Morphology of Membranes Formed from Polysulfone/ Polyethersulfone/N-methyl-2-pyrrolidone/Water System by Immersion Precipitation

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Abstract : The polysulfone(PSf)/polyethersulfone(PES) blend membranes were prepared by an immersion precipitation method. N-methyl-2-pyrrolidone(NMP) was used as a solvent and water as a nonsolvent. The composition of the coagulation bath and the dope polymer concentration as well as the blend ratio of two polymers were varied. The membrane morphologies were interpreted on the basis of the phase diagram of the PSf/PES/NMP/water system. As the solvent content in the coagulation bath increased in the single polymer system, the number of macrovoids decreased and the morphology was changed from finger-like to cellular structure. In the given bath condition phase separation occurs earlier for the solutions of PSf/ PES blend than for those of single polymer. A horizontally layered structure and horizontal protuberances inside the macrovoid were observed for the membranes formed from PSf/PES blend solutions. This peculiar structure formation can be interpreted by a PSf-rich/PES-rich phase separation followed by a polymer-rich /polymer-lean phase separation during the exchange of solvent and nonsolvent.

Introduction

In the previous work, we reported the liquid-liquid phase separation behavior in a quaternary system of polysulfone(PSf)/polyethersulfone(PES)/N-methyl -2-pyrrolidone(NMP)/water.[1] The present work treats the morphology formation in this system by a phase inversion method. It would be interesting to investigate the PSf/PES blend membrane because PES is slightly less hydrophobic than PSf.[2-5] PSf

and PES are important polymers as membrane materials due to the chemical resistance, mechanical strength, thermal stability and transport properties.[2,6] There are a number of studies on the morphology of the PSf and PES membranes prepared by phase inversion methods.[7-19] Changing the conditions of the dope solution and coagulation bath, one can obtain various structures of membrane.[7-15] Many studies also deal with the dry/wet phase inversion.[12, 14-17]

For the quaternary systems involving two polymer components, the morphological study is hardly

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found in the published literature.[20-23] Boom *et al.*[20] studied the system of PES/poly(vinyl pyrrolidone) (PVP)/NMP/water. They found that the addition of PVP to the ternary system suppresses the formation of macrovoids in the sublayer and the appearance of nodular structure in the top layer follows a mechanism of spinodal decomposition during the very early stages of the immersion step. Tam *et al.*[21] used a copolymer of PES and polyetherethersulfone(PEES) to show the membrane morphologies with adding PVP as an additive. Gas permeation through PSf/polyimide(PI) miscible blend membranes was investigated by Kapantaidakis *et al.*[22] Recently, Wang *et al.*[23] observed the morphologies of the blend membrane composed of cellulose acetate(CA) and polyacrylonitrile(PAN) with varying compositions.

In this work, we prepared the PSf/PES blend membranes by immersion precipitation. NMP was used as a solvent and water as a nonsolvent. The composition of the coagulation bath and the dope polymer concentration including blend ratio of two polymers were varied. The membrane morphologies were interpreted in conjunction with the phase diagram of the PSf/PES/NMP/water system.[1] The effects of liquid demixing by polymer/liquid phase separation and by polymer/polymer phase separation were discussed when PSf/PES blends were used in the membrane formation.

Experimental

Materials. Polysulfone, Udel P-3500 (M_n = 33,500 g/mol and M_w = 50,800 g/mol), from Amoco Performance Products and polyethersulfone, Ultrason E6020P (M_n = 11,000 g/mol and M_w = 58,000 g/mol, porous flake), from BASF were used after sufficient drying. NMP of micropure electronic grade from International Specialty Chemical (ISP) was used as received. Distilled water was used as a nonsolvent.

Membrane Preparation. The polymer solution of 20 and 30 wt% total polymer concentration in NMP were cast on a glass plate and immersed into a coagulation bath of water and NMP mixture. The temperatures of the polymer solution and the bath were kept constant at 20°C. Blend

ratios in weight bases between PSf and PES in the polymer solution were 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100. The weight ratios between water and NMP in the coagulation bath were 100/0, 80/20, 60/40, 40/60, and 20/80. The initial thickness of the cast film was 100 μm. The membranes were washed in water by overflowing for 48 h and freeze-dried for the morphology observation.

Morphology Observation. Dried membranes were cut into a proper size and frozen in liquid nitrogen, then fractured to observe the cross-section. Morphologies of the membranes were examined with a scanning electron microscope (Leica, Cambridge 240).

Results and Discussion

Experimental Phase Diagram. The experimental phase diagrams[1] of the quaternary system are shown in Figure 1, in which two polymers are lumped together keeping the blend ratio of PSf and PES constant. The cloud point curves of the solution containing the blends of PSf and PES do not fall in between those of the pure polymers. As the blend ratio between PSf and PES decreases from 100/0 of wt PSf/wt PES, the cloud point
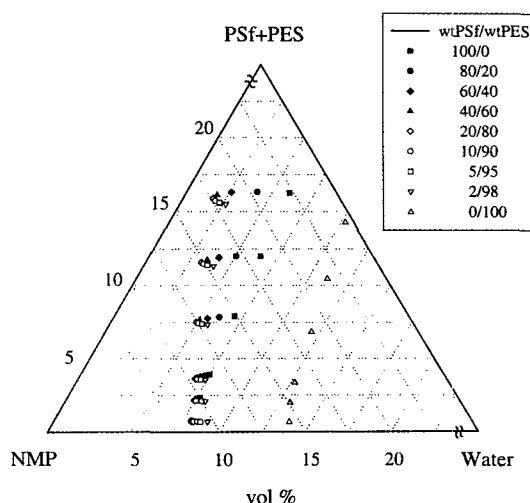
Figure 1. Experimental cloud points for the quaternary system of PSf/PES/NMP/water at 20 °C with various weight ratios of PSf and PES.[1] Components of PSf and PES were lumped together and concentration was converted into vol%.

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curve goes closer to the solvent-polymer axis. Below a certain value around 20/80 of wt PSf/wt PES, the cloud point curve moves back toward that of PES. The cloud points at low concentration of polymer show little shift toward the polymer-solvent axis as the blend ratio varies. The cloud points in the region of higher concentration of polymer, however, show significant move toward the axis. The experimental phase diagrams indicate that the phase separation occurs with the addition of smaller amount of water when the polymer solution contains the PSf/PES blends. Thus, the miscible region in the solution of the blends decreased compared to the cases of the pure polymer components.

It was found that two types of phase separation can be obtained for the PSf/PES/NMP/water system depending on the total polymer concentration[1]: when the total polymer concentration is above a certain value (the critical point value), the solution shows a PSf-rich/PES-rich phase separation (polymer/ polymer phase separation) with the addition of nonsolvent; otherwise it shows a polymer-rich/polymer-lean phase separation (polymer/liquid phase separation). In addition, when more water is introduced to the solution of higher concentration of total polymer than the critical concentration, a secondary polymer-rich/polymer lean phase separation can be attained with the PSf-rich and PES-rich phases formed in the primary phase separation process. This is because the water content of the polymer-rich phase in equilibrium with the polymer-lean phase is beyond that of the region of polymer/polymer phase separation. The previous study[1] showed that the calculated binodal curves based on the Flory-Huggins theory fitted the experimental cloud points well and the model described appropriately the phase separation behavior of the quaternary solution.

Morphology of PSf and PES Membranes. The SEM micrographs of the cross-sections for PSf and PES membranes prepared under varying conditions of the dope polymer concentration (20, 30 wt% polymer in NMP) and the coagulation bath (0/100, 40/60, 80/20 NMP/water) are shown in Figure 2 and Figure 3, respectively. In each case, as the amount of solvent in the bath increases, the number of macrovoids decreases
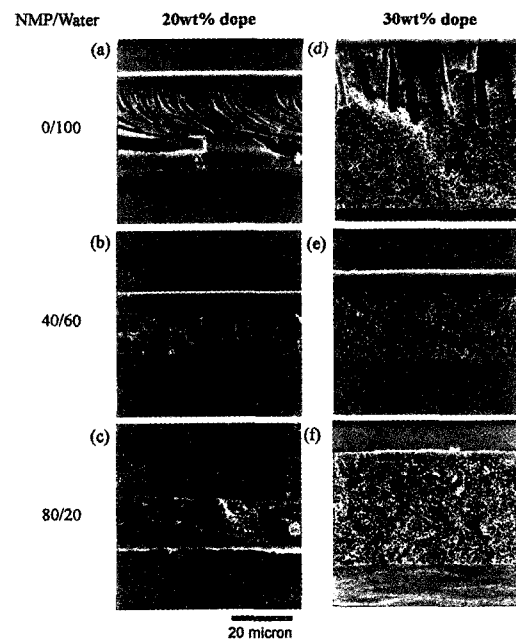

Figure 2. SEM micrographs of the cross-sections for PSf membranes; dope polymer concentration (20, 30 wt% polymer in NMP) and coagulation bath composition (0/ 100, 40/60, 80/20 NMP/water) were varied.
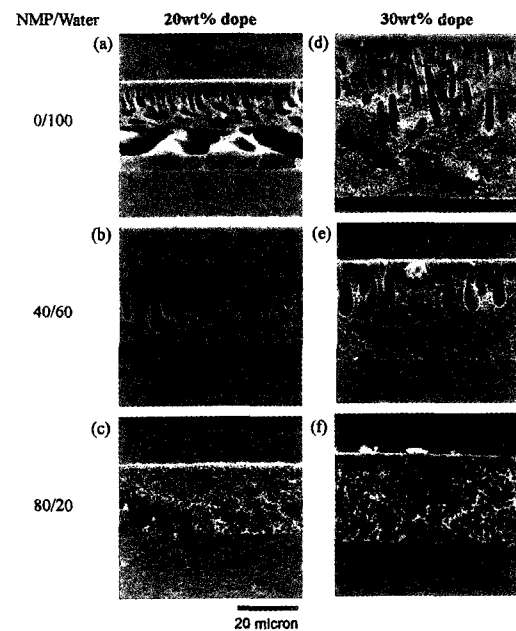

Figure 3. SEM micrographs of the cross-sections for PES membranes; dope polymer concentration (20, 30 wt% polymer in NMP) and coagulation bath composition (0/100, 40/60, 80/20 NMP/water) were varied.

and the morphology is changed from finger-like to cellular structure. With high content of nonsolvent in the bath, the solvent-nonsolvent exchange in the interface would be very rapid, resulting in the instantaneous precipitation.[24,25] When the time for the solution passed through the metastable region in the phase diagram is short enough to cause insignificant amount of nuclei to form, there may be strong chance for the phase separation to occur by spinodal decomposition. Thus, macrovoids are formed by the spinodal decomposition mechanism and small cells around the macrovoids are formed by the mechanism of nucleation and growth in the secondary phase separation since the macrovoid (primary polymer-poor phase) acts as a local coagulation bath of high solvent content during the secondary phase separation.[26]

The solvent content in the coagulation bath influences the growth of cells in the sponge-like structure. This can be exemplified by observation of the different location of membrane thickness for the cross-section of the membrane prepared in a coagulation bath of pure water as can be seen in Figure 4. The surface of polymer solution contains a large amount of nonsolvent due to the fast diffusion process. Then highly concentrated polymer solution of the polymer-rich phase due to
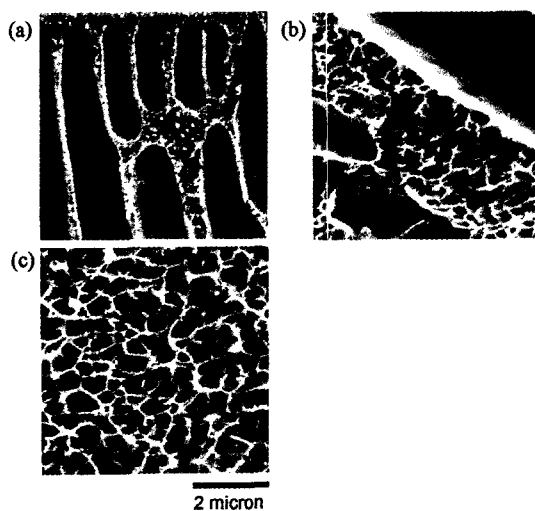

2 micron

Figure 4. SEM micrographs of the cross-sections for a PES membrane formed from a dope solution of 20 wt% polymer in NMP and a coagulation bath of pure water (a, top region; b, middle region; c, bottom region).

phase separation is obtained,[27] and high viscosity of the polymer-rich phase suppresses the growth of the cell. Inside the surface, the diffusion of nonsolvent becomes slow due to the decrease in the concentration gradient of nonsolvent and as a result, the lower part in the polymer solution film feels the environment as the coagulation medium that contains solvent more. In this case the solidification rate is slow so that larger cells can be formed.

When the solvent-nonsolvent exchange occurs at the interface between polymer solution and coagulation medium, the rate of solvent diffusion in the polymer solution into the coagulation medium is higher than that of nonsolvent diffusion in the coagulation medium into the polymer solution. This might be caused by high miscibility between solvent and nonsolvent and hydrophobic characteristics of polymer. Due to the differences in diffusion, the polymer solution contracts. As the polymer concentration increases the viscosity of the solution increases and the rate of solvent-nonsolvent exchange decreases. This makes the contraction of the polymer solution film less and the rate of coagulation slow. In the SEM micrographs of the cross-section of the membranes in Figure 2 and 3, the membranes become thicker and the cell size of the sponge-like structure is bigger with the higher polymer concentration of the dope solution. The tendency for macrovoid formation decreased due to slower mass transfer with higher viscosity of 30 wt% polymer concentration.

Comparison of the structure formation for PSf and PES membranes obtained under the same conditions of the dope polymer concentration and of the coagulation bath composition is complicated by the competition between thermodynamics and kinetics of mass transfer. In the ternary phase diagram, the PES system has a wider homogeneous region than the PSf system. On the other hand, the rate of water penetration would be higher in the PES solution due to enhanced hydrophilicity. When the effect of higher rate of water penetration is dominant, the PES solution is in a situation of higher nonsolvent content in the bath than the PSf solution (Figure 2e and Figure 3e). When the thermodynamic effect is more dominant, however, the PES solution
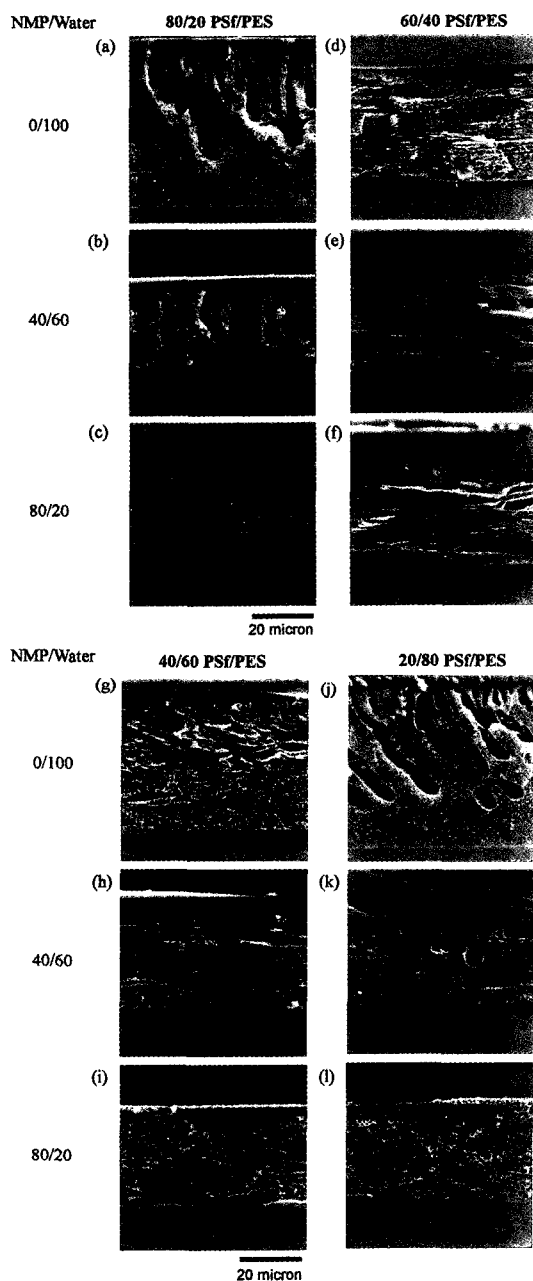
Figure 5. SEM micrographs of the cross-sections for PSf/PES blend membranes formed from a dope solution of 30 wt% total polymer in NMP; blend ratio of PSf and PES (80/20, 60/40, 40/60, 20/80 PSf/PES) and coagulation bath composition (0/100, 40/60, 80/20 NMP/water) were varied.

has a longer period for the growth of domain (polymer-lean phase) than the PSf solution. Thus,

slower solidification in the PES solution gives rise to bigger cell size (Figure 2f and Figure 3f) and less tendency for macrovoid formation (Figure 2c and Figure 3c).

Morphology of PSf/PES Blend Membranes.
The miscible region in the phase diagram decreased for the solutions of PSf/PES blend compared to those of the single polymer components (Figure 1). It is expected that in the given bath condition phase separation occurs earlier for the quaternary system than for the ternary system. In other words, the solutions of polymer blend are under a coagulation bath of higher water content than the solutions of single polymer. This expectation is true when the series of 80/20 PSf/PES blend is compared with those of pure PSf (Figure 5a, b, c and Figure 2d, e, f). A greater extent of macrovoid formation and a smaller cell size of the sponge-like structure are observed for the solutions of polymer blend. Similar trends are followed by comparison of the cases of 20/80 PSf/PES blend and pure PES, although the tendency for macrovoid formation is less clear.

There is a distinctive feature for the morphology of membranes formed from PSf/PES blend solutions as is seen in Figure 5; a horizontally layered structure especially for the series of 60/40 and 40/60 PSf/PES and horizontal protuberances inside vertical macrovoid are observed. The layered structures for the system of 40/60 PSf/PES blend under two different conditions of coagulation bath are shown in Figure 6 with higher magnification. The cell size of the membranes is smaller in the upper region than in the lower region, which is a similar result to the cases of single polymer. The unusual structure formation seemed to be caused by a polymer/polymer phase separation. This is not shown in the membranes made of single polymer. Because the concentration of 30 wt% total polymer in NMP is much above the critical concentration, a PSf-rich/PES-rich phase separation should occur during the very early stages of water penetration and a polymer-rich/polymer-lean secondary phase separation follows when more water diffused into the solution.

The particular structure may be interpreted by considering multi-layers in the whole thickness of polymer solution during the exchange of solvent
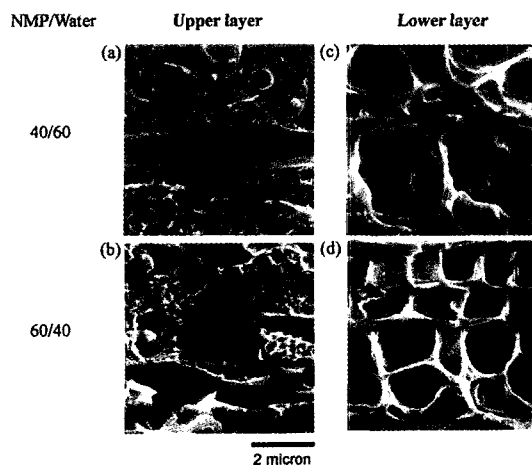
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NMP/Water   Upper layer   Lower layer

2 micron

Figure 6. SEM micrographs of the cross-sections for 40/60 PSf/PES blend membranes (a and b, upper region; c and d, lower region) formed from a dope solution of 30 wt% total polymer in NMP and different bath compositions (a and c, 40/60 NMP/water; b and d, 60/40 NMP/water).

and nonsolvent. The first layer (top layer) contacting with coagulation bath is separated into a PSf-rich phase and a PES-rich phase (polymer/polymer phase separation) at the beginning of immersion. Then the PSf-rich phase is separated into a polymer-rich phase and a polymer-lean phase (polymer/liquid phase separation) but the PES-rich phase is still in homogeneous state because the PES system needs more nonsolvent to induce phase separation. In the second layer a polymer/polymer phase separation followed by a polymer/liquid phase separation also occurs before the PES-rich phase in the first layer is separated. Third layer, fourth layer, and fifth layer etc., are separated via a similar mechanism to former cases. With more ingress of water, the PES-rich phase is separated into a polymer-rich phase and a polymer-lean phase and in whole layers the polymer/liquid phase separation would eventually occur. The horizontal protuberance inside macrovoid may be explained by the superposition of the layered structure formation by polymer/polymer phase separation and the feature observed in the single polymer system.

The layered structure formation seemed to be related to the relative amount of each phase and the mobility of the phases after phase separation.

As can be seen in Figure 5, the horizontal ladder-like structure is observed more easily in the series of 60/40 and 40/60 PSf/PES than in the series of 80/20 and 20/80 PSf/PES. The layered structure was not observed clearly for the solutions of 20 wt% total polymer concentration, which indicates that the multi-layers by polymer/polymer phase separation is destroyed before solidification due to rapid diffusion in the medium of low viscosity.

Conclusions

The PSf/PES blend membranes were prepared by immersion precipitation. NMP was used as a solvent and water as a nonsolvent. As the content of solvent in the coagulation bath increased in the single polymer system, the number of macrovoids decreased and the morphology was changed from finger-like to cellular structure. The cell size in the sponge-like structure became large with higher amount of solvent in the bath.

In the given bath condition phase separation occurs earlier for the solutions of PSf/PES blend than those of single polymer because the miscible region in the phase diagram decreased for the quaternary system. A horizontally layered structure and horizontal protuberances inside macrovoid were observed for the membranes formed from PSf/PES blend solutions. This peculiar structure formation can be interpreted by a PSf-rich/PES-rich phase separation followed by a polymer-rich/polymer-lean phase separation during the exchange of solvent and nonsolvent in imaginary multi-layers of the whole thickness of polymer solution. The layered structures were related to the relative amount of each phase and the mobility of the phases after phase separation.

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