the cross-cut adhesion test according to JIS K5400. Each emulsion film on the plate was immersed in distilled water for one day at 25 or 40 °C. After the emulsion film was taken out from water, the water droplets were wiped off with filter paper, and then cut into 25 squares (5×5) of 4 mm^2 by cutting at 2-mm intervals. A pressure-sensitive adhesive tape (Nitto Electric, Osaka, Japan) was put on the film surface, made to firmly adhere using a 2-kg roller (one round trip) and then peeled off rapidly. This procedure was repeated several times, and the percentage of film squares remaining on the plate was counted.

Minimum film-forming temperature (MFT)

MFT of each emulsion was measured on an aluminium plate having a temperature slope (0.4 °C/cm) in the presence of silica gel to keep the relative humidity at 0%. MFT was determined as the border between the transparent part and the white powder part by optical observation.

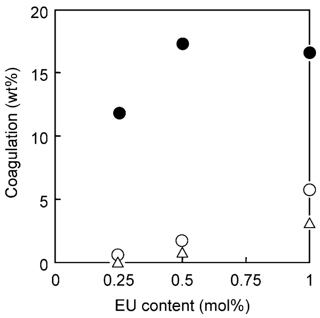

Fig. 1 Relationships between the methacrylamide ethylethyleneurea (EU) content (mol%) and the percentage of coagulation during emulsifier-free emulsion copolymerizations of *n*-butyl methacrylate (BMA) and EU by batch (●), seeded-batch (○), and starved-fed (△) monomer addition methods

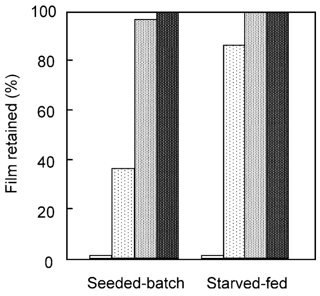

Fig. 2 Percentages of films, which were immersed in water for one day at 25 °C, retained after the 100-times cross-cut adhesion tests. These films were prepared from poly(BMA)/BMA-EU copolymer [PBMA/P(BMA-EU)] emulsions produced by the seeded-batch and starved-fed monomer addition methods. EU contents (mol%): *white* 0; *light grey* 0.25; *grey* 0.5; *black* 1.0

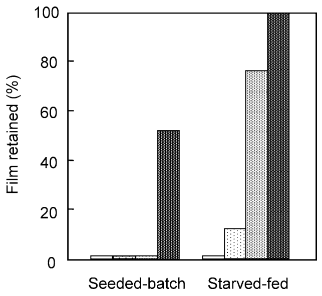

Fig. 3 Percentages of films, which were immersed in water for one day at 40 °C, retained after the 5-times cross-cut adhesion tests. These films were prepared from PBMA/P(BMA-EU) emulsions produced by the seeded-batch and starved-fed monomer addition methods. EU contents (mol%): *white* 0; *light grey* 0.25; *grey* 0.5; *black* 1.0

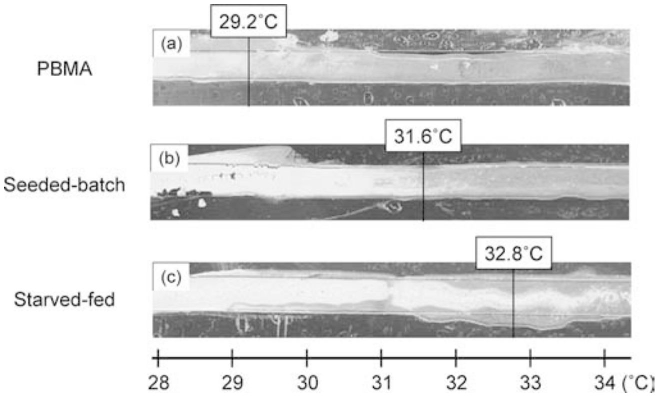

Fig. 4a–c Photographs of emulsion films of the PBMA (**a**) and PBMA/P(BMA-EU) particles produced by the seeded-batch (**b**) and starved-fed (**c**) monomer addition methods on an aluminium plate having a temperature slope (0.4 °C/cm). EU contents (mol%): **a** 0; **b, c** 0.25

Results and discussion

Figure 1 shows relationships between the EU content below 1 mol% and the percentages of coagulation during emulsifier-free emulsion copolymerizations and seeded emulsion copolymerization with batch, seeded-batch, and starved-fed monomer addition methods. Each conversion was almost 100% by gravimetric measurement. In all cases, the percentage of the coagulations increased with an increase in EU content. Especially, in case of the batch system, it was more than 10 wt% in any EU content. Such a phenomenon has often been observed in emulsion copolymerization of water-soluble monomer [8]. The result may be explained by the idea that water-soluble EU-rich polymers were prepared in the water phase during the copolymerization. On the other hand, in case of the seeded-batch system, the percentage of the coagulations was less than 5 wt%. The lowest percentage was found in the starved-fed system. This good result should be based on retardation of the formation of water-soluble EU-rich polymers owing to a decrease in the EU concentration in aqueous media during copolymerization with the starved-fed monomer addition method.

Figures 2 and 3 show wet adhesion properties (estimated by the 100-times and 5-times cross-cut tests) of films on an alkyd resin plate prepared from the emulsifier-free PBMA/P(BMA-EU) emulsions produced in the seeded-batch and starved-fed systems, which were immersed for one day in water at 25 °C and 40 °C, respectively. In the case of 0 mol% EU content, all of the films were completely peeled off from the alkyd resin plate by the one-time cross-cut test. However, in the PBMA/P(BMA-EU) emulsion films produced in the starved-fed system, even in only 0.25 mol% EU content, 86% film remained; in 0.5 mol% EU content, 100% film remained. The wet adhesion property of the emulsion film at 40 °C was clearly better in the starved-fed system than in the seeded-batch system.

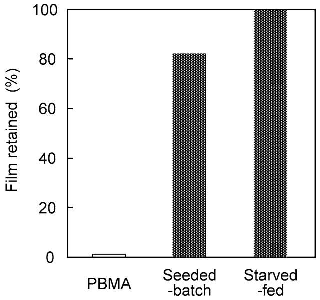

Fig. 5 Percentages of films on the stainless steel, which were immersed in water for one day at 25 °C, retained after the 100-times cross-cut adhesion tests. These films were prepared from the PBMA and PBMA/P(BMA-EU) (EU content 1.0 mol%) emulsions produced by the seeded-batch and starved-fed monomer addition methods

Figure 4 shows the photographs of the PBMA film and both PBMA/P(BMA-EU) emulsion films (EU content, 0.25 mol%) dried on the aluminium plate having a temperature slope. Supposing that EU is homogeneously distributed in the particles, the Tg of the PBMA/P(BMA-EU) (EU content, 0.25 mol%) is calculated to be 30.1 °C by Fox's equation using Tg values of the PBMA and PEU which are, respectively, 30 °C [9] and 87 °C (by catalog). That is, in this EU content, Tg of PBMA/P(BMA-EU) was almost equal to that of PBMA. MFT of the PBMA emulsion was about 29.2 °C. On the other hand, MFT of the PBMA/P(BMA-EU) composite emulsion produced by the seeded-batch system was 31.6 °C and higher than that of the PBMA emulsion. Furthermore, the PBMA/P(BMA-EU) composite emulsion produced by the starved-fed system had the slightly higher MFT of 32.8 °C, than that by the seeded-batch system. It is well known that Tg of the polymer at the particle surface layer affects MFT [10, 11]. These results suggest that larger amounts of EU were localized at the composite particles produced in the starved-fed system than in the seeded-batch system. In the case of slow monomer feeding, because the PBMA seed particles are not swollen with the second monomers, the viscosities of the seed particles must be high through the copolymerization. Thus, the copolymerization should occur not inside the particles but at the surface layer, resulting in the localization of EU groups at the particle surface layer.

Figure 5 shows the wet adhesion property of the film prepared from the PBMA emulsion and PBMA/P(BMA-EU) emulsion (EU content, 1 mol%) produced in the seeded-batch and starved-fed systems on the stainless steel plate. The PBMA emulsion film, which did not contain EU, was completely peeled off from the plate by the one-time cross-cut test. In the PBMA/P(BMA-EU) emulsions produced by the seeded-batch and starved-fed systems, the percentage of the retained films were respectively 82% and 100% after the 100-times cross-cut tests. These results show that the emulsion film containing EU has the good wet adhesion, not only for the alkyd resin but also for the stainless steel.

Conclusion

It was concluded that the polymer particles (produced in a colloidal stable state by the emulsifier-free seeded emulsion copolymerization of BMA and EU with PBMA seed particles utilizing the starved-fed monomer additional method) predominantly localized a large amount of EU at the particle surface layer, and its emulsion film had a superior wet adhesion property for not only the alkyd resin but also for the stainless steel.

References

1. Kreis RW, Sherman AM (1988) The waterborne & higher-solids coating symposium, 222
2. Siesel B (1998) Progress in Organic Coating 34:214
3. Kameya M (2000) Finechemical 29(9):17
4. Matsuda M (2001) J Adhesion Soc Japan 37:24
5. Matsuda M, Sugitani T, Goh HB (1999) Tosou & Toryou 591:35
6. Rhone-Poulenc Technical Bulletin (1995) SIPOMER WAM-II
7. Okubo M, Matsuda M, Terada A, Kagawa Y, Kondo S (2003) J Appl Polym Sci (in press)
8. Vijayendran BR (1979) J Appl Polym Sci 23:893
9. Brandrup J, Immergut EH, Grulke EA,(1999) Polymer Handbook, 4th edn. Wiley, New York
10. Vandezande GA, Smith OW, Bassett DR (1997) Vinyl acetate polymerization. In: Lovell PA, El-Aasser MS (eds) Emulsion polymerization and emulsion polymers. Wiley, New York, pp 563–587
11. Bassett DR, Hamielec AE(1981) ACS Symposium Series 165:371