

Preparation of Two-Layer Film Having Porous Structure by Emulsion Blend Technique

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ABSTRACT: A two-layer film consisting of a tacky layer (air side) and a porous nontacky layer (release-paper side) was prepared by casting blend emulsion on a release paper, in which 150-nm 2-ethylhexyl acrylate–2-methoxyethyl acrylate–acrylic acid terpolymer particles having high storage stability and 542-nm ethyl acrylate–methyl methacrylate copolymer particles having low storage stability were dispersed. Both emulsion particles were produced by emulsifier-free emulsion copolymerizations. The difference of

tackiness between both surfaces increased with increases in the film-formation time and the concentration of electrolytes in the blend emulsion, and resulted in the two-layer film. The film had a high water vapor permeability, which is also needed for medical adhesive tape. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2027–2033, 2003

Key words: morphology; storage stability; tackiness; emulsion blend; medical tape

INTRODUCTION

Film preparation from polymer emulsion has advantages, with respect to environmental problems such as volatile organic compounds, over films prepared from polymer solution. There are many practical applications of emulsion films such as water-based paints, high-quality papers, floor coatings, and adhesives. In these applications, weak points are low water resistance and reduction of adhesion strength caused by the localization of emulsifier.^{1–5} In particular, adhesion is very sensitive to the presence of emulsifier at the film–substrate interface. Compared to films containing emulsifier, films prepared from polymer emulsion produced by emulsifier-free emulsion polymerization had high water resistance⁶ and good adhesion.^{1–3} On the other hand, a film cast from emulsifier-free polymer emulsion having low colloidal stability had a porous structure resulting from the coagulation of particles during the drying process, and the porous film was characterized by lower water resistance than that of emulsifier-containing emulsion films.^{7,8} Such a porous emulsion film must have high water vapor permeability, which is needed for medical adhesive tape.

Two kinds of emulsions were blended for the purpose of improvement of properties such as film-form-

ing ability and mechanical properties.^{9–12} In our previous study,¹³ it was found that two-layer emulsion films could be prepared from blend emulsions, in which two kinds of polymer particles having different colloidal stabilities were dispersed. In previous studies,^{14,15} the influences of the particle sizes and amounts of surfactant on the formation of the two-layer structure were examined in detail.

In this study, the two-layer film, in which one layer has tackiness and the other has nontackiness and a porous structure, was prepared as a model film for use as medical adhesive tape.

EXPERIMENTAL

Materials

Ethyl methacrylate (EA), 2-ethylhexyl acrylate (EHA), 2-methoxyethyl acrylate (MEA), acrylic acid (AA), and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Potassium persulfate (KPS, Nacalai Tesque Inc., Kyoto, Japan) was purified by recrystallization. Guaranteed reagent-grade copper chloride (CuCl_2), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and sodium sulfate were used as received from Nacalai Tesque. Deionized water with a specific resistance of $5 \times 10^6 \Omega \text{ cm}$ was distilled.

Emulsifier-free emulsion polymerization

EHA–MEA–AA terpolymer [P(EHA–MEA–AA)] and EA–MMA copolymer [P(EA–MMA)] particles were produced by emulsifier-free emulsion copolymeriza-

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TABLE I
Recipes for the Preparations of P(EHA-MEA-AA)^a (49/50/1, w/w/w) and P(EA-MMA)^b (40/60, w/w) Particles by Emulsifier-Free Emulsion Copolymerizations

Ingredient	P(EHA-MEA-AA) ^a	P(EA-MMA) ^b
EHA (g)	19.6	—
MEA (g)	20.0	—
AA (g)	0.40	—
EA (g)	—	32.0
MMA (g)	—	48.0
KPS (g)	1.44	0.8
Na ₂ S ₂ O ₃ (g)	0.88	—
CuCl ₂ (g)	0.14	—
Water (g)	760	720
<i>D_h</i> ^c (nm)	150	542

Abbreviations: EHA, 2-ethylhexyl acrylate; MEA, 2-methoxyethyl acrylate; AA, acrylic acid; EA, ethyl acrylate; MMA, methyl methacrylate; KPS, potassium persulfate; P(EHA-MEA-AA), EHA-MEA-AA terpolymer; P(EA-MMA), EA-MMA copolymer.

^a In flask; N₂; 70°C; 6 h; stirring rate, 200 rpm.

^b In flask; N₂; 70°C; 12 h; stirring rate, 200 rpm.

^c Hydrodynamic diameter measured by dynamic light scattering.

tions for 6 and 12 h, respectively, at 70°C under a nitrogen atmosphere under the conditions listed in Table I as follows. In the former polymerization, first water, Na₂S₂O₃, and all the monomers were poured into a 1-L four-neck flask, and the temperature of the mixture was increased to 70°C with stirring by an anchor-type stirrer. Next, KPS and CuCl₂ were added as an aqueous solution. The latter polymerization was carried out under a similar procedure expect for using only KPS initiator. The conversions were almost 100% by gravimetric measurement. The hydrodynamic diameters of the two kinds of particles were measured at room temperature by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan) at the light-scattering angle of 90°.

Estimation of sedimentation rates of particles

Each emulsion (polymer concentration, 5.0 wt %) was poured into a test tube (ϕ 12 mm). Sedimentation of the particles was evaluated from an increasing rate of the volume fraction of the upper clear layer at 25°C. During the measurement, the test tube was capped to prevent water evaporation.

Preparation of blend emulsion film

The pH value of emulsion, in which the P(EHA-MEA-AA) and P(EA-MMA) (1/1, w/w) particles were blended, was adjusted to 10.0 with ammonium aqueous solution. Films were prepared by casting the blend emulsion on release paper at 35 ± 2°C in desiccators under relative humidities of 50, 55, and 75%,

which were adjusted with magnesium nitrate, sodium bromide, and sodium chloride saturated aqueous solution, respectively. Compared with them, the film was prepared at 35 ± 2°C in an open system in air. Film-formation time is designated as the time at which the transparent part of the film attains 80%. The dry thickness of all films was about 100 μm.

Measurement of tackiness

The tackiness of air-side and release-paper-side surfaces of the blend emulsion film was measured by peeling test. The peeling test was carried out as follows. The air-side or the release-paper-side surfaces of the films was appended to a polyethylene terephthalate (PET) film with double-coated tape. The opposite-side surface of the film having a width of 10 mm was stuck onto a Bakelite plate using a roller (2 kg) at a round trip. The 180° peeling test of the blend emulsion film from the Bakelite plate was carried out five times for each sample at room temperature with a tensile tester (Autograph AGS-1kND; Shimadzu Seisakusho Corp., Kyoto, Japan) at a speed of 300 mm/min and the average value was taken.

Electron microscopy

Both surfaces of the blend emulsion film and cross sections, which were prepared by breaking the film in liquid nitrogen, were observed with a scanning electron microscope (SEM, S-2500; Hitachi Seisakusho Corp., Ibaraki, Japan).

Whitening rate of film in water

The variation in optical density of the blend emulsion film (20 × 25 mm) was recorded as a function of dipping time in water at 30°C with an incident wavelength of 610 nm. The portion in contact with water was limited to one side of the specimen, that is, the air-side or release-paper-side (bottom-side) surface, as described in detail in a previous study.⁷

Permeability of water vapor

A cup (diameter, 60 mm), into which distilled water was poured, was covered with a sample film and was placed in a desiccator in which a large amount of calcium chloride was kept to maintain a perfect drying atmosphere. In the desiccator, the atmosphere was stirred. Water permeation from the cup was always carried out from the release-paper side to the air side of the film at 40 ± 2°C for 5 h. The following equation was used for the calculation of the degree of moisture permeation (P_w):

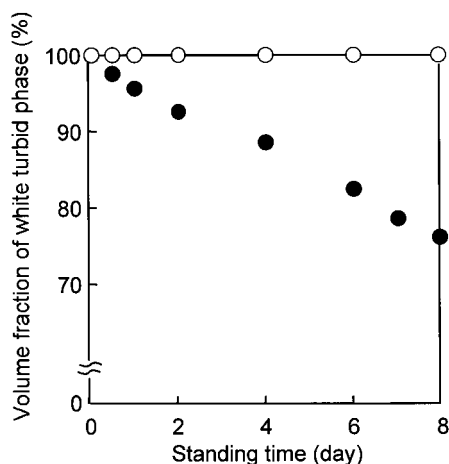


Figure 1 Sedimentation curves for 2-ethylhexyl acrylate–2-methoxyethyl acrylate–acrylic acid terpolymer [P(EHA–MEA–AA)] (49/50/1, w/w/w) (○) and ethyl acrylate–methyl methacrylate copolymer [P(EA–MMA)] (40/60, w/w) (●) emulsions prepared by emulsifier-free emulsion copolymerizations under conditions shown in Table 1.

$$P_w \text{ (g m}^{-2} \text{ 24 h}^{-1}\text{)} = [24 \times (a_1 - a_2)]/S$$

where a_1 and a_2 are, respectively, the weight of water before and after the permeation measurement for 1 h; and S is the area of filtration ($2.8 \times 10^{-3} \text{ m}^2$). The measurement was carried out five times for each sample and the average value was taken. Each error was less than 2.7% for all measurements.

Critical coagulation concentration

To estimate the difference of colloidal stabilities, critical coagulation concentration (CCC) values, which are standards for the colloidal stability of the emulsion to which electrolytes are added, for P(EHA–MEA–AA) and P(EA–MMA) emulsions were measured by the following procedure.^{8,16} First, each emulsion was purified by ion-exchange resin, and various concentrations of sodium sulfate aqueous solution were separately added to the emulsion. The initial coagulation rate at each sodium sulfate concentration was obtained from a relationship between time and absorbance of each emulsion measured by a spectrophotometer (Model 100-50; Hitachi Corp.) at 20°C with an incident wavelength of 470 nm. In the case of low sodium sulfate concentration, the initial slope at the absorbance versus time profiles increased significantly with an increase in the sodium sulfate concentration. The initial slopes at each sodium sulfate concentration are defined as the slow flocculation constant (K_s). The initial slope became constant at a certain sodium sulfate concentration. This initial slope is defined as the rapid flocculation constant (K_r). The sodium sulfate concentration at an intersection point of the two lines

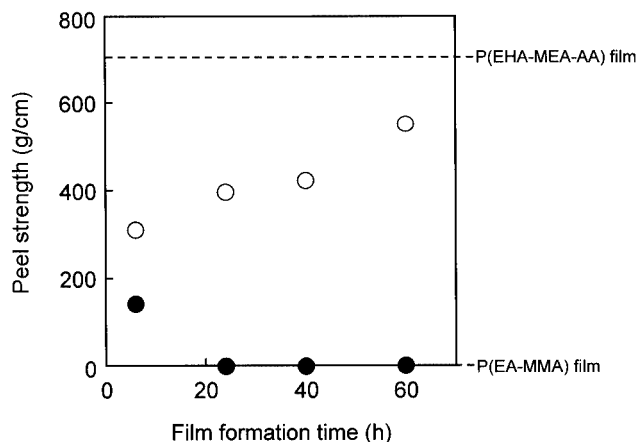


Figure 2 Relationships between film-formation time and peel strength for P(EHA–MEA–AA)/P(EA–MMA) (50/50, w/w) blend emulsion films. Measurement surfaces: ○, air side; ●, release-paper side.

in the logarithmic plots of K_r/K_s and the sodium sulfate concentration is a CCC value.

RESULTS AND DISCUSSION

Figure 1 shows the sedimentation curves of P(EHA–MEA–AA) and P(EA–MMA) emulsions prepared by emulsifier-free emulsion copolymerizations under conditions shown in Table I, from which electrolytes were removed by ion-exchange resin. In the P(EHA–MEA–AA) emulsion, the clear layer did not appear within 8 days, whereas in the P(EA–MMA) emulsion, the clear layer attributed to the sedimentation of the particles appeared at the top end. According to a previous study,¹³ this result suggests that there is a

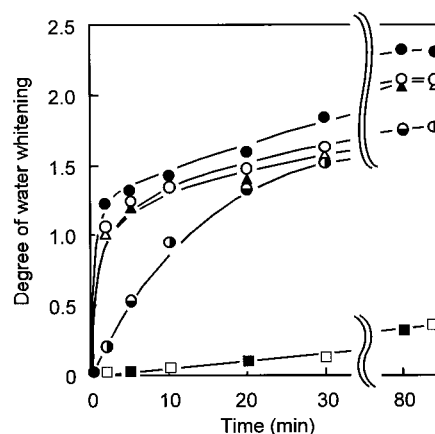


Figure 3 Variations of degree of whitening of P(EA–MMA)/P(EHA–MEA–AA) blend emulsion films (○, ●, ◐, ◑), P(EHA–MEA–AA) emulsion film (△, ▲), and melt pressed P(EA–MMA) emulsion film (100°C, 50 kg/cm², 20 min) (□, ■) in water at 25°C. Adsorption direction: ○, ◐, △, □, air side → release-paper side; ●, ◑, ▲, ■, release-paper side → air side. Film-formation time: ◐, ◑, 6 h; ○, ●, 40 h. Wave length, 610 nm.

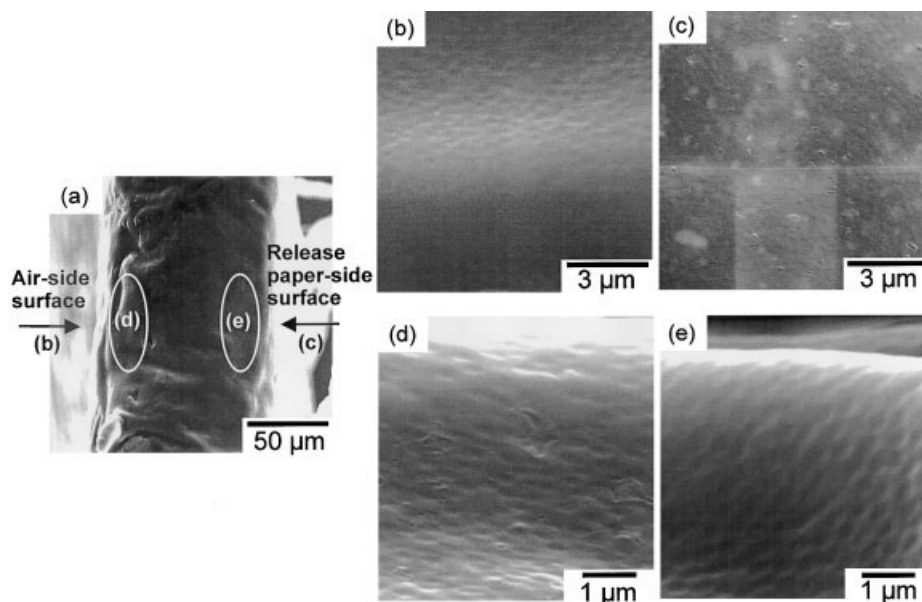


Figure 4 SEM micrographs of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion film: (a) cross section; (b) air-side surface; (c) release-paper-side surface; (d) cross section near the air side; (e) cross section near the release-paper side. Film-formation time, 6 h.

possibility of preparing a two-layer film by casting a blend emulsion (1/1, w/w) of the P(EHA-MEA-AA) and P(EA-MMA) particles.

Figure 2 shows the tackiness of the blend emulsion films prepared for different film-formation times. The film-formation times of 24, 40, and 60 h were adjusted with magnesium nitrate, sodium bromide, and sodium chloride saturated aqueous solutions, respectively. The film-formation time without the saturated salt aqueous solutions was 6 h. Hereafter, the films

will be shown as 6-, 24-, 40-, and 60-h films. There were great differences in the tackiness between both the surfaces of each film. The tackiness at the air-side surface increased with an increase in the film-formation time and approached that of the P(EHA-MEA-AA) film, whereas at the release-paper-side surface it disappeared at the film-formation time of 24 h and over. The difference in the tackiness between both surfaces increased with the increase in the film-formation time. That is, an asymmetrical film having a high

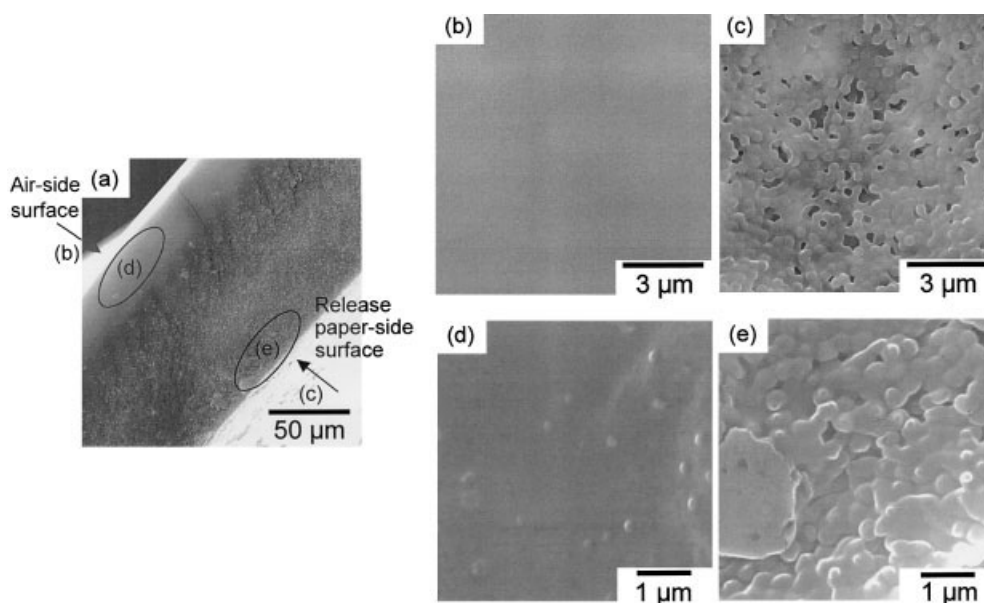


Figure 5 SEM micrographs of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion film: (a) cross section; (b) air-side surface; (c) release-paper-side surface; (d) cross section near the air side; (e) cross section near the release-paper side. Film-formation time, 40 h.

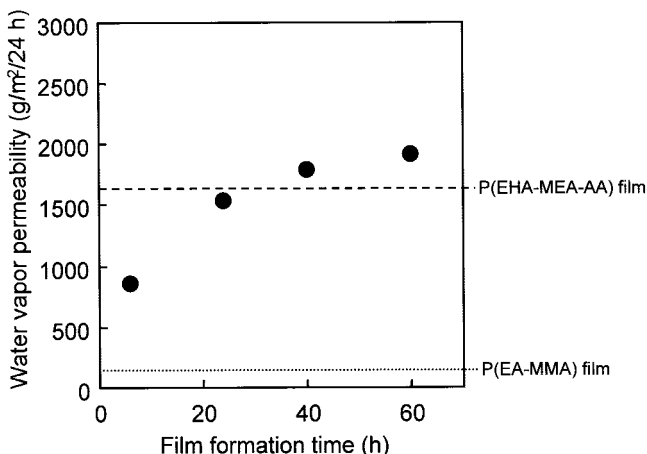


Figure 6 Relationships between film-formation time and water vapor permeability of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion films from release-paper side to air side.

tacky surface (air side) and a nontacky one (release-paper side) was prepared.

Figure 3 shows variations of degree of whitening of the P(EHA-MEA-AA)/P(EA-MMA) blend emulsion films, P(EHA-MEA-AA) emulsion film, and melt-pressed P(EA-MMA) emulsion film as a function of dipping time in water. In the P(EHA-MEA-AA) emulsion film, the whitening rates at air side and release-paper side were the same. This result was also observed in the melt-pressed P(EA-MMA) film and 6-h film. These results suggest that these films had homogeneous structures. On the other hand, in the 40-h film, the whitening rate at the air side was nearly equal to that of the P(EHA-MEA-AA) film and was slightly less than that at the release-paper side. Assuming that 40-h film has a simple two-layer structure, which consists of the P(EHA-MEA-AA) at the air side and the P(EA-MMA) at the release-paper side, the whitening rate at the release-paper-side surface must be equal to that of the melt-pressed P(EA-MMA) film; however, the rate was the highest, which suggests that there is a pore structure at the release-paper-side surface.

Figures 4 and 5 show SEM micrographs of the surfaces and cross sections of the 6- and 40-h films, respectively. The 6-h film had a similar morphology among both the surfaces and the cross sections. That is, the 6-h films had a comparatively homogeneous structure in which the two kinds of particles mixed randomly, whereas the 40-h films consisted of a dense structure at the air side and a porous structure at the release-paper side. The porosity at the release-paper-side surface and the smoothness at the air-side surface increased in magnitude with the increase in the film-formation time. In the release-paper side, the 24-h film had a few pores, and the 60-h film had many pores.

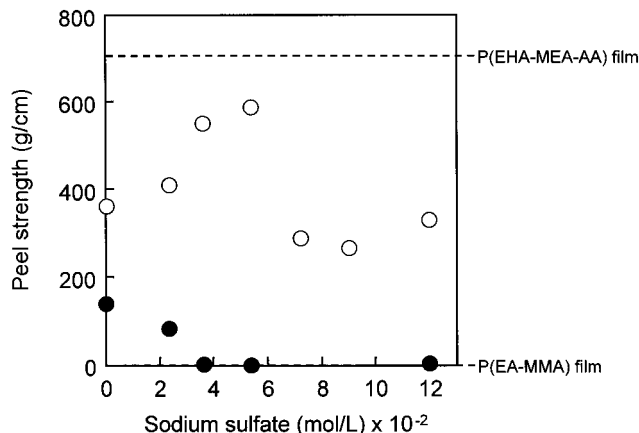


Figure 7 Relationships between sodium sulfate and peel strengths at air-side (○) and release-paper-side (●) surfaces of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion films. Film-formation time, 6 h.

It is an absolute requirement for a medical adhesive tape to have high adhesiveness at one side and high water vapor permeability. The two-layer structure having the porous structure may be useful for use as a medical adhesive tape.

Figure 6 shows a relationship between the film-formation time and the water vapor permeability of the blend emulsion films. The water vapor permeability increased with the increase in the film-formation time. This result was in substantial agreement with the results on the porosity of the films as shown in Figures 3, 4, and 5. Moreover, the water vapor permeabilities of the 40- and 60-h films were higher than that of the homogeneous P(EHA-MEA-AA) emulsion film having the same thickness (100 μm). The high water vapor permeabilities of the 40- and 60-h films seem to be based on the high porosity in the films. The P(EA-

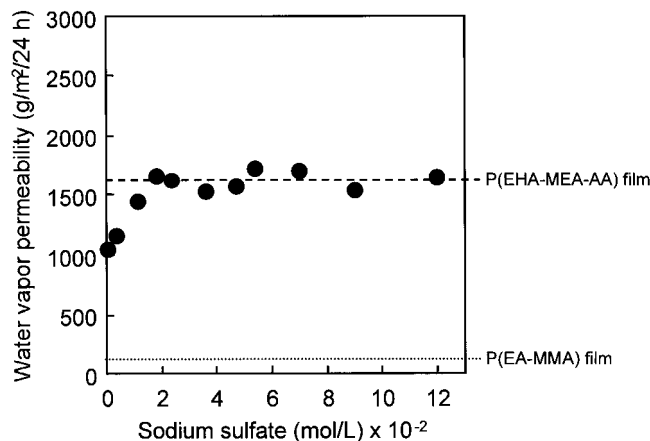


Figure 8 Relationships between sodium sulfate and water vapor permeability of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion films from release-paper side to air side. Film-formation time, 6 h.

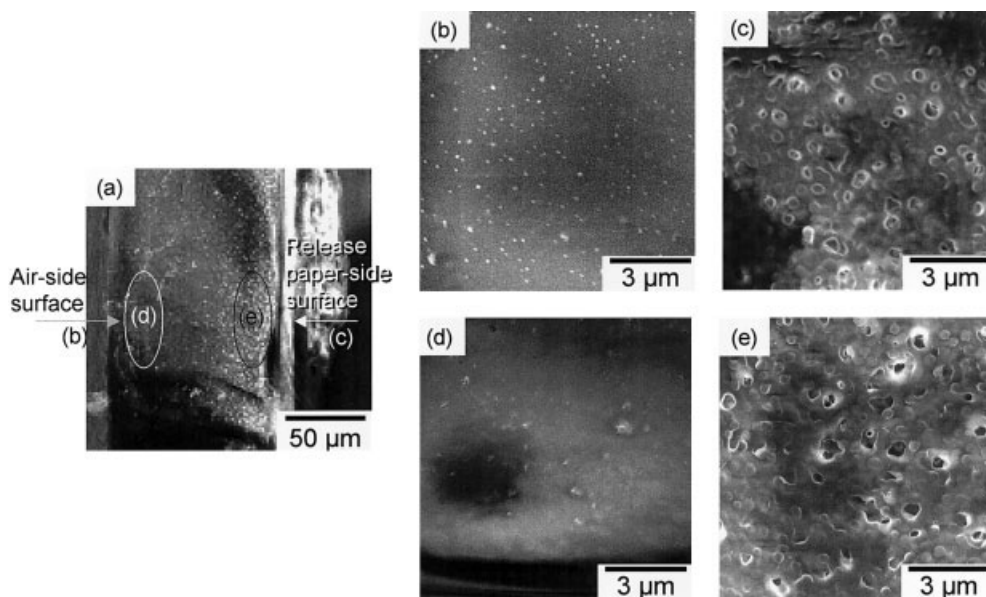


Figure 9 SEM micrographs of P(EHA-MEA-AA)/P(EA-MMA) (50/50, w/w) blend emulsion films (film thickness, 100 μm): (a) cross section; (b) air-side surface; (c) release-paper-side surface; (d) cross section near the air side; (e) cross section near the release-paper side. Sodium sulfate: 2.3×10^{-2} mol/L. Film-formation time, 6 h.

MMA) emulsion film, which had no pores, had the lowest water vapor permeability.

The CCC values of the P(EHA-MEA-AA) and P(EA-MMA) emulsions were determined to be 0.365 and 0.120 mol/L, respectively. Thus it is expected that a two-layer film having a porous structure may be prepared in a short film-formation time by the addition of sodium sulfate.

Figure 7 shows the relationships between the sodium sulfate concentration and peel strength at both surfaces of the 6-h films. The difference in the peel strength between both surfaces increased with an increase in the sodium sulfate concentration. The peel strength at the air-side surface increased with the sodium sulfate concentration below 0.054 mol/L and decreased above this value. The increase in the peel strength below 0.054 mol/L seems to be caused by earlier sedimentation of the P(EA-MMA) particles during the film-formation process. Decrease in the peel strength above 0.054 mol/L may be caused by the presence of sodium sulfate at the air-side surface of the film. In the case of 0.12 mol/L, the peel strength was increased from 390 to 440 g/cm by washing the film surface.

Figure 8 shows the relationship between the sodium sulfate concentration and the water vapor permeability of the 6-h films. The water vapor permeability increased with the increase in the sodium sulfate concentration, and attained a constant value above 0.023 mol/L, which was equal to that of the P(EHA-MEA-AA) film. The water vapor permeability of the P(EHA-MEA-AA) film was not increased by the increase of the sodium sulfate concentration.

Figure 9 shows SEM micrographs of the surfaces and cross sections of the 6-h film prepared at 0.023 mol/L of sodium sulfate, at which the water vapor permeability attained the saturated value as shown in Figure 8. A porous structure was clearly observed at the surface layer on the release-paper side. These results suggest that the addition of sodium sulfate may increase the solid content in blend emulsion to prepare the two-layer film.

CONCLUSIONS

From the above results, it is clear that the two-layer film having the porous structure and tackiness/non-tackiness asymmetric surfaces was successfully prepared by controlling the colloidal stabilities of the P(EHA-MEA-AA) and P(EA-MMA) particles, which indicates one method by which a high-grade medical adhesive tape may be prepared.

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