

Preparation of Asymmetric Film by Blending Two Kinds of Polymer Emulsions Having Greatly Different Storage Stabilities

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SYNOPSIS

Two kinds of anionic polymer emulsions with different particle sizes were blended and cast on a release-paper at 30°C. One was poly(butyl acrylate) emulsion, and the other was ethyl acrylate–methyl methacrylate (1 : 1, weight ratio) copolymer emulsion. They were produced by emulsifier-free emulsion polymerization. The blend films prepared in an appropriate range of the blend ratio had a great difference in tackiness between both surfaces: The air-side surface exhibited tackiness and the release-paper side showed nontackiness. The forming mechanism is discussed.

INTRODUCTION

In previous articles, we have reported that two-layer composites¹ and asymmetric films² having a difference in tackiness between both surfaces were prepared using an emulsion-blend technique. In the latter films, sodium dodecyl sulfate (SDS)-containing ethyl acrylate–methyl methacrylate copolymer [P(EA–MMA)] emulsion and emulsifier-free poly(butyl acrylate) (PBA) emulsion were blended. The bottom-side surface exhibited tackiness, whereas the air-surface showed nontackiness. It was concluded that the formation of such an asymmetric film in which the air-side surface consists mainly of P(EA–MMA) and the bottom-side one consists mainly of PBA is derived from the difference in the colloidal stabilities of both particles. In this study, we tried to prepare an asymmetric polymer film having opposite surfaces in tackiness to the film mentioned above from emulsifier-free blend emulsion of PBA and P(EA–MMA).

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EXPERIMENTAL

Materials

Butyl acrylate (BA), ethyl acrylate (EA), and methyl methacrylate (MMA) were purified by reduced pressure distillation under a nitrogen atmosphere. Reagent-grade potassium persulfate (KPS) and Na₂S₂O₃ were purified by recrystallization. Cupric sulfate (CuSO₄) was of extra pure grade. Deionized water was distilled.

Emulsion Polymerization

Both series of PBA and P(EA–MMA) emulsions were prepared by emulsifier-free emulsion polymerization in a glass flask. The polymerization conditions are listed in Tables I and II. PBA–LL, PBA–L, and P(EA–MMA)–L emulsions were prepared by seeded emulsion polymerization, where their seed particles were swollen with monomers for 72, 24, and 48 h at 2°C, respectively, prior to the polymerizations.

Determination of Particle Size

Average particle size was determined using dynamic light scattering spectroscopy with a dynamic laser

Table I Preparation of a Series of PBA Emulsions*

Sample Designation	PBA-S	PBA-M	PBA-L	PBA-LL
BA (g)	20	40	20	60
PBA-M (mL)			100	
PBA-L (mL)				100
KPS (mg)	220	120	100	150
Na ₂ S ₂ O ₃ (mg)	130			
CuSO ₄ (mg)	1			
Water (g)	178	155	80	160
Time (h)	10	24	45	45
Solid (%)	10.1	20.1	19.7	24.0
PD (nm)	280	460	550	940

* Atmosphere, nitrogen; temp, 70°C. Abbreviations: BA, butyl acrylate; KPS, potassium persulfate; PD, particle diameter.

particle analyzer (Otsuka Electronics, Potal LPA-3000/3100). In both series of emulsions, the particle diameter increases in the order of PBA-S < PBA-M < PBA-L < PBA-LL and of P(EA-MMA)-S < P(EA-MMA)-M < P(EA-MMA)-L.

Storage Stability

Each emulsion in which the polymer concentration was about 20 wt % was put in a test tube with an inside diameter of 12 mm. The storage stability was estimated by an increase in the volume fraction of the clear layer due to the sedimentation of particles as a function of standing time at 25°C. During the measurement, the top was capped to remove water evaporation.

Tackiness of Film Surfaces

PBA and P(EA-MMA) emulsions prepared were blended at room temperature, and the films having

a dry thickness of about 0.8 mm were cast on a release-paper at 30°C. The air-side or the bottom-side surface of the dried film stripped from the release-paper was adhered onto a glass plate using a double-coated tape. A polyethylene terephthalate (PET) film (thickness, 90 μm) having a width of 10 mm was stuck onto the other surface using a roller (weight, 380 g). The 180 peeling test of the PET film from the surfaces was carried out at room temperature with a tensile tester (Shimadzu Seisakusho Corp., Autograph SD-100-2) at a speed of 200 mm/min.

RESULTS AND DISCUSSION

Figure 1 shows the storage stabilities of both series of PBA and P(EA-MMA) emulsions used. In the cases of PBA-S, -M, and -L and P(EA-MMA)-S emulsions, the clear layer did not appear within the

Table II Preparation of a Series of P(EA-MMA) Emulsions*

Sample Designation	P(EA-MMA)-S	P(EA-MMA)-M	P(EA-MMA)-L
EA (g)	25	20	20
MMA (g)	25	20	20
P(EA-MMA)-M (mL)			100
KPS (mg)	430	50	100
Na ₂ S ₂ O ₃ (mg)	250		
CuSO ₄ (mg)	4		
Water (g)	946	172	220
Time (h)	8	25	45
Solid (%)	4.8	19.2	19.3
PD (nm)	180	420	540

* Atmosphere, nitrogen; temp, 70°C. Abbreviations: EA, ethyl acrylate; MMA, methyl methacrylate; KPS, potassium persulfate; PD, particle diameter.

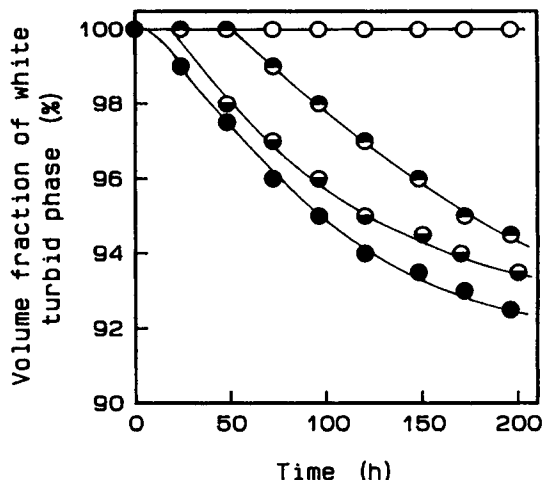


Figure 1 Storage stabilities of both series of PBA and P(EA-MMA) emulsions used: (○) PBA-S, -M, and -L and P(EA-MMA)-S; (●) P(EA-MMA)-M; (●) PAB-LL; (●) P(EA-MMA)-L.

standing time of 200 h. Whereas in the cases of P(EA-MMA)-L, and -M and PBA-L emulsions, the clear layer due to the sedimentation of the particles appeared at the top end. In both series of PBA and P(EA-MMA), the storage stability decreased with an increase in their particle diameters.

PBA and P(EA-MMA) emulsions were blended in various pairs, and the tackiness of both surfaces of the film cast from each blend emulsion was measured. PBA emulsion films had tackiness, whereas P(EA-MMA) emulsion films did not.

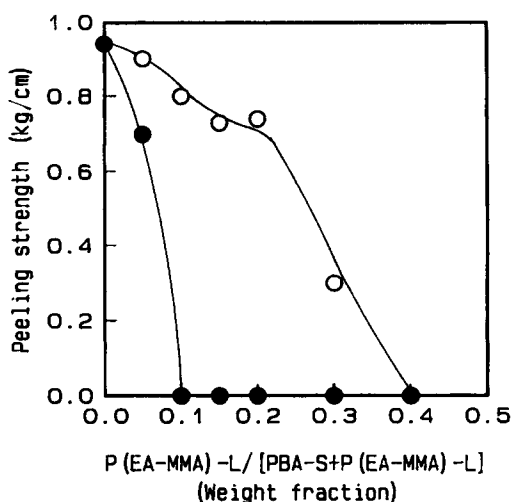


Figure 2 Peeling strengths of PET film from the surfaces of air side (○) and bottom side (●) for PBA-S/P(EA-MMA)-L-blend emulsion films.

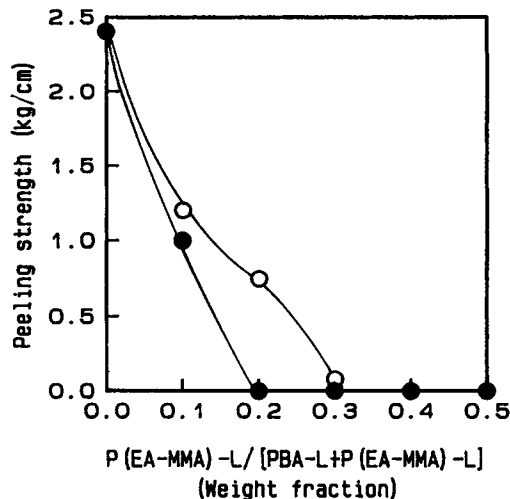


Figure 3 Peeling strengths of PET film from the surfaces of air side (○) and bottom side (●) for PBA-L/P(EA-MMA)-L-blend emulsion films.

Figure 2 shows the tackiness of the films cast from blend emulsions of PBA-S/P(EA-MMA)-L, in which P(EA-MMA)-L had lower storage stability than did PBA-S. The films had a great difference in tackiness at both surfaces in a range of blend ratio from 0.15 to 0.3: The air-side surfaces exhibited tackiness, whereas the bottom-side surfaces did not. The asymmetric surface property in the tackiness was in the reverse of that of the film prepared in the previous work² in which the bottom-side surface exhibited tackiness and the air-side surface did not.

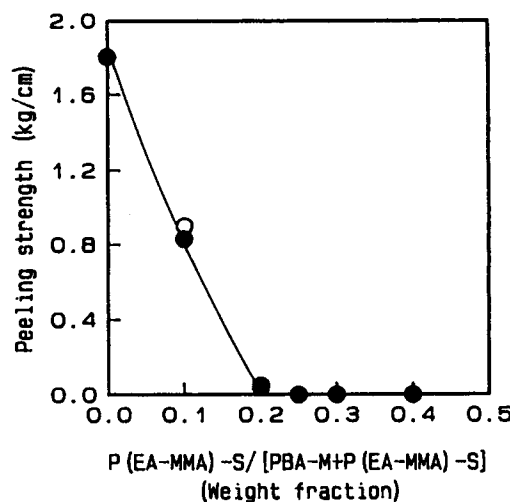


Figure 4 Peeling strengths of PET film from the surfaces of air side (○) and bottom side (●) for PBA-M/P(EA-MMA)-S-blend emulsion films.

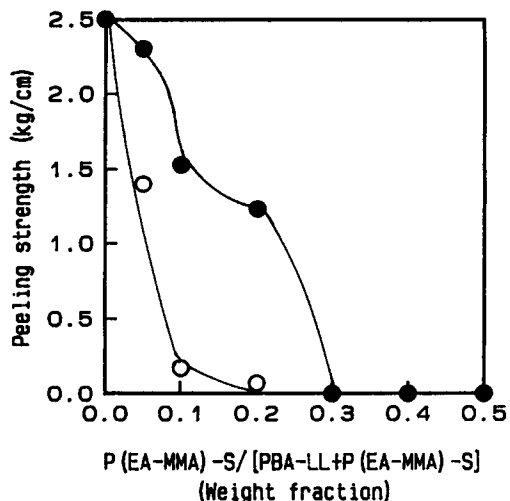


Figure 5 Peeling strengths of PET film from the surfaces of air side (○) and bottom side (●) for PBA-LL/P(EA-MMA)-S-blend emulsion films.

Figures 3 and 4 show the tackiness of the films cast from the blend emulsions of PBA-L/P(EA-MMA)-L and PBA-M/P(EA-MMA)-S, respectively. In the former, there was difference in the storage stabilities between them, but the difference seems to be smaller than that in PBA-S/P(EA-MMA)-L blend emulsion because the diameter of PBA-L was larger than that of PBA-S, whereas in the latter there was no obvious difference. In the comparison with the PBA-S/P(EA-MMA)-L

blend film shown in Figure 2, it is clear from Figures 3 and 4 that as the difference in the storage stabilities between PBA and P(EA-MMA) emulsions blended decreased the difference in the tackinesses between both surfaces of the blend films decreased. This tendency agreed well with that obtained in various emulsion blend systems of poly(ethyl acrylate) and poly(methyl methacrylate).¹

Figure 5 shows the tackiness of the films cast from blend emulsions of PBA-LL/P(EA-MMA)-S, in which PBA-LL had lower storage stability than did P(EA-MMA)-S. In the P(EA-MMA) content ranging from 0.1 to 0.2, the air-side surface exhibited a high tackiness about 1 kg/cm, whereas the bottom-side surface showed almost no tackiness. The asymmetry of the films in tackiness was similar to that of the films shown in Figure 2.

In such ways, asymmetric films can be prepared from polymer blend emulsion by utilizing the difference in storage stabilities between original emulsions.

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