일반강연 I-2

상전이법에 의한 Polyimide/DMSO/물 계의 비대칭막 제조 메카니즘

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Mechanism of Membrane Formation with Polyimide/DMSO/Water System by Phase Inversion

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1. Introduction

Phase inversion is a well-known process for preparing a variety of asymmetric membranes [1-3]. In this process, a homogeneous polymer solution consisting of a polymer and an adequate solvent with or without an additive is cast on a glass plate and immersed in a coagulation bath. The diffusive exchange of solvent and nonsolvent introduces liquid-liquid phase separation, i.e. a polymer-rich and a polymer-lean phases in the casting solution to lower the mixing Gibbs free energy. The successive solidification of the phase-separated solution leads to a porous, asymmetric structure. Thus, the morphology and performance of membranes strongly relies on the thermodynamics as well as kinetics of the phase separation [4-6].

It is well known that systems exhibiting high mutual affinity of solvent with nonsolvent yield the finger-like structure owing to instantaneous demixing [3,7-9]. Several researchers have reported that membranes prepared with DMSO/water as well as NMP/water pairs showed a finger-like structure, irrespective of polymers [8-12].

However, polyimde/DMSO/water system used in this study gave a typical sponge-like structure of membrane unlike previous other reports. Therefore, the formation of the unexpected morphology was investigated thermodynamically as well as kinetically. First, thermodynamic phase diagrams have been constructed for polyimide/DMSO/water and polyimide/NMP/water systems, which include the binodal and spinodal curves, gelation point, and tie-line for phase separations. The polyimide used here is Matrimid 5218 of Ciba-Geigy Co, which has excellent chemical resistance, long-term thermal stability and transport properties suitable for membranes. Secondly, the phase separation kinetics have been monitored by measuring the intensity of transmitted light with time. The rates of phase separation for both systems were compared to elucidate their effect on membrane morphology.

2. Theory

For polymer solutions, Flory-Huggins theory is used to describe the thermodynamic behavior of polymer/solvent/nonsolvent system [13]. Gibbs free energy of mixing in a ternary system can be conveniently formulated by the following equation on the basis of the theory of Tompa [14].

3. Experimental

3.1. Materials

Polyimide (PI) used was Matrimid 5218 supplied by Ciba-Geigy Co. Mw and Mn of PI are 80,000 and 46,000, respectively, measured by GPC. The solvents were dimethylsulfoxide (DMSO, Aldrich), N-methyl-2-pyrrolidinone (NMP, Aldrich). Distilled water was used as a nonsolvent.

3.2. Membrane preparation

Asymmetric PI membranes were prepared by a wet phase inversion process. Polymer solutions were cast uniformly on a glass plate with a 200㎛doctor blade and immersed into a coagulation bath at 8OC within a second. Membranes were kept in a nonsolvent bath for a day, dried in air, and then characterized. All membrane formation was conducted at 30-40% relative humidity and room temperature.

4. Results and discussion

The membrane morphology of PI/DMSO/water system had a typical sponge-like structure unlike PI/NMP/water system. To elucidate the membrane formation mechanism, the kinetics and thermodynamics of the phase separation were investigated. According to the light transmission experiment, the large difference in the phase separation kinetics of two systems was not shown. However, the phase diagrams exhibited unique thermodynamic properties of PI/DMSO/water system in comparison with PI/NMP/water system: 1) The miscibility gap and metastable region of PI/DMSO/water system were exceptionally narrow, 2) Its gelation point, where the membrane structure may be determined mostly, was very close to the binodal curve compared to that of PI/NMP/water system, and 3) the tie-line passing through the gelation point was nearly parallel to the polymer-solvent axis, leading to the high concentration of the polymer-rich phase and consequent vitrification. In condition that the kinetics of two systems are similar, the thermodynamic characteristics of PI/DMSO/water system may inhibit to proceed the phase separation further and undergo insufficient liquid-liquid phase separation, which induce the unexpected sponge-like structure.

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