Colloid Polym Sci (2002) 280: 574–578
DOI 10.1007/s00396-001-0644-1

ORIGINAL CONTRIBUTION

Masayoshi Okubo
Akira Ito
Masahiro Okada
Toyoko Suzuki

Variation of the morphology of a carboxylated polymer film by alkali treatment

Received: 22 August 2001
Accepted: 21 November 2001
Published online: 5 April 2002

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

M. Okubo (✉) · A. Ito · M. Okada
Division of Molecular Science, Graduate School of Science and Technology
Kobe University, Kobe 657-8501, Japan
E-mail: okubo@cx.kobe-u.ac.jp
Tel.: +81-78-8036161
Fax: +81-78-8036205

M. Okubo · T. Suzuki
Department of Chemical Science and Engineering, Faculty of Engineering
Kobe University, Kobe 657-8501, Japan

Abstract The variation of the morphology of a carboxylated polymer film cast from tetrahydrofuran solution, in which styrene/methacrylic acid copolymer particles produced by emulsion copolymerization were dissolved, before and after alkali treatment at temperatures higher than the glass-transition temperature was observed with a scanning electron microscope. The treated film had a porous structure. This result provides important evidence for the formation mechanism of the multihollow structure in submicron-sized, carboxylated polymer emulsion particles by the stepwise alkali/acid method and the alkali/cooling method which the authors proposed.

Keywords Multihollow structure · Alkali swelling · Morphology · Particle

Introduction

Recently, we found that submicron-sized styrene/butyl acrylate/methacrylic acid terpolymer [P(S-BA-MAA)] particles produced by emulsion terpolymerization were changed to those having many hollows within them by stepwise treatments with alkali and acid [1]; this was named the stepwise alkali/acid method. In following work, the effects of some factors in the alkali-treatment [2,3] and the acid-treatment [4] processes on the formation of the multihollow structure were examined in detail. Moreover, in order to prepare multihollow polymer particles having a high glass-transition temperature (T_g), P(S-MAA) particles were treated by the stepwise alkali/acid method [5], and the formation mechanism of the multihollow structure was proposed as follows [6,7]. In the alkali-treatment process, a lot of small water pools are formed in the particle owing to absorption of water by ionized carboxyl groups. The water pools seem to act as "primary" hollows. In the acid-treatment process, the water pools coagulate to decrease the interfacial area between the deionized P(S-MAA) and water for the achievement of a thermodynamically more stable state, which results in the multihollow structure.

Furthermore, P(S-MAA) particles, in which the MAA content exceeded 8 mol%, were changed to those having the multihollow structure by alkali treatment at a temperature higher than the T_g and subsequent cooling; this was named the alkali/cooling method [8]. The effects of the molecular weight of the base polymer, the particle size [9], and the kind of alkali [10] on the formation of the multihollow structure were clarified. In the formation mechanism proposed from the results, it is assumed that the hollow structure has already been formed in the

alkali-treatment process and that it is fixed in the cooling process.

However, the formation of a hollow structure in the alkali-treatment process at a temperature higher than the T_g has not been confirmed directly until now.

In this article, the possibility of the formation of the multihollow structure in the alkali-treatment process is clarified by examining mainly the variation of the morphology of a P(S-MAA) (92/8 molar ratio) film before and after the alkali treatment at a temperature higher than the T_g.

Experimental

Materials

S and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate was purified by recrystallization. Commercial grade poly(oxyethylene nonyl phenyl ether) nonionic emulsifier (Emulgen 911, Kao Co., Japan) was used as received. Analytical grade potassium hydroxide was used as received. Deionized water with a specific resistance of 5×10^6 Ωcm was distilled.

Production of polymer particles

P(S-MAA) (92/8 molar ratio) and P(S-BA-MAA) (50/42/8 molar ratio) particles were produced by emulsion polymerizations at 70 °C under the conditions listed in Table 1. In both emulsions, the residual monomers were not detected by gas chromatography and there were no coagulated particles; therefore, the polymer compositions of the particles obtained should be equivalent to those in the polymerization recipes.

Preparation of cast film

P(S-MAA) and P(S-BA-MAA) particles prepared by emulsion polymerizations were separated from the medium by centrifugation, and dried. The dried particles were dissolved in tetrahydrofuran. Each solution was cast onto paper coated with mold-release agent and dried at room temperature for 2 days and under reduced pressure for 1 day. The thickness of each film was about 100 μm.

Table 1. Recipes of emulsion polymerizations

	Styrene/butyl acrylate/methacrylic acid (molar ratio)	
	92/0/8[a]	50/42/8[b]
Styrene (g)	56	1.63
Butyl acrylate (g)	–	1.65
Methacrylic acid (g)	4.0	0.21
Potassium persulfate (mg)	240	14
Emulgen 911 (g)	3.3	0.32
Water (g)	540	31.5
T_g (°C)[c]	106	10

[a]In a flask: N_2; 24 h; 120 rpm
[b]In a sealed tube: N_2; 24 h; shaking rate 120 cycles/min (3-cm strokes)
[c]Calculated by Fox's equation [12]

Alkali treatment

The cast films were, separately, immersed in alkaline solution, the pH of which was adjusted to 13.0 with KOH in test tubes. The test tubes were immersed in an oil bath under various conditions (temperature, time). After the treatment, each film was cooled in air to room temperature. The films were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

Results and discussion

Photographs of P(S-MAA) (92/8, molar ratio) film in KOH aqueous solution (pH 13.0) at room temperature for 1 h, at 150 °C for 1 h, and at room temperature after the alkali treatment are shown in Fig. 1. The film before raising the temperature to 150 °C was transparent. The film at 150 °C and that subsequently cooled to room temperature were clouded. These results suggest that the alkali treatment at a temperature higher than the T_g changed the film from a homogeneous structure to a heterogeneous one, and the change was kept in the cooling process.

SEM photographs of cross-sections of the P(S-MAA) films before and after the alkali treatment at 150 °C shown in Fig. 1 are displayed in Fig. 2. The film before the treatment had a homogeneous structure. On the other hand, the film after the treatment had a multihollow structure, which was similar to that in the particles treated by the alkali/cooling method [8]. It is obvious that the whitening of the film in KOH aqueous solution (pH 13.0) at 150 °C for 1 h, shown in Fig. 1c, was due to the heterogeneous structure.

SEM photographs of cross-sections of the P(S-MAA) films after the alkali treatment at an initial pH of 13.0 for 1 h at different temperatures are shown in Fig. 3. The film treated at 50 °C was transparent and did not

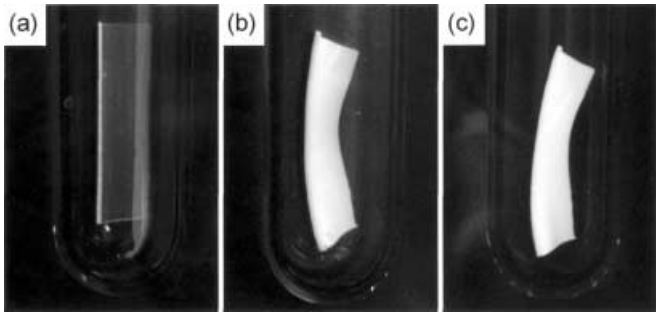

Fig. 1. Photographs of styrene/methacrylic acid copolymer [*P(S-MAA)*] (92/8 molar ratio) film in KOH aqueous solution (pH 13.0) **a** at room temperature for 1 h, **b** at 150 °C for 1 h, and **c** at room temperature after the heat treatment

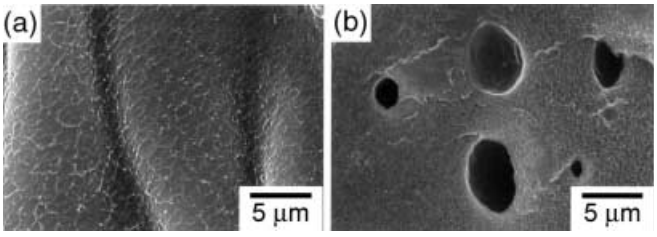

Fig. 2. Scanning electron microscope (*SEM*) photographs of cross-sections of P(S-MAA) (92/8 molar ratio) films **a** before and **b** after the alkali treatment at an initial pH of 13.0 at 150 °C for 1 h

have the multihollow structure as shown in Fig. 3a. The films became turbid at a temperature above 60 °C, and had the multihollow structures as shown in Fig. 3b–f. In previous work [8], the multihollow structure in P(S-MAA) (86/14 molar ration) particles was formed in alkali treatment at a temperature above 70 °C, which seems to be based on the fact that the T_g of the copolymer in the particles decreased from 112 °C to about 70 °C by the plasticization due to water adsorption [11]. These results indicate that there is a close connection in the formations of multihollow structures between the particle and the film.

SEM photographs of cross-sections of the P(S-MAA) films after the alkali treatment at an initial pH of 13.0 and 150 °C for different times are shown in Fig. 4. For treatment times longer than 5 min, the multihollow structure was observed in the whole of the film. For each alkali-treatment time, the film became turbid (the data have been omitted) and the turbidity remained after cooling to room temperature. This indicates that the whitening of the film in the alkali treatment was caused by the formation of a heterogeneous structure, which was equivalent to the multihollow structure. These results suggest that the multihollow structure was already formed in the alkali-treatment process.

SEM photographs of the surfaces of the P(S-MAA) films after the alkali treatment at an initial pH of 13.0 and 150 °C for different times are shown in Fig. 5. Before the treatment, the film surface was smooth. Each

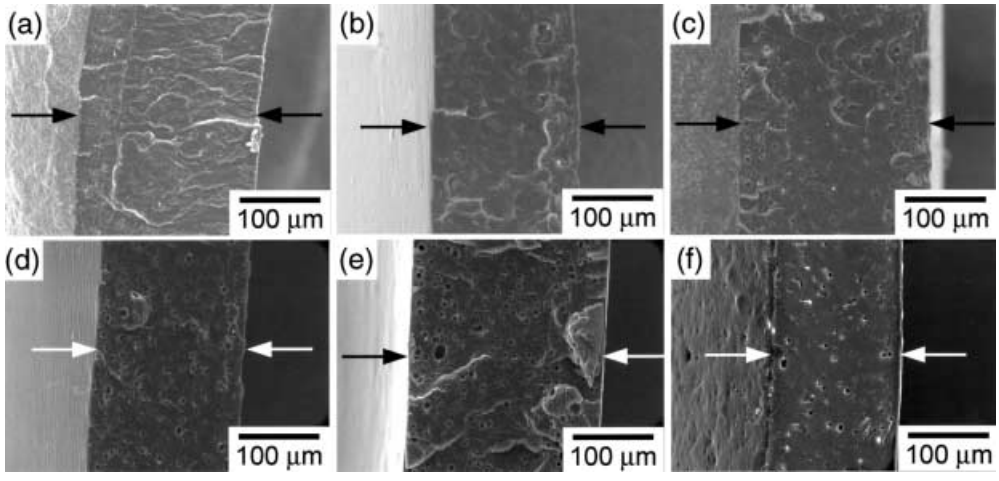

Fig. 3. SEM photographs of cross-sections of P(S-MAA) (92/8 molar ratio) films after the alkali treatment at an initial pH of 13.0 for 1 h at different temperatures (°C): **a** 50; **b** 60; **c** 80; **d** 100; **e** 120; **f** 150. The *arrows* show the surfaces of the films

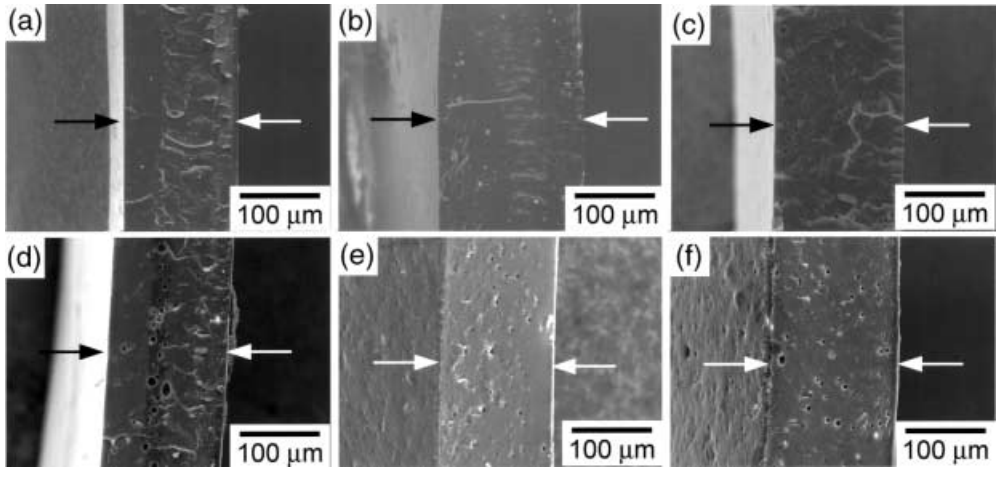

Fig. 4. SEM photographs of cross-sections of P(S-MAA) (92/8 molar ratio) films after the alkali treatment at an initial pH of 13.0 and 150 °C for different times (min): **a** 0; **b** 1; **c** 5; **d** 15; **e** 30; **f** 60. The *arrows* show the surfaces of the films

treated film had an uneven surface which was quite different from the inner structure shown in Fig. 4. The states of the surface and the inside were similar to the skin and sponge layers, respectively, of an asymmetric ultrafiltration membrane. To get more information on in situ alkali swelling state of film, a P(S-BA-MAA) (52/40/8 molar ratio) emulsion having a MAA content of 8 mol% and a T_g of 10 °C was produced by emulsion terpolymerization and was cast to prepare a film.

Optical micrographs of the inner structures of the P(S-BA-MAA) film in the alkali-treatment process at an initial pH of 13.0 and 20 °C for different times are shown in Fig. 6. Before the alkali treatment, the film was homogeneous. Water pools appeared in the alkali-treatment process for each treatment time and the number of water pools became larger with the treatment time. Observation at the different depths of focus in the film indicates that the structure was formed in the whole of the film.

From these results, it is concluded that in the alkali-treatment process at a temperature higher than the T_g of the base polymer, a multihollow structure is formed inside the carboxylated polymer film and is fixed in the cooling process. We propose the formation mechanism of the multihollow structure inside the carboxylated particle by the alkali/cooling method as follows. First, the carboxyl groups inside the particle are neutralized by alkali treatment at a temperature higher than the T_g [3]. Because of the osmotic pressure due to the ionized carboxyl groups, H_2O molecules penetrate inside, and the H_2O molecules around the carboxyl group become a small water pool, which drastically increases the interfacial area between ionized P(S-MAA) and water. In order to obtain a thermodynamically more stable state, the water pools coagulate to decrease the interfacial area. In case when the MAA content is small (less than 8 mol%), the multihollow structure is difficult to ob-

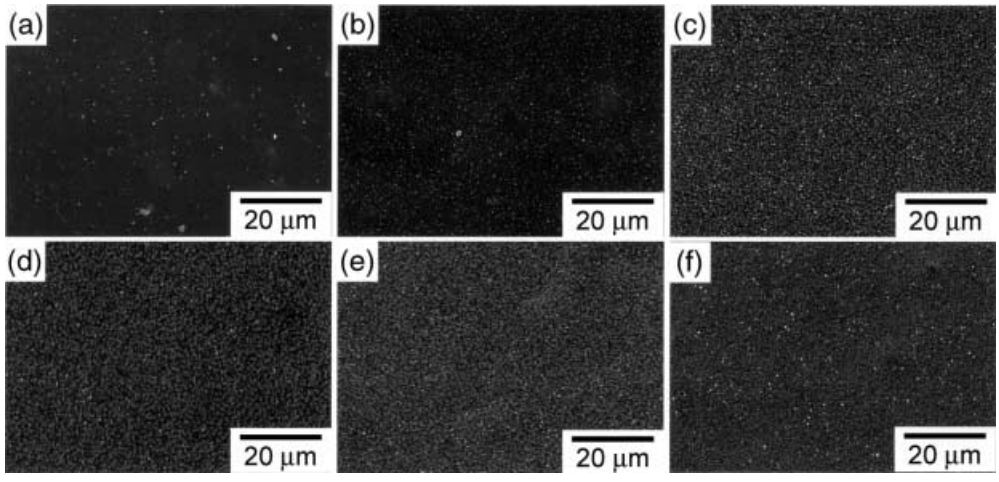

Fig. 5. SEM photographs of surfaces of P(S-MAA) (92/8 molar ratio) films after the alkali treatment at an initial pH of 13.0 and 150 °C for different times (min): **a** 0; **b** 1; **c** 5; **d** 15; **e** 30; **f** 60

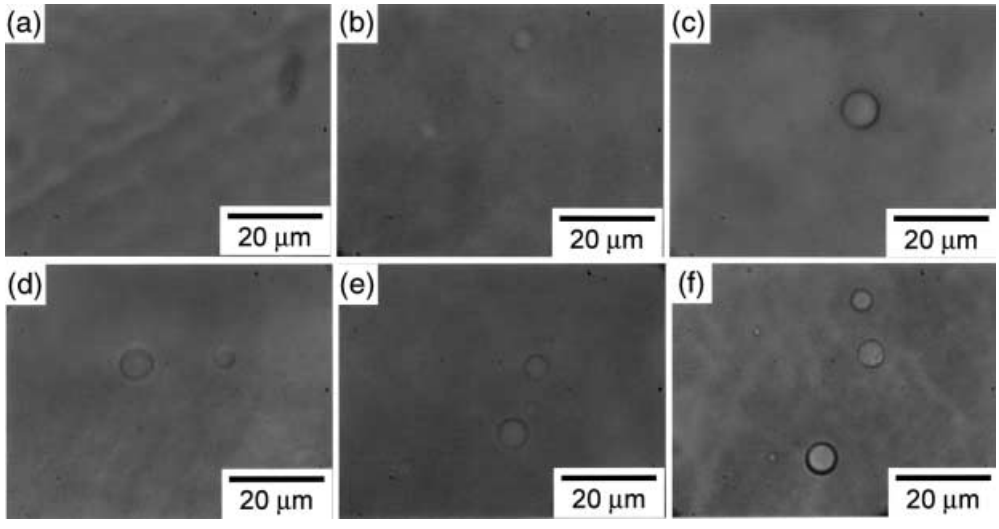

Fig. 6. Optical micrographs of inner structures of P(S-butyl acrylate-MAA) (50/42/8 molar ratio) films in the alkali-treatment process at an initial pH of 13.0 and 20 °C for different times (min): **a** 0; **b** 1; **c** 5; **d** 15; **e** 30; **f** 60

serve with a transmission electron microscope because the rate of the coagulation is too slow [7]. On the other hand, in case when the MAA content is high enough (more than 8 mol%), the rate is fast because the number of water pools inside the particle is large, and results in the multihollow structure in a short time. Finally, in the cooling process, the multihollow structure is fixed because the molecular movement is frozen.

References

1. Okubo M, Kanaida K, Fujimura M (1990) Chem Express 5:797
2. Okubo M, Ichikawa K, Fujimura M (1991) Colloid Polym Sci 269:1257
3. Okubo M, Ichikawa K, Fujimura M (1992) In: Daniels ES, Sudol ED, El-Aasser MS (eds) Polymer latexes: preparation, characterization, and applications. ACS symposium series 492. American Chemical Society, Washington, DC, p 282
4. Okubo M, Ichikawa K (1994) Colloid Polym Sci 272:933
5. Okubo M, Ito A, Hashiba A (1996) Colloid Polym Sci 274:428
6. Okubo M, Sakauchi A, Okada M (2002) Colloid Polym Sci 280:38
7. Okubo M, Sakauchi A, Okada M (2002) Colloid Polym Sci (in press)
8. Okubo M, Ito A, Kanenobu T (1996) Colloid Polym Sci 274:801
9. Okubo M, Ito A, Nakamura M (1997) Colloid Polym Sci 275:82
10. Okubo M, Nakamura M, Ito A (1997) J Appl Polym Sci 64:1947
11. Okubo M, Xu D, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:246
12. Fox TG (1956) Bull Am Phys Soc 1:123