

# Morphology of Composite Film Prepared by Polymerizing Styrene in Poly(vinyl Chloride) Film

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## Synopsis

Styrene and the styrene-additive mixtures (kerosene, dioxane, ethylene dichloride, or dioctylphthalate) were soaked into a poly(vinylchloride) film and then styrene was polymerized. Subsequently, poly(styrene) was extracted with  $\text{CCl}_4$  and the microporous membrane was obtained, of which the morphology was studied. It is elucidated that the additives affect the morphology of the resultant composite films.

## INTRODUCTION

A cation exchange membrane is prepared by the paste method<sup>1,2</sup> and the soaking method.<sup>3</sup>

**Paste Method.** A paste, mainly consisting of styrene (St), divinylbenzene (DVB), an initiator of radical polymerization, and fine poly(vinyl chloride) (PVC) powder, is coated onto a PVC cloth as a reinforcing material, and St and DVB are copolymerized by heating. Thus the base membrane is prepared and then sulfonated with concentrated sulfuric acid to obtain the cation exchange membrane.

**Soaking Method.** A PVC film is immersed in a mixture of St, DVB, an initiator of radical polymerization, and an additive to control the swelling of the PVC film. Subsequently, the swollen PVC film is taken out and heated to copolymerize St and DVB. Thus the base membrane is obtained, onto which cation exchange group is introduced by sulfonation with concentrated sulfuric acid.

In these cation exchange membranes, the cation exchange resin component is finely and continuously dispersed in the PVC gel phase. Also, the cation exchange resin component ( $\text{Fe}^{+++}$  form) is selectively decomposed and removed by treating with an  $\text{H}_2\text{O}_2$  aqueous solution, and the microporous membrane of PVC is obtained.<sup>4-8</sup> However, when no DVB is used, the flat cation exchange membrane is not easily obtained, and the flat microporous membrane also is not prepared.

We have now succeeded in preparing a microporous film by using no DVB. Poly-St, polymerized in a PVC film, was extracted out of the composite film of poly-St and PVC with the use of  $\text{CCl}_4$ . The resultant PVC film was microporous but has lower water permeability. Then we have found that its morphology was interesting, showing the polymerizing behavior of St in the PVC gel phase.

## EXPERIMENTAL

### Materials

All the reagents used were of commercial grade. St was washed with a dilute NaOH aqueous solution and water, dried over anhydrous  $\text{CaCl}_2$ , and distilled under reduced  $\text{N}_2$  atmosphere before use. PVC film was of commercial grade and 0.1 mm thick, containing 25% of dioctylphthalate (DOP).

### Preparation of the Microporous Film

The PVC film was immersed in a mixture of St-benzoylperoxide (BPO) or St-BPO-additive at  $40^\circ\text{C}$  for 2 h. The BPO/St and St/additive ratios were 0.015 and 3 by weight, respectively. Kerosene, dioxane, ethylene dichloride, and DOP were used as the additive without any purification. The swollen PVC film was taken out, wrapped with cellophane film, and heated at  $110\text{--}120^\circ\text{C}$  for 15 h, applying some pressure on the film surface by using iron plate. St was thus polymerized, and the base film was prepared. Subsequently, the base film was immersed in  $\text{CCl}_4$  to extract poly-St. Renewing  $\text{CCl}_4$ , the extraction was carried out until no turbidity was observed when the extracting solution was added to excess methanol.

### Measurement of Water Permeability

Water permeability of the microporous film was measured by using a cell similar to that in the previous paper,<sup>9</sup> when the applied pressure was  $3\text{ kg/cm}^2$  and the effective film area was  $6.15\text{ cm}^2$ .

### Scanning Electron Microscopy

The surface and the cross section of the microporous film were observed by using a scanning electron microscope (JSM-50A from JEOL Ltd.). The cross section was prepared by breaking the film dipped in liquid  $\text{N}_2$ . The specimens were freeze-dried, fixed on a cylindrical Cu disk, and then coated with a thin Au layer by using a vacuum metalizer.

## RESULTS AND DISCUSSION

When a monomer is polymerized in a film of another polymer (polymer A) and the resultant polymer (polymer B) is incompatible with the polymer A, the polymer B separates out of the polymer A during the polymerization. If the polymer B can be extracted out of the polymer A with an appropriate solvent, a microporous film of the polymer A is obtainable. The polarity balance among the polymer A, the polymer B, and the solvent is important to obtain a good microporous film. After some preliminary experiment, we studied on the combination of PVC-poly-St- $\text{CCl}_4$ . It was preliminarily elucidated that when poly-St polymerized in the unplasticized PVC film, poly-St was not easily extractable, and the preparation of the microporous film was difficult. Accordingly, a plasticized PVC film was used in this study.

Table I shows some film properties before and after the polymerization of St and the extraction. Some expansion from the PVC film to the base film is observed and also some shrinkage from the base film to the microporous film.

TABLE I  
 Properties of the Films<sup>a</sup>

No.	Additive	Base film		Microporous film	
		Dimension (cm × cm)	Weight increase	Dimension (cm × cm)	Water content (g H <sub>2</sub> O/g wet film)
1	None	5.1 × 6.1	0.36	4.9 × 5.9	0.49
2	Kerosene	5.0 × 5.4	0.23	5.0 × 5.4	0.07
3	Dioxane	5.2 × 6.2	0.42	4.9 × 5.9	0.50
4	Ethylene dichloride	5.1 × 6.6	0.48	5.0 × 6.4	0.55
5	DOP	5.2 × 6.4	0.43	4.8 × 6.4	0.50

<sup>a</sup>Weight increase = (weight of base film - weight of PVC film)/weight of base film.

Water content = (wet weight - dry weight)/wet weight. Dimension of PVC film, 5 cm × 5 cm.

The weight increase of nos. 3-5 is larger than that of no. 1, and on the other hand, the weight increase of no. 2 is less than that of no. 1. This is explainable in terms of the affinity of St and the St-additive mixtures for PVC. Namely, the good solvent for PVC is effective as additive to make the PVC film more swollen, and, on the other hand, kerosene (poor solvent for PVC) suppresses the swelling of the PVC film. The weight increase means the increase of the extractable component consisting of the additive, DOP, and poly-St. All the extractable component is removed except in the case of no. 2. Water content shows the porosity of the microporous film, and the water content of no. 2 is very small. This shows that poly-St is essentially unextractable in the case of no. 2. A poor solvent for PVC is inadequate as the additive.

Table II shows that the water permeability of the microporous film is very small. This is owing to the presence of the skin layer at the surface of the microporous film. The PVC film itself has a skin layer as shown in Figure 1, and, furthermore, St soaked in the part near the film surface should migrate away during the polymerization. This should be one of the reasons why the phase separation of poly-St at the film surface was not enough to make the microporous structure applicable as a microporous filter. In order to remove the skin layer, the film surface was carefully shaved with a razor-blade to make the surface dull. Thus the water permeability of the shaved film, no. 1, increases. Furthermore, in order to make it easier to remove the skin layer, it was found that dipping the base film in tetrahydrofuran for a few seconds was

 TABLE II  
 Water Permeability of Microporous Films

No.	Appearance of film	Water permeability ( $\times 10^{-3}$ mL/cm <sup>2</sup> min kg cm <sup>-2</sup> )			
		Nontreatment	After shaving with razor blade		After tetrahydrofuran treatment
			One surface	Both surfaces	
1	Rather dull	1.6	2.6	8.3	8.1
4	Glossy	0.2	—	—	7.6
5	Glossy	0	—	—	8.3

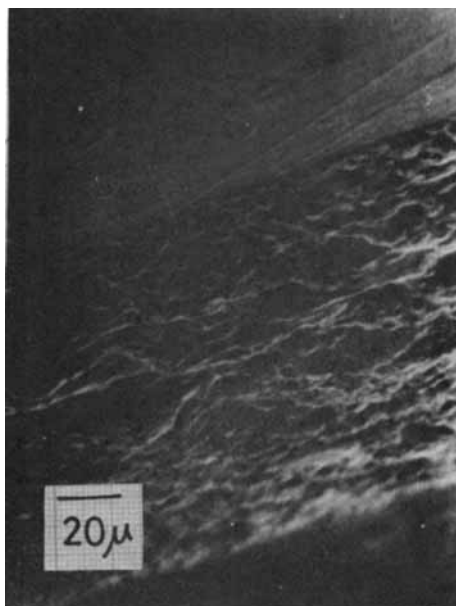


Fig. 1. Scanning electron micrograph of the cross section of the PVC film.

effective. In fact, the water permeability increases. Considering that the porosity is pretty large, the small water permeability is difficult to understand, and exclusion of the skin layer may be still imperfect.

Figure 2 shows an example of the porosimetry curve by using Model 1520 SM from the Carlo Erba Scientific Instruments Div. The average pore size is  $0.05 \mu\text{m}$ , and the pore size distribution is rather narrow. This means that the phase separation of poly-St uniformly occurs in the PVC gel phase during the polymerization. Also, polyethylene latex (particle size,  $0.1 \mu\text{m}$ ) could not pass

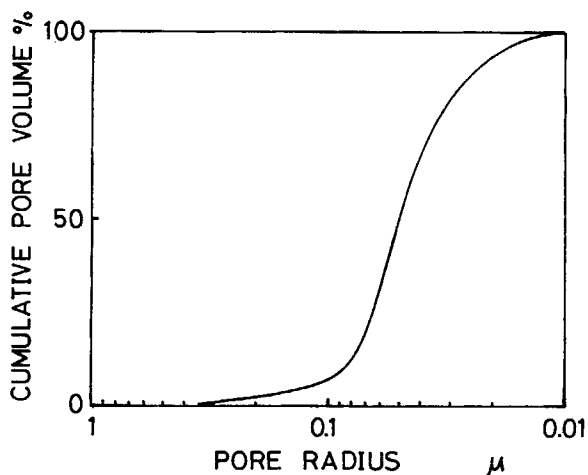


Fig. 2. Pore size distribution of a microporous film of the PVC-poly-St system. Porosity 53% and 0.12 mm thick.



Fig. 3. Scanning electron micrograph of the surface of the microporous film, no. 1.

through these films. The dimension of the film does not change by drying at room temperature. When the microporous film is once dried, the film becomes water-unwettable. However, it is possible to make the film water-wettable again by treating with methanol.

Figure 3 shows the surface of the microporous film, no. 1. Fine craze can be observed, which might be formed by extracting poly-St and/or drying. The

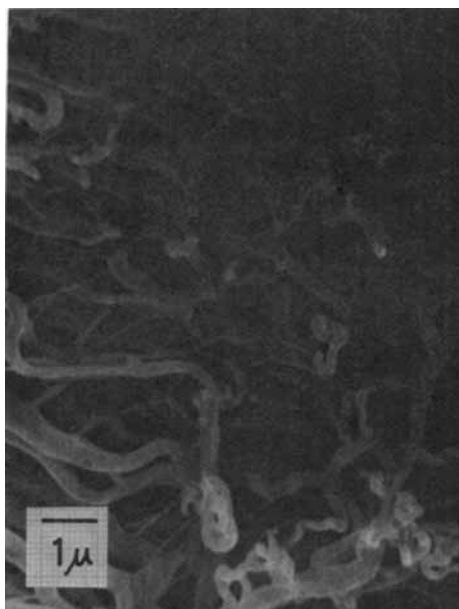


Fig. 4. Scanning electron micrograph of the cross section of the microporous film, no. 1.

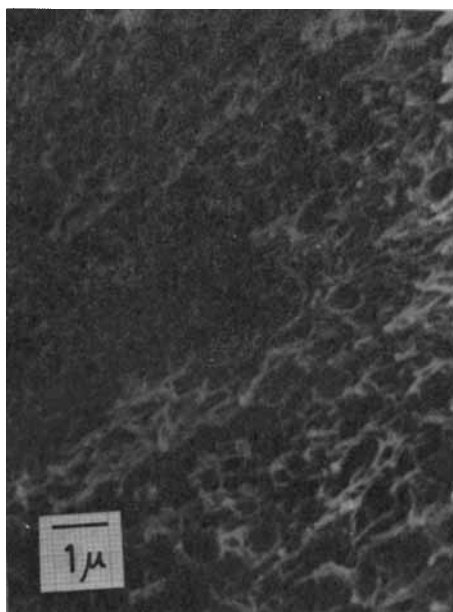


Fig. 5. Scanning electron micrograph of the cross section of the microporous film, no. 3.

surface is significantly different from the structure of its cross-section, as shown in Figure 4. These results verify the presence of the skin layer and support the increase in the water permeability by shaving the film surface with a razor-blade or the tetrahydrofuran treatment.

Figures 5 and 6 show the cross section of the microporous films, nos. 3 and 5. In the case of no. 1, the PVC phase is of three-dimensional string network,

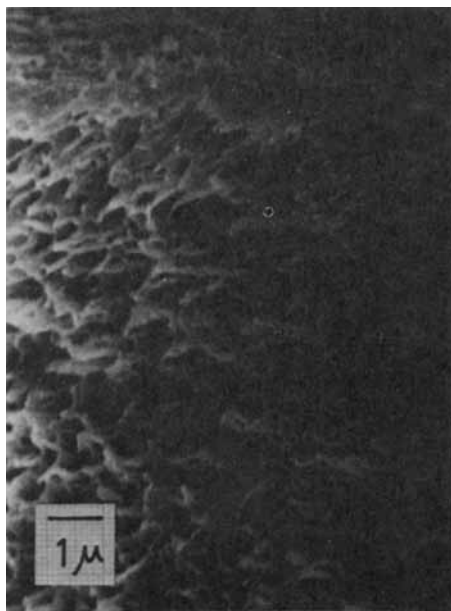


Fig. 6. Scanning electron micrograph of the cross section of the microporous film, no. 5.

and this pattern is very much different from that prepared by copolymerizing St and DVB in the PVC gel phase.<sup>6</sup> Namely, when the microporous membrane is obtained from the cation exchange membrane prepared by the soaking method or the paste method, its structure is like an aggregation of minute cells. This difference should be ascribed to the copolymerizing behavior of St and DVB. When St and DVB copolymerize in a PVC gel phase, the polymerizing poly-St separates out of the PVC gel phase, and then DVB (a crosslinking agent) promotes the phase separation. From the comparison of the patterns among nos. 1, 3, and 5 as shown in Figures 4-6, the additives (dioxane and DOP) are effective to make the phase-separated poly-St more finely dispersed in the PVC gel phase. Here, it is meaningful to note that the film porosities are almost the same. Now, the additive effect described above is inexplicable. However, it might be interesting to study the relation between the state of the phase separation and the mechanical properties of the composite film.

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