非對稱型 逆滲透膜의 構造 調整機構에 對하여

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The Mechanism for Regulating the Structure of "Skinned" Type Membranes

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Abstract

Optical microscopy was used to investigate the phenomena involved in the precipitation of cellulose acetate membranes cast from various binary solutions containing 20% (wt.) of acetone, acetic acid and dioxane, respectively. It was observed that the high rate of precipitation induced convection flows in the cast polymeric solution during precipitation by cold water. The formation of membrane defects such as voids and large cavities as observed by previous workers could well be attributed to the occurrence of such convection flows. The driving forces for their occurrence could, however, not be properly accounted for by the gradients of buoyant force and surface tension force. The magnitude of the net volume flow rate between the solvent and the non-solvent phases could explain the convection flow. The extension of air-exposure period before precipitation was a convenient way for eliminating membrane defects.

Introtuction

Manufacturing asymmetric porous cellulose acetate membranes for reverse osmosis applications involves generally the following steps:[8] (i)casting the polymer solution as a thin film on a surface; (ii) evaporation of the solvent from the film surface; (iii) immersion of the film in an appropriate gelation medium such as cold water; and finally (iv)shrinking the membrane by contact with hot water. During evaporation period a membrane skin or thin layer of dense polymer is formed at the air surface as a result of the establsihed solvent gradient. Coagulation preserves or fixes this structure which acts as a salt-selective layer. The matrix or porous region on which this skin rests is formed during coagulation by polymer precipitation resulting from the competing processes of non-solvent penetration and solvent extraction.

During the past few years, solvent evaporation rates and equilibrium phase separation conditions in the surface region have been quantitatively studied for the development of the improved membranes, notably by Sourirajan and his coworkers.[3-6] Large voids or imperfections in the backing porous matrix have been found in many cases. However, the study on the factors governing their formation has been meager, although it is one of the most important problems associated with the practical application of high-

pressure reverse osmosis techniques.

Recently, Frommer and Matz[1] made optical and scanning electron microscopic studies on the mechanism of the formation of imperfections for membranes made from various binary solutions containing only cellulose acetate and solvent. They proposed a general mechanism that the formation of large finger-like cavities in membranes originates from convection flows induced in the cast fluid polymeric solution due to a high rate of precipitation of polymer from the cast solution. The high rate of precipitation was generally associated with a high tendency of the non-solvent to penetrate and mix with the solvent. On the other hand, the fluidity of the casting solution was found to play an interrelated part in controlling convection flows. These two parameters have not yet been quantitatively related, however. Also, the same general mechanism was not qualitatively applied to the acetone-cast membranes. The object of the present work is to re-examine the driving forces which can account for the formation of convection cells and to check the possibility of utilizing the extension of air-exposure period and the stabilizing effect of surface active agent added to the non-solvent for eliminating membrane defects.

Experimetal

Three binary solutions were prepared using acetone, acetic acid and dioxane as solvents and used for manufacturing membranes and optical microscopic studies. All binary solutions contained 20% (wt.) of Eastman's type E-398-3 cellulose acetate (acetyl content 39.8%; molecular weight 35,000).

Solutions were cast as a 0.3 mm film at ambient temperature ($\sim$24°C) on a glass plate (10×25 cm). They were precipitated in an ice-water bath immediately after their casting. Two minute-evaporated acetone-cast and dioxane-cast membranes were also manufactured for studying the effect of airexposure period on the membrane structure. The influence of a surface active agent was examined with a dioxane-cast membrane precipitated in ice-cold water containing 0.5% (w. t) sodium dodecyl benzene sulfonate. All membranes were annealed in a water bath at 80°C for 30 minutes and stored in water.

A drop of the casting solution was placed on a microscope slide and covered with a cover-slide to form a thin circular film. The slides were carefully cleaned with cleaning solution before use. Drops of water were then applied in contact with periphery of the cover slide. These drops were immediately drawn by capillary forces in between the microscope slides to form a circular water-polymer solution interface. Dark field microscopy was used to observe and follow the formation of light scattering zones such as interfaces between homogeneous phases and turbid areas. Two different air-exposure periods were chosen: 30 seconds and 90 seconds. All photomicrographs were taken two minutes after contact with water.

Results and Discussion

Our observations of the manufactured membranes are summarized in Table 1. Membranes No. 2 and No. 4 were transparent whereas the other membranes were white and opaque. The extension of air-exposure

Table 1. Manufacturing Conditions and Observation of the Cellulose Acetate Membranes Cast from Various Binrary Solutions

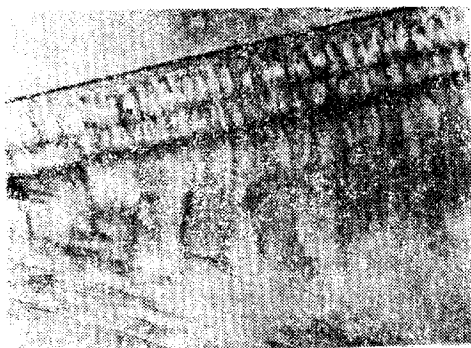| Memberane No.	Casting Solution	Air-Exposure Period	Gelation Medium	Observation
1	CA-acetone	0 min	Ice-cold water	White and opaque
2	CA-acetone	2	//	Transparent
3	CA-acetic acid	0	//	//
4	CA-dioxane	0	//	White and opaque
5	CA-dioxane	2	//	//
6	CA-dioxane	0	0.5% SDBS Aqueous solution	//
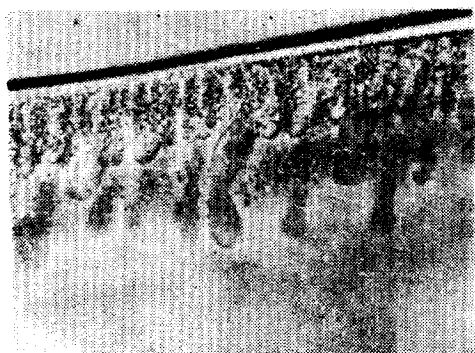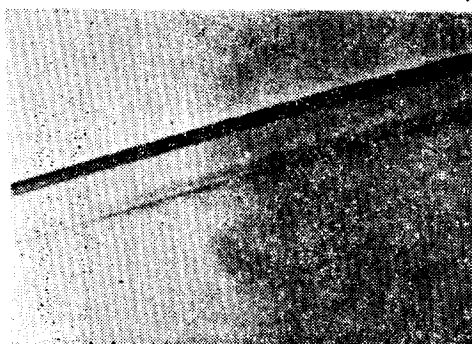
0. 5 Min.   1. 5 Min.

Fig. 1   Acetone-cast solution in contact with water

0. 5 Min.   1. 5 Min.

Fig. 2   Acetic acid-cast solution in contact with water
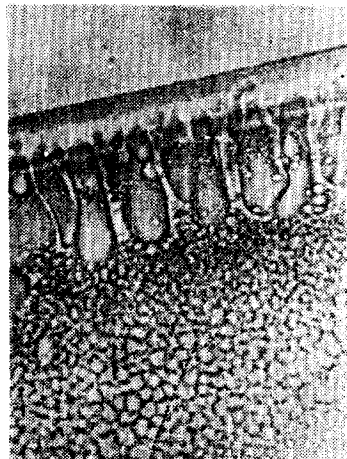
0. 5 Min.   1. 5 Min.

Fig. 3   Dioxane-cast solution in contact with water

0. 5 Min.　　　　　　　　　　　　　　　1. 5 Min

Fig. 4　Dioxane-cast solution in contact with SDBS aqueous solution

period effected the change in an acetone-cast membrane but not a dioxane-cast membrane. The surface active agent did not cause any observable change in a dioxane-cast membrane. All membranes were thinner than the original cast films and the increasing order of partial shrinkage was acetone>dioxane>acetic acid.

Typical pictures of precipitation phenomena observed through an optical microscope are shown in Figures 1 through 4. The homogeneous region between a polymer-water interface and a turbid zone represents the precipitate formed during the air-exposure period before contact with water. The turbid zone displays the precipitate formed thereafter. The coagulated structures are seen to be quite different depending on the nature of the solvents and on the air-exposure period. The relative rate of penetration of the precipitation front from the periphery of a circular droplet towards its center is in the order acetone <acetic acid <dioxane. The extension of air-exposure period reduces significantly the rate of penetration and makes the structure more uniform. There is no observable effect caused by the surface active agent used.

It is obvious that membranes are opaque when they contain many pores larger than the range of the visible spectrum (04-0.7μ) which scatter light. Acetic acid-cast membranes must therefore be of more uniform structure than those cast from other solvents. By similar reasoning, two minute-evaporated acetone-cast membranes must contain pores smaller than those of non-evaporated membranes. Optical photomicrographs show that precipitation structures for opaque membranes exhibit more turbid and cavity-like zones and that in such cases the rates of precipitation are high. It is also possible for anyone to observe that a high rate of precipitation induces the convection flow in the polymeric solution. It is therefore understood that a large extent of formation of cavities in membranes must be associated with a high rate of precipitation, as Frommer also proposed.

It may be simply considered that the precipitation of polymer takes place when the concentration of the non-solvent in the polymeric solution reaches a certain value (C) at the precipitation point. For a simple case where the film shrinkage is not allowed during its formation as in the optical microscope experiments, it follows from the precipitation condition that

$$C = \frac{J_w dt}{J_w dt + [(d\delta)\rho x - J_s dt] + (d\delta)\rho(1-x)}$$

where $\delta(t)$ is the depth of precipitation from the surfaces,

J_w and J_s respectively the influx of non-solvent and the outflux of solvent,

ρ the density of the casting solution,

x the weight fraction of the solvent in the casting solution.

Rearranging this equation for the rate of precipitation yields

$$\frac{d\delta}{dt} = \frac{1}{\rho} \left[\frac{1-C}{C} J_w + J_s \right]$$

This equation may well apply to the precipitation from the binary polymeric solution, It shows that the rate of penetration of the precipitation front is expected to decrease with (a) decrease in J_w; (b) decrease in J_s; (c) increase in C; and (d) increase in ρ. Decrease in J_w and J_s will be achieved by extending the air exposure period because a thicker membrane skin is formed. Other factors being constant, a use of the solvent having a lower tendency of mixing with the non-solvent will decrease the rate of precipitation through the decrease in J_w and J_s. For the solvents studied, Frommer, Matz and Rosenthal[2] reported the essentially same values ($\sim$30wt. %) for C. These expected results are in accordance with our observations except for the case of acetone-cast membranes. The relative initial tendencies of the non-solvent and the solvent to dissolve in each other are in the order, acetone$<$ acetic acid$<$dioxane, judging from the data on the heat of mixing collected by Frommer and Matz.[1] This fact indicates that the extent of formation of cavities does not depend simply on the absolute magnitude of the rate of precipitation. Frommer, Matz and Rosenthal[2] measured the direction and magnitude of osmotic flows using membranes cast from 20% dried E-398-3 cellulose acetate in tetraethyl phosphate(TEP). The results are given in Table 2.

In the case of dioxane and acetone, there is a net volume flow from the solution into the water compartment. When acetic acid is used as the solvent, there

Table 2. Direction and Magnitude of Volume Flow Through a Porous C/A Membrane Separating Water from A 2:3 Water–Solvent Solution

Solvent in the 2:3 Water- Solvent Solution	Direction	Magnitude μl/cm^2 min. 100 mircrons
Dioxane	Solution to Water	0. 08
Acetic Acid	Not Detectable	—
Acetone	Solution to Water	0. 1*

*Measurement by the authors

is no volume flow through the membrane to either direction. Although the measurement is made with a TEP-cast membrane, the relative magnitude of the net volume flow is in agreement with the observed relative shrinkage of the membranes. These data suggest that the net volume flow from the solution into the water phase results in convection flows in a polymeric solution and hence growing of the cavities in the precipitated layer. Associated with this mechanism, the extent of convection flows will depend on the the fluidity of the polymeric solution. The increasing order of the observed viscosity of the polymeric solutions was acetic acid$>$dioxane$>$acetone. Combining these two parameters then explains the unique feature of acetone-cast membrane.

At this point, it is necessary to examine finally what other driving forces could induce convection flows in the polymeric solution. Since buoyancy-driven convections are not expected in the optical microscope experiments, there must be driving forces other than density gradients. Since the structures of membranes were unaffected by the way a cast membrane was immersed in the non-solvent bath, they were not the driving forces in the membrane-manufacturing process, either. One may then speculate the surface tension-driven convection mechanism. To clarify this possibility, we first observed the patterns near the water-organic solvent interface during their mixing. They are briefly summarized in Table 3. Interfacial turbulence was observed except for the acetone-water system. The influence of the surfactant on the resulting precipitation structure for dioxane-casting solution was virtually negligible. Therefore,

Table 3. Mixing Patterns for the Water-Organic Systems

System	Mixing Patterns	
	Upper Phase	Lower Phase
Acetone (upper) Water (lower)	No turbuleece Stable	No turbulence Stable
Water (upper) Acetic acid (lower)	Turbulence Calms down rapidly	Turbulence Calms down slowly
Water (upper) Dioxane (lower)	Turbulence Calms down slowly	Turbulence Calms down slowly

the surface tension-driven mechanism was not the effective one, either.

Conclusions

For better mastering of the art of membrane manufacturing, an extensive more quantitative understanding of the present problem is highly required. Our qualitative ideas and observations lead to the following conclusions:

(1) The formation of membrane defects is generally ascribed to the high rate of precipitation, but should accompany the net volume flow from the casting solution into the non-solvent phase.

(2) The extension of the air-exposure period is a very convenient way for regulating the structure of skinned type membranes when they are made from a highly volatile solution.

(3) Driving forces for convection flows induced in the polymeric solution cannot be explaind by surface tension or buoyant force gradients.

References

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