Effect of Solvent Mixture on the Formation of Asymmetric Polyimide Membrane and Gas Permeation

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The effects of solvents (DMAc, NMP, 1,4-dioxane) and nonsolvents (H_2O, Methanol, n-hexane) on the morphology of 6FDA-*p*-TeMPD polyimide membrane, prepared by the wet phase inversion method, were studied.

In the polymer/solvent/nonsolvent ternary system, the binodal curve, the coagulation value and the relative light transmission were measured, and the solubility parameter difference was calculated. The onset state and rate of liquid-liquid demixing were predicted and the morphology of membrane was analyzed. It is found that the finger-like pores are formed within uncontinued polymer nodules of membrane when the binodal curve is close to the polymer-solvent (P-S) axis, the coagulation value is small, the reduction of light transmission is easy to occur and the order of solubility parameter difference ($\Delta\delta_{i-j}$) is $\Delta\delta_{S-NS} > \Delta\delta_{P-NS} > \Delta\delta_{P-S}$.

The dense skin with small nodules and the sponge type sublayer with macrovoid are formed in case that the binodal curve is distant from the P-S axis, the onset time of liquid-liquid demixing is long and the order of $\Delta\delta_{i-j}$ is $\Delta\delta_{P-NS} > (\Delta\delta_{S-NS} \leqq \Delta\delta_{P-S})$

The thick layer of fine nodule coagulation and loosely grown sublayer of nodules appear when the binodal curve is distant from the P-S axis, the onset time of liquid-liquid demixing is very long and the order of $\Delta\delta_{i-j}$ is $\Delta\delta_{S-NS} > (\Delta\delta_{P-NS} \leqq \Delta\delta_{P-S})$.

In consideration of the effects of each solvent and nonsolvent on membrane porphology, the proper solvent-nonsolvent pairs were selected for the formation of asymmetric membrane having thin, dense skin layer and porous support sublayer. Also, it was found that the solubility parameter differences and binodal curves are a good criterion for the selection of the solvent-nonsolvent pair.

To control the solubility parameter differences meaning the exchange rate between the solvent and nonsolvent and being easily calculated, dioxane-DMAc and dioxane-NMP solvent mixtures were used.

In dioxane-DMAc solvent mixtures, as DMAc increases, $\delta_{d,smix}$ a little decreases, $\delta_{p,smix}$ largely increases and $\delta_{h,smix}$ a little increases. In the solubility parameter differences, as DMAc increases, $\Delta\delta_{p\ smix}$ a little decreases and $\Delta\delta_{smix\ NS}$ increases. When DMAc becomes to more than 60 wt.%, $\Delta\delta_{p\ smix}$ is smaller than $\Delta\delta_{smix\ NS}$. In this case, the binodal curve comes distant from P-S axis, and the coagulation value

becomes large, the onset time of liquid-liquid demixing is long. When the w.t. percent of dioxane-DMAc is 60-40, the thin skin layer, porous layer and sponge-like layer with macropore are developed sufficiently(Fig. 1).

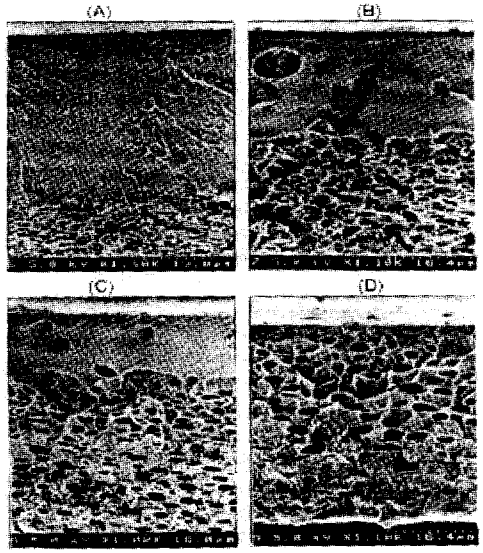

Fig. 1. Effect of solvent mixture on membrane morphology.
solvent mixture(dioxane-DMAc);(A)9-1, (B)8-2, (C)7-3, (D)6-4.

Also, in dioxane-NMP solvent mixture, a similar trend appeares. As NMP increases, $\Delta\delta_{p\ smix}$ decreases and $\Delta\delta_{smix\ NS}$ increases. When NMP becomes to 60 wt.%, $\Delta\delta_{p\ smix}$ and $\Delta\delta_{smix\text{-}NS}$ are equal to each other. It is found by SEM photographs that the thin skin layer, porous sublayer and sponge-like layer with macropore are formed when $\Delta\delta_{p\text{-}smix}$ is equal to $\Delta\delta_{smix\text{-}NS}$.

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