

Studies on Suspension and Emulsion. LIV. Shrinkage of Polymer Emulsion Film Having Asymmetric Porous Structure

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Synopsis

It was found that the film cast on a glass plate from emulsifier-free ethyl acrylate–methyl methacrylate copolymer emulsion when separated from there shrank and curled immediately. This film had an “asymmetric” porous structure. It was discussed the relationship between the porous structure and the shrinkage due to the residual internal stress produced during film formation.

INTRODUCTION

In an earlier article¹ we suggested that the film cast on a glass plate from emulsifier-free ethyl acrylate–methyl methacrylate copolymer emulsion has an “asymmetric” porous structure. In a following article,² its formation mechanism was studied from the viewpoint of emulsion stability during drying.

Moreover, in these experiments it was acknowledged that the above emulsion film when separated from the glass plate shrank immediately. In addition, it curled against the opposite side as compared with the usual polymer emulsion film. These behaviors seem to be due to the residual internal stress produced in the film formation process. As the internal stress affects the cohesive and adhesive qualities of coating, it is important in the field of coating and adhesive industries.³ However, to our knowledge, there are few reports on the shrinkage studies of polymer emulsion cast film in the literature.⁴ Therefore, in this article, we tried to clarify this point.

EXPERIMENTAL

Materials

Ethyl acrylate (EA) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Potassium persulfate and sodium sulfate were reagent-grade. Commercial-grade sodium dodecyl benzene sulfonate (DBS) was used after drying and deionized water was distilled with a Pyrex distillator.

Emulsion Polymerization

Emulsifier-free EA—MMA (60/40, w/w) copolymer emulsion was prepared by emulsifier-free emulsion copolymerization with potassium persulfate as initiator at 70°C. The solid content was 15%. The number-average diameter

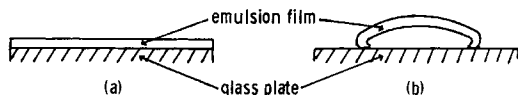


Fig. 1. Emulsion film before (a) and after (b) freeing from glass plate.

determined with a disk centrifuge sedimentometer (Union Giken Co., PA-101) was $0.50 \mu\text{m}$ (standard deviation:0.04). The glass transition temperature of this copolymer measured with a differential scanning calorimeter, Daini Seikosha Model SSC/560S, using a $5^\circ\text{C}/\text{min}$ heating rate, was 18.2°C .

The emulsion was cast on a glass plate ($10 \times 10 \text{ cm}$) in a film thickness of ca. 0.1 mm . The emulsion film was smoothly freed without elongating from the glass plate by dipping dried pieces in water at 30°C for 1 h. The water content in film before dipping was less than 1% w/w. The length of the now-free film was measured, and the shrinkage was calculated according to following equation:

$$\text{shrinkage (\%)} = 100 \times (L_0 - L)L_0$$

where L_0 and L are the lengths of film before and after separation from the glass plate, respectively.

Whitening Rate of Film in Water

The variation in optical density with each dipping time of film of $5 \times 20 \text{ mm}$ in water was recorded at 30°C , with incident light in a wavelength of 660 nm . Here, as described in detail in an earlier article,¹ the portion in contact with water was limited to one side of the specimens, namely, the film–air or film–substrate (glass) interface in the process of film formation, hereafter abbreviated as air side and glass side, respectively.

RESULTS AND DISCUSSION

When EA—MMA copolymer emulsion film was freed from the glass plate in water, it shrank and curled immediately, as shown in Figure 1. Similar curling was observed in film without freeing cast on aluminum foil, $250 \mu\text{m}$ in thickness. Thus the shrinkage was greater at the glass side than the air side. The states of shrinkage and curling were maintained even if the film continued to be dipped in water after freeing from the glass plate. Therefore, it is clear that they were not due to the partial water absorption on the air side during dipping in water to free from the glass plate. Though we can often observe the curling phenomenon of emulsion film, it curls generally against the opposite side shown in Figure 1. This suggests that the distribution of residual internal stress in the emulsion film used in this work is different from that in usual emulsion film. When sample pieces without freeing were maintained at 30°C after the completion of film formation at 30°C , the shrinkage decreased with the standing time, reaching a constant value, 3%, after 15 days. In the case of polyethyl acrylate emulsion film, oppositely, it expanded because of water absorption to free from the glass plate in water.

Figure 2 shows the shrinkage in the case where the sample pieces were kept at different temperatures for 1 h after the completion of film formation at 30°C . The shrinkage decreased with the elevating of the treating temperature. When the emulsion particles were allowed to absorb toluene before film formation, the shrinkage decreased.

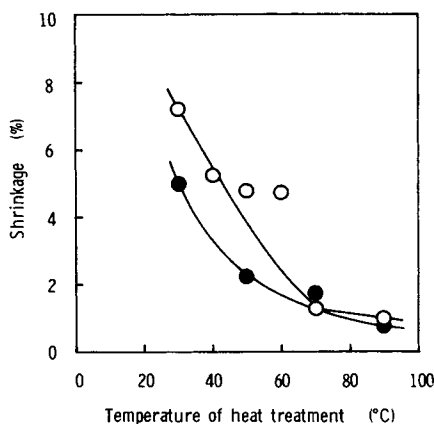


Fig. 2. Effect of heat treatment for 1 h on the shrinkage of emulsifier-free EA—MMA copolymer emulsion films: (○) original emulsion; (●) toluene-containing emulsion.

The above results suggest that the internal stress produced was greater on the glass side than on the air side, and was reduced by large scale molecular motion allowed by the addition of toluene (a plasticizer).

The effect of porosity in film, controlled by the emulsion stability during film formation according to the earlier article,² on the shrinkage was investigated.

Figure 3 shows the shrinkage of films from emulsions having different stabilities formed at different temperatures. The emulsion stability was changed by the post-addition of anionic emulsifier or ionic salt. As will be seen, in the case of post-stabilized emulsion, the shrinkage was almost same, but, in the case of post-unstabilized emulsion, it was smaller, as compared with the original emulsion. In addition, regardless of emulsion stability, the shrinkage decreased with an elevating of formation temperature.

Figure 4 shows the effect of emulsion stability on the whitening rate of emulsion films in water. Regardless of the portion of water permeation, as the emulsion stability increased, the whitening rate decreased. In addition, regardless of emulsion stability, the whitening rate based on water permeation on

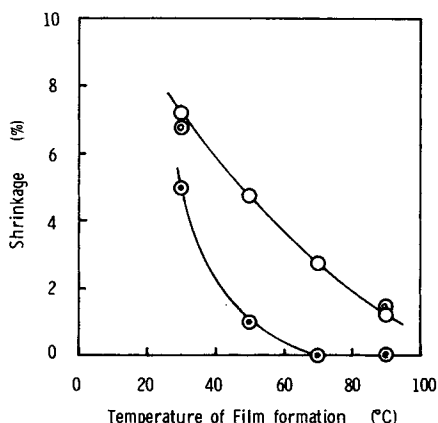


Fig. 3. Effect of the emulsion stability during film formation on the shrinkage of EA—MMA copolymer emulsion films: (○) without additive; (⊙) post-addition of DBS; (⊖) post-addition of Na₂SO₄.

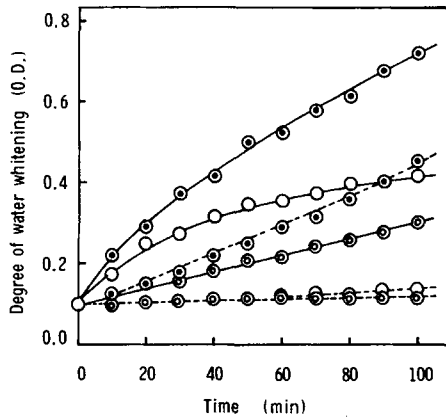


Fig. 4. Effect of the emulsion stability during film formation on the whitening rate of EA—MMA copolymer emulsion films: (O) without additive; (⊙) post-addition of DBS; (●) post-addition of Na_2SO_4 . Water absorption direction: (—) air side \rightarrow glass side; (---) glass side \rightarrow air side.

the air side was larger than that on the glass side. These results show that these films have asymmetric porous structure and their degree of asymmetry and porosity increased with a reduction in emulsion stability as reported in detail in the previous articles.^{1,2} In the same measurement for films prepared at different temperatures shown in Figure 3, it was found that the degrees of porosity at both sides increase with an elevating of temperature.

Figure 5 shows the relationship between the whitening rate and shrinkage. As will be seen, the whitening rate based on water permeation on the air side was not related to the shrinkage, but that on the glass side appeared to correlate with the shrinkage. In addition, as the whitening rate of film on the air side the degree of curling of the films without freeing cast on the aluminium foil decreased.

From the above results, the shrinkage behavior seems to be as follows. In the particle coagulation process via close packing, polymer molecules in particles must move in large-scale motion. If they cannot move satisfactorily, internal stress is produced in the film, resulting in shrinkage when it is freed. At this time, the porous structure in film which is formed by flocculation before close packing

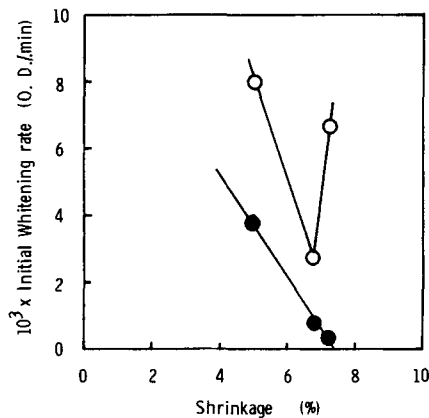


Fig. 5. Relationship between the initial whitening rate and the shrinkage of EA—MMA copolymer emulsion films. Water absorbing direction: (O) air side \rightarrow glass side; (●) glass side \rightarrow air side.

must reduce the internal stress. Thus, as the emulsion film used in this work has an asymmetric porous structure, the porosity being larger on the air-side than on the glass-side, it shrank and curled, as shown in Figure 1.

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