Phase Behavior and Morphological Studies of Polysulfone Membranes; The Effect of Alcohols Used as a Non-solvent Coagulant

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Abstract: In this study, asymmetric polysulfone membranes were prepared by the phase inversion method and the casting solutions were containing N-methyl-2-pyrrolidone (NMP) as a solvent. Deionized water and various alcohols (methanol, ethanol, and propanol) were used as a coagulation medium in preparing asymmetric polysulfone membranes. This study investigates the effect of alcohol coagulants having different solubility parameters as a pore-former on the construction of porous structures and their pure water permeation properties. Asymmetric polysulfone membranes immersed in the pure alcohol coagulation bath solution showed the typical sponge-like structures and the reduced water permeability as compared with those of polysulfone membranes precipitated in the pure water coagulation bath solution. In the water/alcohol mixtures, asymmetric polysulfone membranes showed the finger-like structures with the sponge-like structures. Therefore, the sponge-like structure of polysulfone membrane was formed under the delayed demixing systems while the porosity of membrane was decreased significantly. The water permeability of polysulfone membrane precipitated in the pure water coagulant showed 164 [L/m² hr] at 14.7 psi. In case of polysulfone membranes prepared in the pure methanol and ethanol coagulant, they showed the water permeability of 56 and 30 [L/m² hr], respectively.

1. Introduction

Synthetic membrane technology has grown up very fast since the first integrally skinned asymmetric cellulose acetate membrane was developed by Loeb and Sourirajan using a phase inversion process [1]. For the preparation of synthetic polymeric membranes, the
phase inversion method has been widely used [2-4]. In this process, a homogeneous polymer solution consisting of polymer and solvent is immersed into a non-solvent coagulation bath, where the interchange of solvent and non-solvent causes the casting solution to be phase-separated [5,6]. During the immersion precipitation, liquid-liquid phase separation was preceded in a polymer solution until the porous structure fixed by vitrification of polymer-rich phases. The phase separation behavior of membrane-forming systems plays a crucial role in the determining morphological properties and the performance [7,8]. Membrane structures, especially pore size, porosity, and pore size distribution, can be controlled for each specific application, which is depended upon the choice of the polymer, solvent, non-solvent, and preparation parameters. Chen et al. [6] reported that if the driving force between solvent and non-solvent is strong enough, the phase inversion membranes showed finger-like structures. On the other hand, if the affinity between solvent and non-solvent is low, the sponge-like structures were constructed in the phase inversion membranes.

Addition of a third component to the casting solution, consisting of a polymer and a solvent, is a widely used method to control membrane morphology. Water-soluble polymers such as polyvinylpyrrolidone (PVP) [9,10], polyethylene glycol (PEG) [11], surfactants [12], and both non-solvent [13] and solvent additives [14] have been commonly used as a third component. Changing the composition in the casting solution or in the coagulation bath is a convenient method to obtain desired membrane structures. Kang et al. reported that finger-like structures were inhibited with addition of PVP in the NMP and DMP systems [15]. Lai et al. reported that the effects of the addition of non-solvent and the evaporation of casting solution on the structure of poly(4-methyl-1-pentene) (TPX) membranes. The addition of non-solvent in casting solution was proved to be an efficient method to elevate the porosity of TPX membranes [13]. Changing the composition in the casting solution or in the coagulation bath is a convenient method to obtain desired membrane structures. Adding solvent in the coagulation bath can delay the occurrence of liquid-liquid demixing in the casting solution and thus results in denser asymmetric membranes [16]. On the contrary, adding non-solvent in the casting solution can increase the porosity of membranes. For example, Pesek and Koros successfully elevated the porosity of asymmetric polysulfone membranes by adding two different non-solvents in the polymer solution [17]. In this study, three kind of alcohols (methanol, ethanol, propanol) according to the different carbon numbers are employed as a non-solvent to investigate the effect on the morphological properties, porous structures, and the permeation properties of polysulfone membranes relative to some variables playing a role in the phase-inversion process, such as coagulation bath solution composition (different non-solvent composition).

2. Experimental

2.1. Materials

Polysulfone (PSf) (Udel P3500) supplied by Amoco was used as a membrane material. N-Methyl-2-pyrrolidone (NMP) from Aldrich as a good solvent for polysulfone was used without further purification. Pure water was used as a coagulant. Methanol, ethanol, propanol obtained from Fluka AG were used as coagulants in the mixture of water/alcohol coagulation bath solutions.

2.2. Preparation of PSf Membrane

PSf membranes were prepared by the immersion-precipitation technique. PSf/NMP solutions consist of 15, 17 and 20 wt% PSf in NMP solution. The compositions of PSf solution and coagulation bath solution are listed in Table 1. Polysulfone solutions were cast uniformly onto a polyester non-woven fabric with a doctor knife having a 200 μm thickness and immediately immersed into a coagulation bath without evaporation at 20°C. Membranes were kept in a coagulation bath for 1 hr, washed with tap water for a day to remove remaining solvent (NMP). All membrane formation was conducted at 50–60% relative humidity and room
Table 1. The Compositions of the Polysulfone Solutions

<table>
<thead>
<tr>
<th>Composition of casting solution (wt%)</th>
<th>Coagulation bath solution (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$	ext{Sf}$</td>
<td>NMP</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
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<td>83</td>
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<td>17</td>
<td>83</td>
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<td>17</td>
<td>83</td>
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* Alcohol: methanol, ethanol, propanol

2.3. Determination of Coagulation Value

The coagulation value can be used as a measure of thermodynamic stability of the polysulfone casting solution. It is determined by the added amount of coagulant (pure alcohol and water/alcohol mixture) in a PSf/NMP polymer solution until the solution became milky-white, representing that the cloud point had been reached. The weight of the added coagulant was used as the coagulation value. The experiment was performed at 20°C and the observed milky-white was stirred for 24 hr until does not dissolve. The ratios of alcohol/water mixture are used 100/0 and 80/20 (vol/vol%), respectively.

2.4. Scanning Electron Microscopy (SEM)

The morphologies of different faces of the PSf membranes were examined using scanning electron microscopy (SEM). The membranes were freeze dried, then frozen in liquid nitrogen and fractured to expose the cross-sectional areas. The dried samples were gold coated and viewed with SEM (S-800, Hitachi, Japan) at 5.0 kV.

2.5. Membrane Porosity

An overall porosity can be calculated with the membrane area (A), the mass (Wm), the thickness (D) and the density ($\rho_p$) of the polysulfone polymer. The percentage porosity was calculated as following equation (Eq. 1).

$$Porosity\, (\%) = \frac{V_m - V_h}{V_m} \times 100$$

$$= \frac{D \cdot A - \left( \frac{W_m}{\rho_p} \right)}{D \cdot A} \times 100 \quad (1)$$

where $V_m$ is the volume of polysulfone membrane and $V_h$ is the volume of polysulfone polymer.

2.6. Pure Water Flux Measurements

To test the performance of the PSf membranes, a common permeation test apparatus was used to measure the pure water flux (see Fig. 1). All test was conducted at 25°C and 0.3 L/min of flow rate at 14.7 psi. Flux was measured by weighing of permeate through the membrane per unit time using the following equation (Eq. 2):

Fig. 1. Apparatus of permeation test used in this study.
\[ Flux \left[ \frac{L}{m^2 \text{hr}} \right] = \frac{Q}{A \times T} \]  \hspace{1cm} (2)

where \( Q \) is the volume of permeate \( (L) \), \( A \) is effective area of membrane \( (m^2) \) and \( T \) is the operating permeation time \( (hr) \).

3. Results and Discussion

3.1. Thermodynamics

Most commercial available membranes are prepared by the immersion precipitation: a polymer solution is cast on a suitable support material and immersed in a coagulation bath containing a non-solvent. Precipitation occurs because of the exchange of solvent and non-solvent. The porous membrane structures ultimately were constructed by the combination of mass transfer and phase separation behavior \([2]\). In order to understand the membrane-forming mechanism by the phase inversion process, the thermodynamics of membrane-forming system should be investigated. The coagulation value can be used as a measure of thermodynamic stability of the casting system. The term of coagulation value was used originally by Ziabicki to represent thermodynamics in dry-wet spinning of fiber \([19]\).

Fig. 2 shows the coagulation values of the PSf solutions when the pure alcohol (methanol, ethanol and propanol) coagulants used, defined as the weight of coagulant required bringing the polymer solution into the liquid-liquid demixing region \([19]\). From the coagulation values, the lower coagulation value indicates that the polymer solution is easier to phase separation, suggesting that the prepared phase-inversion membranes have more porous structures.

The coagulation value is related with the morphological properties, porous structures, and permeation properties of the PSf membrane. Fig. 3 shows the coagulation value of the PSf casting solution when the mixture of alcohol/water coagulant used as a coagulation solution. As a result, the coagulation value increases with increasing the molecular weight of alcohol coagulant and the coagulation value decrease when the water used coagulant in the mixture of alcohol/water coagulation bath solution as compared with the pure alcohol coagulants. From the Fig. 2 and 3, we expected that the membrane structures, such as the sponge-like structure and the finger-like structure could be controlled by the alcohol coagulants having the different molecular weight and the mixture of alcohol/water. The morphological properties and the water permeation performances of PSf membranes prepared by the phase-inversion method using the various alcohols and the mixtures of alcohol/water coagulation solutions will be discussed later with the cross-sectional SEM images.
and the results of the pure water flux.

3.2. Morphological Properties of PSf Membranes

Smolders et al. [16] suggested that the formation mechanism of macrovoids could be split into two stages: initiation and growth. In the initiation stage, the nucleation of the polymer-poor phase resulting from liquid-liquid demixing can initiate the formation of macrovoids. In the growth stage, the nuclei expand to macrovoids because the diffusional flow of solvent from the polymer solution to the nuclei is larger than the flow of coagulant from the nuclei to the polymer solution. Therefore, instantaneous demixing is preferred in the initiation stage and delayed demixing is required to provide appropriate environments for the growth of macrovoids.

Fig. 4 shows that the porous structures of PSf membranes prepared by the phase-inversion method using the water coagulation solution as a function of the concentration of PSf solution. All of the PSf membranes immersed in the pure water coagulation bath formed the finger-like structures (macrovoids structure). By increasing the concentration of PSf solution, the membrane structures were changed from the finger-like structures to the sponge-like structures. Fig. 5 shows cross-sectional images of the PSf membranes prepared by immersed in the mixtures of the water/methanol coagulation solution. As a result, the PSf membranes immersed in the pure methanol coagulant obtained the sponge-like structures while the finger-like structures were constructed in the PSf membranes prepared using

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the mixtures of water/methanol coagulant. The formation mechanism of macrovoids for coagulant/solvent/polymer ternary systems has been studied extensively [16,20,21]. In a coagulant/solvent/polymer ternary system (with no additives), instantaneous demixing or very short delay time is required to initiate the formation of macrovoids (finger-like structure) [16]. Figs. 6 and 7 show the membrane structures prepared using other alcohol coagulants (ethanol and propanol). Generally speaking, the macrovoids are formed in case of instantaneous demixing and the sponge-like structures are built in case of delayed demixing. As a result, the membrane structures (sponge-like structure or finger-like structure) could be controlled by the demixing time of solvent and non-solvent. With increasing the composition of alcohol in the coagulation bath solution, the membrane morphology was changed from the finger-like structure to the sponge-like structure. J. Y. Lai et al. [13] explained that the relationship between solubility-parameter difference and phase separation behavior. The larger solubility-parameter difference between the polymer and the mixture of solvent and non-solvent indicates that the polymer is less compatible with the mixture, suggesting that the system is easier to phase separation. As a result, with an increasing solubility-parameter difference the porosity is increased and the PSf membranes prepared by the phase-inversion method obtained the finger-like structures.

3.3. Pure Water Permeabilities of PSf Membranes

Fig. 8 shows the relationship between the membrane porosity and the pure water flux. The porosity and
pure water flux of the PSf membranes prepared by the phase-inversion method were decreased with the containing alcohol coagulants in the water/alcohol coagulation bath solutions as compared with those of the PSf membranes immersed in the pure water coagulation bath solution. Furthermore the membrane porosity and pure water flux were decreased with increasing the molecular weight of alcohol coagulants. As shown in the relationship between the membrane porosity and the pure water flux, the PSf membrane that was immersed in the mixture of water/ethanol (80/20 vol/ vol%) coagulation bath solution showed 75% porosity and 121 [L/m^2hr]. Fig. 9 shows the pure water flux of PSf membranes with the various PSf concentrations. As expected, the water flux decrease with increasing the PSf concentration. N. Scharnagl et al. [22] explained

Table 2. Pure Water Permeabilities of Polysulfone Membranes

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Composition of casting solution (wt%)</th>
<th>Pure water flux [L/m^2hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSf</td>
<td>NMP</td>
</tr>
<tr>
<td>PS 15</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>PS 17</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>PS 20</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3. The Relationship between the Water Permeability and the Solubility-parameter of Coagulation Bath Solution

<table>
<thead>
<tr>
<th>Coagulation bath solutions (vol %)</th>
<th>$\beta$* (L/cm^2)$^{1/2}$</th>
<th>Pure water flux** [L/m^2hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>48.10</td>
<td>164</td>
</tr>
<tr>
<td>Water/Methanol=80/20</td>
<td>44.38</td>
<td>139</td>
</tr>
<tr>
<td>Water/Ethanol=80/20</td>
<td>43.74</td>
<td>121</td>
</tr>
<tr>
<td>Water/n-Propanol=80/20</td>
<td>43.38</td>
<td>95</td>
</tr>
<tr>
<td>Water/Methanol=50/50</td>
<td>38.80</td>
<td>123</td>
</tr>
<tr>
<td>Water/Ethanol=50/50</td>
<td>37.20</td>
<td>111</td>
</tr>
<tr>
<td>Water/n-Propanol=50/50</td>
<td>36.30</td>
<td>88</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.50</td>
<td>56</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26.30</td>
<td>30</td>
</tr>
</tbody>
</table>

* Solubility parameters of the coagulation bath solution
** Pure water flux of PS 17
that the membrane properties depend upon the formation parameter. The most important parameters are the concentration of polymer, the type of solvent, and the composition of precipitation solutions. They showed the pure water permeability of polyacrylonitril (PAN). From their results, the pure water flux decrease with increasing PAN polymer concentration. From the result, the PS 17 showed the 164 [L/m²·hr] at 14.7 psi. The solubility parameter of the mixture of water/alcohol coagulation bath solution and the pure water flux are listed in Table 3. The pure water flux was decrease by the containing alcohol coagulants in the coagulation bath solution and with the increasing alcohol coagulant composition. As explained above, the solubility parameter difference between polymer solution and coagulation bath solution was an important factor for the formation of membrane structures. From the results, the PSf membrane that was immersed in the ethanol coagulation solution showed the lowest water permeability. In case of immersed in the water coagulation solution, the PSf membranes showed the higher water permeability than those of the other membranes immersed in the pure alcohols and the mixtures of water/alcohol coagulation solutions.

4. Conclusion

The addition of alcohol non-solvents (methanol, ethanol, propanol) in the coagulation bath solutions was proved to be an efficient method to formation the sponge-like structure of polysulfone membranes. The coagulation values increases with the increasing the molecular weight of alcohol coagulants and the coagulation values decreased when the pure water used as a coagulant in the mixtures of water/alcohol coagulation bath solutions. The coagulation values were related with the morphological structures and permeation properties of the PSf membranes. The larger solubility-parameter difference between the polymer solution and the non-solvent indicated that the polymer is less compatible with the mixture, suggesting that the system is easier to phase separation. As a result, with an increasing solubility-parameter difference between polymer solution and coagulation bath solution the porosities were increased and the PSf membrane obtained the finger-like structures. From the pure water permeabilities, the PSf membrane immersed in the pure water coagulation bath solution showed the highest water permeability as compared with those of the PSf membranes immersed in the pure alcohol and the water/alcohol mixtures.

The sponge-like structures were constructed in the PSf membranes when the alcohol coagulation bath solutions were used as a coagulation solution and their PSf membranes showed the lowest water permeability. In this study, the structural properties, the porous structures, and the permeation performances of the PSf membranes were importantly influenced by the difference solubility-parameter between polymer solution and non-solvent.

Acknowledgement

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References

6. T. H. Young and L. W. Chen, “Pore mechanism