

**상전이법에 의한 제조된 폴리이미드/PVP/용매/물
계의 상거동 및 형태학적 연구**

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**Phase Behavior and Morphological Studies of
Polyimide/PVP/Solvent/Water Systems
by Phase Inversion**

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1. Introduction

The roles of additives in the structures of membranes are dependent on the system used.¹⁻³ Several researchers have reported that the addition of a third component into a dope solution could induce or suppress macrovoid formation in asymmetric membranes. Smolders et al.⁴ demonstrated that the addition of water promoted the macrovoid formation in the system of cellulose acetate/acetone/water with the delayed demixing, while suppressed it in the system of cellulose acetate/1-4 dioxane/water with the instantaneous demixing. Wang et al.⁵ have reported that the addition of surfactants in the casting solution could induce or suppress macrovoids, depending on the miscibility between the added surfactant and the coagulant. Lai et al.⁶ also found that macrovoid formation could be suppressed or induced depending on the content of nonsolvent additives such as n-butanol, cyclohexanol. In this study, the roles of PVP which can suppress or induce macrovoid formation will be studied in polyimide (PI) systems with varying solvents in a pure water coagulant and interpreted in terms of the miscibility gap, the viscosity of the polymer solution,

polymer-polymer phase separation and overall porosity.

2. Experimental

Polyimide (PI) used was Matrimid 5218 supplied by Ciba-Geigy Co. Its M_w and M_n are 80,000 and 46,000, respectively, characterized by GPC. The solvents were dimethylformamide (DMF, Junsei), N-methyl-2-pyrrolidinone (NMP, Aldrich), γ -butyrolactone (GBL, Aldrich), dimethylsulfoxide (DMSO, Aldrich). Distilled water was used as a coagulant. Polyvinylpyrrolidone (PVP, M_w 40,000, Polysciences) was used as a polymer additive. All chemicals were used without further purification.

A series of polymer solutions with 15 wt% of PI concentration were prepared in vials with teflon-lined cap. Different amounts of PVP and water were added to the PI solutions and PI/PVP solutions, respectively. Then the solutions were mixed in a shaking water bath for 1-2 days at elevated temperature (60-80°C) until the complete dissolution was obtained. Thereafter the solutions were cooled to 25°C and the cloud points were observed visually. Especially, the concentration of PVP making the PI solution turbid was adopted as the solubility gap of PVP.

3. Results and discussion

3.1. Thermodynamics of PI/PVP/Solvent Systems

The term PVP solubility gap represents a measure of the amount of PVP causing the phase separation of polymer solutions. The solubility gaps for PVP in four PI solutions, $\chi_{PI/Solvent}$ and $\Delta\delta_{PVP/Solvent}$ are presented. $\chi_{PI/Solvent}$ was determined from the activity coefficient by UNIFAC method. However, $\Delta\delta$ was used instead of χ in PVP/solvent pair, because of unobtainable group contribution parameters of PVP. Though the solubility of PI and PVP in four solvents and the compatibilities between PVP and PI are excellent (solubilities of two polymers in four solvents were more than 20 wt%, according to our measurement), the addition of small amounts of PVP in PI/DMSO and PI/GBL solutions induced phase separation, i.e., a PI rich phase and a PVP rich phase. It is well known that the

phase separation polymer1/polymer2/solvent systems is ascribed to the polymer-polymer phase separation, i.e., a polymer1 rich (polymer2 lean) phase and a polymer2 rich (polymer1 lean) phase. The low solubility gaps for PVP in PI/DMSO and PI/GBL solutions can be explained in terms of the low affinities of DMSO and GBL to both PI and PVP (high $\chi_{PI/DMSO}$, $\chi_{PI/GBL}$ and high $\Delta\delta_{PVP/DMSO}$, $\Delta\delta_{PVP/GBL}$) whereas the high solubility gap for PVP in PI/NMP solution in terms of high interactions of PI/NMP and PVP/NMP. The solvent power for PI was also confirmed by the dilute solution viscosities. Namely, DMSO and GBL have poorer solvency than NMP and DMF for PI.

3.2. Overall Porosity

Though the effect of PVP on the membrane morphology was quite different, the result of overall porosity was consistent, irrespective of solvents used. That is, the overall porosity increased with the increasing content of PVP in PI solution, as represented in Table 5. It should be noted that PI/DMSO membrane without PVP possess high porosity unlike GBL system, in spite of the similar sponge-like structure between two systems. The differences of porosity between two systems may be caused from the different membrane formation mechanism. The mechanism of membrane formation for PI/DMSO/water system was described well in our previous study.¹⁵ Especially, the effect of PVP on the increase of the overall porosity was drastic in GBL system. These results of overall porosity can be attributed to the soluble property of PVP in water, which leaches out of the membrane during precipitation. One may say that the larger content of PVP exists in the polymer-lean phase in GBL system than NMP and DMF system. Therefore, the macrovoid formation in GBL system becomes more vigorous.

4. References

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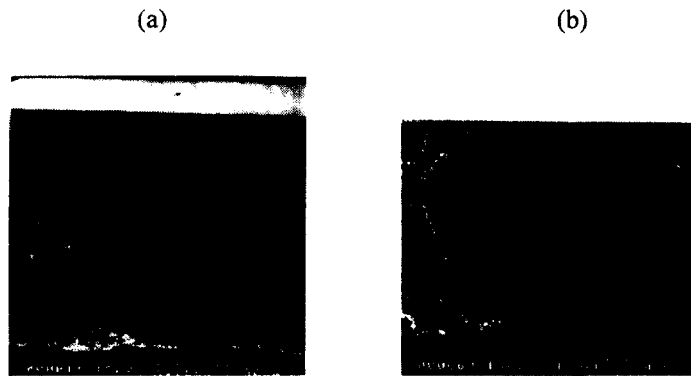


Figure 1. Promotion of macrovoid formation with addition of PVP
(a) PI/PVP/GBL=15/3/82 wt% (d) PI/PVP/DMSO=15/1/84 wt%.