

## Preparation of a Polyimide Nanofiltration Membrane for Lubricant Solvent Recovery

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**ABSTRACT:** Polyimide (PI) membrane has been proven to be an efficient approach for solvent recovery. However, the inherent fragility of the PI membrane limits the range of separation conditions and process economics. In this study, copolyimides were synthesized from 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and 4,4'-biamino-3,3'-dimethyldiphenyl-methane (DMMDA) by chemical imidization in a two-step procedure. Then, a PI nanofiltration (NF) membrane was prepared through a phase-inversion process for solvent recovery from lube oil filtrates. The results indicated that the immersion of the PI (BTDA-DMMDA) NF membrane in a 1,6-diaminohexane/ethanol crosslinking agent solution carried on the chemical crosslinking modification, which could effectively improve the solvent resistance of the NF membrane. Moreover, the addition of inorganic salt in the polymer solution further enhanced the solvent resistance and pressure resistance of the membrane, which was favorable for the solvent recovery. The lubricant rejection was above 93%, and the solvent flux was about 30 L m<sup>-2</sup> h<sup>-1</sup> with the NF membrane prepared in optimum conditions, and this membrane showed great potential for future development in the application of solvent recovery from lube oil filtrates. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40338.

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### INTRODUCTION

Solvent lube oil dewaxing processes are practiced worldwide in refineries. In this process, the solvent must be recycled from lube oil by refrigeration for economic reasons. For most feeds, the overall production and dewaxed oil yield are limited by the solvent circulation and refrigeration capacity.<sup>1</sup>

Compared with conventional separation techniques, membrane separation has several advantages, including a high energy efficiency, low power consumption, easy operation and control, and low capital costs.<sup>2</sup> Nanofiltration (NF) technology is widely used in drinking water, wastewater, and industrial applications. In all applications, the membrane surface and pore structure characteristics play a significant role in the transport of water and solute molecules through the membrane.<sup>3,4</sup>

Polymeric membranes nowadays are used for a wide range of industrial separation applications extending from microfiltration to reverse osmosis.<sup>5</sup> The proper selection of the membrane material is fundamentally important for the separation properties of prepared membranes. Among all of the polymer mem-

branes used, aromatic polyimides (PIs) have excellent thermal and chemical stability, so PI membranes have been widely used in the fields of gas separation and wastewater treatment.<sup>6</sup> White and Nitsch<sup>7</sup> demonstrated that a PI membrane manufactured from a copolymer of diaminophenylindane with benzophenone tetracarboxylic dianhydride had excellent rejection characteristics (99%) for the separation of light hydrocarbon solvents from lube oil filtrates. However, the inherent fragility of PI membranes limits the range of separation conditions and the process economics.

Currently, chemical crosslinking is believed to be more efficient for suppressing plasticization,<sup>8,9</sup> and this can significantly improve the solvent resistance and pressure resistance. Staudt-Bickel and Koros<sup>10</sup> have shown that the swelling effects due to a high partial CO<sub>2</sub> pressure can be successfully reduced by the chemical crosslinking of free carboxylic acid groups with ethylene glycol as a crosslinking agent. Wind and coworkers<sup>11,12</sup> found that covalent and ionic crosslinking were also associated with the traditional posttreatment for suppressing the plasticization of (4,4'-hexafluoroisopropylidene) diphthalic anhydride

(6FDA)-based PI through thiol reagents; this proved that diol crosslinking is also effective for plasticization suppression in PI membranes. Chen et al.<sup>13</sup> reported that bis(3-aminopropyl) tetramethyldisiloxane as a new crosslinking agent was used to produce PI membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. The crosslinking was shown to effectively decrease the permeability and increase the ideal selectivity and separation factor of CO<sub>2</sub>/CH<sub>4</sub> separation. To the best of our knowledge, there is no published information quantitatively describing the solvent resistance of crosslinked PI membranes.

In this study, poly(amic acid)s (PAAs) derived from 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and 4,4'-biamino-3,3'-dimethyldiphenyl-methane (DMMDA) were prepared by low-temperature-solution polymerization in *N*-methyl-2-pyrrolidinone (NMP), and then, PAA was imidized to form PIs. 1,6-Diaminohexane (DAH) was proposed as a crosslinking agent to produce crosslinked PI membranes for lubricant solvent recovery. The structure and thermal properties of PAA and PI were confirmed by Fourier transform infrared (FTIR) spectroscopy or thermogravimetric analysis (TGA), respectively. The preparation conditions of the PI NF membranes with a phase-inversion process was investigated. The solvent resistances of the crosslinked PI and PI membrane containing a certain amount of inorganic salt additive were analyzed, and the morphology of the PI membrane with the addition of inorganic salt ZrCl<sub>4</sub> was also characterized with scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

The main monomers BTDA and DMMDA were purchased from Sigma-Aldrich. NMP (used after dehydration) was supplied by Sinopharm Chemical Reagent Factory (China). *N*-Butyl titanate with 98% purity was purchased from Dingrui Chemical Technology Co., Ltd. (China). Other reagents, such as acetic anhydride and pyridine, were purchased from Shanghai Reagent Factory (China) and were used directly without further treatment.

### Synthesis of the PI Material

A typical procedure for polymerization was as follows: an equimolar mixture of DMMDA and BTDA was added to NMP with a total concentration of 10 wt %; the solution was stirred in an ice-water bath for 12 h under a nitrogen atmosphere to form a viscous PAA solution. Then, an equimolar mixture of acetic anhydride and pyridine was added to the solution and reacted for 12 h at room temperature to prepare a PI solution. Under vigorous stirring with deionized water, the solution was subsequently deposited, then washed several times in deionized water, and dried in a vacuum oven at 50°C for 6 h to afford a PI solid powder.

### Preparation of the Crosslinked PI Membrane

The NF PI membranes were prepared via a phase-inversion process. The procedure was as follows. An amount of PI was dissolved in 10 mL of NMP to prepare the casting solution. Then, 2 g of polyethylene glycol (PEG) 200, 3 g of maleic acid, and 0.5 g of the inorganic salt ZrCl<sub>4</sub> were added to the previous solution under a heat lamp at 50°C for 24 h until a uniform

casting solution was formed. The solution was filtered to remove undissolved materials and dust particles. After degassing, the PI solution was cast onto the support fabric with a density of 0.5 mm. The solvent in the membrane partially evaporated for a period at a certain temperature and relative humidity (RH), and then, the membrane was immersed in a coagulation bath of ethanol containing 5 wt % of the crosslinking agent DAH. Then, the nascent membrane was treated successively by isopropyl alcohol, hexane, and the mixed solution of butanone/toluene/lubricants (with a quality ratio of 2:2:1) for 1 day, respectively. Finally, the membrane was kept in a dust-free environment for drying. The preparation procedure of the PI material and the chemical crosslinking modification of the PI membrane are shown in Figure 1.

### Measurement and Characterization

The feed fluid was a mixture of butanone, toluene, and lubricants with a quality ratio of 2:2:1. The solvent flux and lubricant rejection test of the composite NF membrane were conducted with self-made test equipment with a membrane area of 0.93 cm<sup>2</sup> (Figure 2). Before measurement, all of the membranes were pretreated with a high pressure drop (3 MPa) for about 30 min, and then, the separation experiment was measured at a 0.5-MPa operation pressure difference. The test liquid was a mixture of butanone, toluene, and lubricants with quality ratio of 2:2:1. The solvent flux ( $F$ ) was achieved by the measurement of the permeation volume that penetrated the unit area membrane per unit time and was calculated as follows:

$$F = V/At$$

where  $V$  is the total volume of the permeate solvent during the experiment,  $A$  represents the effective area of membrane (0.93 cm<sup>2</sup>), and  $t$  denotes the operation time. The lubricant rejection rate was determined by the measurement of the amount of lubricants in the retentate side, and the feed solution was determined at operation pressure of 3 MPa. The rejection ( $R$ ) was calculated as follows:

$$R = M_r/M_o$$

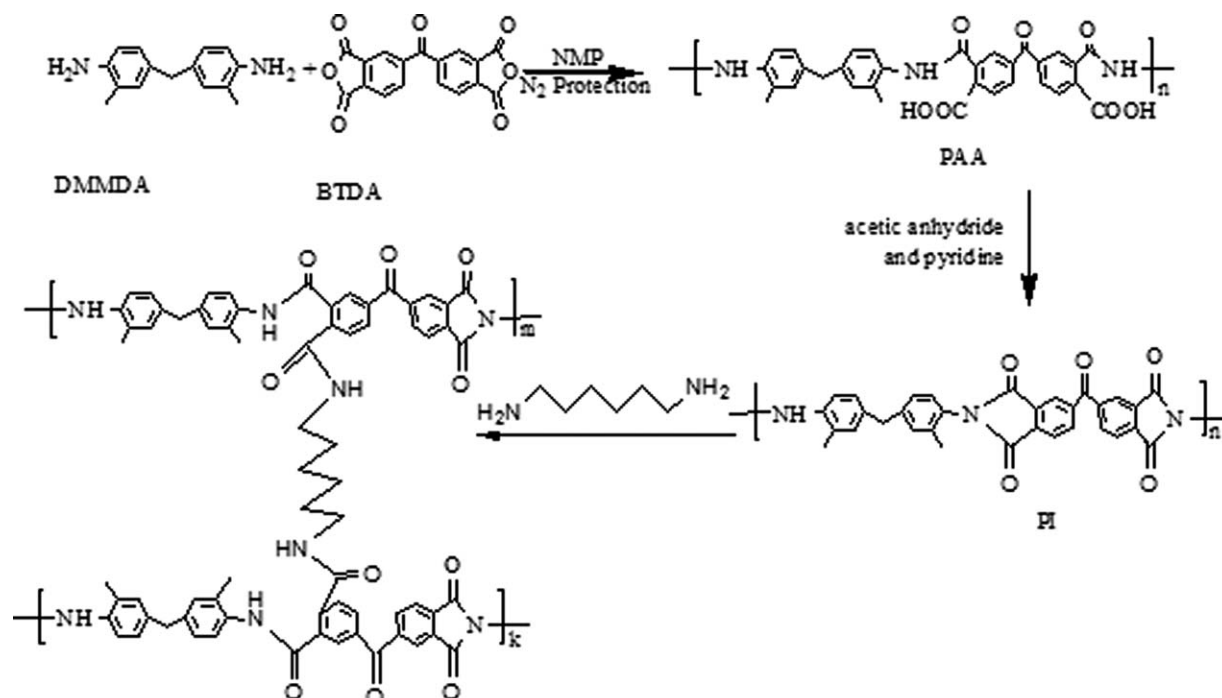
where  $M_r$  and  $M_o$  are the quality of lubricants in the retentate side and the feed solution, respectively.

The FTIR spectra of the PAA and PI were obtained with a 170SX FTIR spectroscopy (Nicolet). The measured wave-number range was between 4000 and 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. All of the original spectra were baseline-corrected with Omnic 6.1 software.

We obtained the decomposition temperatures from a PerkinElmer TGA Pyris 1TGA instrument by heating the polymer from 50 to 750°C at a heating rate of 20°C/min under an air atmosphere.

The surface and cross sections of the membranes prepared with and without the inorganic salt ZrCl<sub>4</sub> were characterized with SEM (S-4800, Hitachi, Japan) after they were coated with a conductive layer of sputtered gold. The cross section was obtained through the snapping of the membranes in liquid nitrogen.

The solvent resistance of the membranes was tested by measuring the volume swelling ratio before and after immersion in



**Figure 1.** Procedure for preparing the PI material and chemical crosslinking modification of the PI membrane.

mixtures of butanone, toluene, and lubricants with a quality ratio of 2:2:1.

The swelling volume rate was defined as follows:

$$\text{Swelling ratio (\%)} = \frac{d_2^2 - d_1^2}{d_1^2} \times 100\%$$

where  $d_1$  and  $d_2$  are the membrane diameters before and after immersion, respectively.

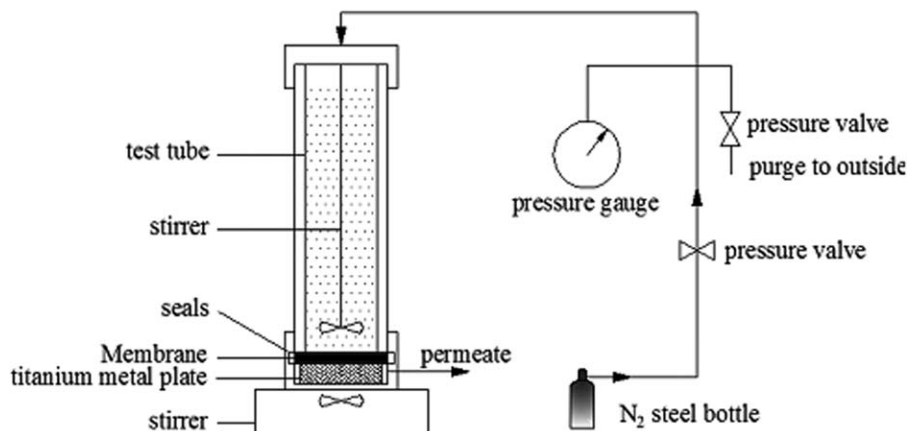
## RESULTS AND DISCUSSION

### Material Characterization

The FTIR spectra of PAA and PI are shown in Figure 3. The peaks in Figure 3(a) at 3429, 1724, and 1631  $\text{cm}^{-1}$  show the presence of amide groups; there was a slight, sharp, and strong peak at 1371  $\text{cm}^{-1}$ , which implied the stretching vibration of the hydroxyls of carboxyl groups.<sup>14</sup> The strong characteristic

absorption peaks at 3440, 1507, and 1302  $\text{cm}^{-1}$  in Figure 3(b) show the presence of amide groups; the intensity wave number of 1662  $\text{cm}^{-1}$  was the absorption peak of tertiary amide, which indicated that the imidization was completed. The peaks at wave numbers 1401 and 725  $\text{cm}^{-1}$  corresponded to the asymmetric stretching vibrations of C–N and the deformation of the imide ring, respectively, which were the characteristic peaks of the PI group.<sup>15</sup>

Figure 4 shows the TGA curves of the unmodified and crosslinking modified PI NF membranes. As compared to that of the unmodified PI membrane, the thermal stability of the crosslinked membrane obtained via immersing in the DAH ethanol solution for 1 h showed a slight decrease with increasing crosslinking degree. This phenomenon may have been due to the fact that DAH was alkaline in the ethanol solution, and this resulted in a small-portion degradation of the polymer during



**Figure 2.** Diagram of the experimental apparatus for testing rejection and flux.

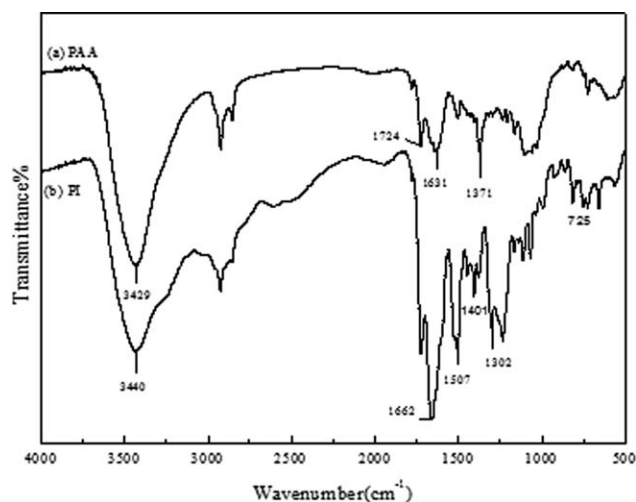


Figure 3. FTIR spectra of (a) PAA and (b) PI.

the formation of the crosslinked effect. However, even though above 700°C the weight loss of the modified PI membrane was less than 50% compared with the that of the other crosslinked PI material.<sup>13,16</sup> This indicated a relatively superior thermal stability. Hence, the thermal stability of the modified membrane was believed to be sufficient for lubricant solvent recovery.

#### Optimization of the Preparation Conditions

It has been well established that the properties of a membrane can be modified by the variation of the casting solution and the film-formation conditions,<sup>17</sup> such as the composition of the polymer solution, the solvent evaporation time and temperature, and the nature and temperature of the coagulation bath.

#### Effects of the Polymer Concentration in the Casting Solution on the Separation Performance of the NF Membranes

The polymer concentration has an important effect on the solvent flux and lubricant rejection. The NF membranes with the polymer concentration in the casting solution varied from 11 to

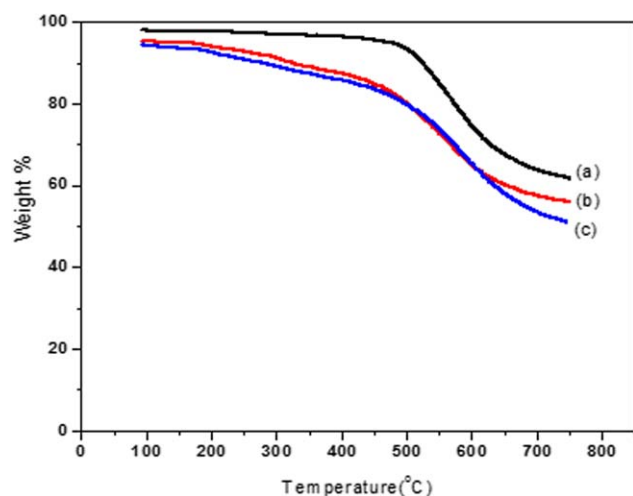


Figure 4. TGA curves of (a) the unmodified PI NF membrane and (b,c) crosslinking-modified PI NF membranes with 1.5 and 2.1 wt% DAH, respectively, in an ethanol coagulation bath. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

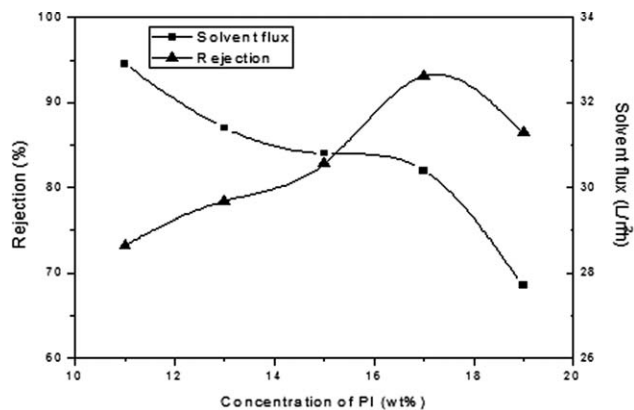


Figure 5. Effects of the polymer concentration on the membrane performance (evaporation time = 50 s, temperature = 32°C, RH = 40%).

19 wt % and were prepared at environmental temperature (32°C) with a RH of about 40%. After 50 s of solvent evaporation, the wet membrane was then immersed in the coagulation bath at a temperature of 30°C. Figure 5 shows the effects of the polymer concentration on the membrane performance.

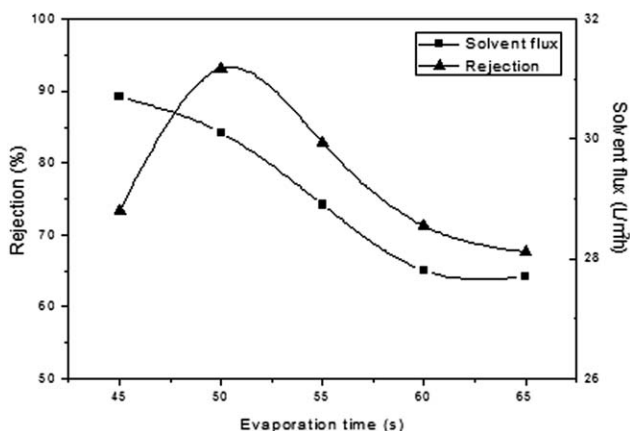
This indicated that the permeation flux decreased, whereas the lubricant rejection rate increased with increasing polymer concentration of the casting solution. When the concentration increased, the polymer molecules were packed even closer, and the coiled chains penetrated with each other;<sup>18</sup> thus, they formed a steric configuration with a smaller free space in the solvent. Consequently, smaller pores were formed across the film. As a result, the diffusive force increased remarkably, and the permeation flux decreased largely, whereas the solvent rejection rate increased. When the results of the solvent flux and lubricant rejection were combined, a concentration of 17 wt % was the optimal condition.

#### Effects of the Solvent Evaporation Time on the Separation Performance of the NF Membranes

To investigate the influence of the evaporation time on the membrane performances and morphologies, the casting solution containing 17 wt % PI was applied to prepare a NF membrane at an RH of about 40% and a temperature of 32°C. After the period of solvent evaporation varied from 45 to 65 s, the wet membrane was then immersed in the coagulation bath at a temperature of 30°C. The results of the solvent flux and lubricant rejection as a function of the evaporation time are presented in Figure 6.

As shown clearly in Figure 5, as the evaporation time increased, the solvent flux of the membrane continuously decreased from the initial higher value of 30.7 L m<sup>-2</sup> h<sup>-1</sup> with a 45-s evaporation time to a relatively lower value of 27.7 L m<sup>-2</sup> h<sup>-1</sup> with a 65-s evaporation time. The experimental results of the solvent flux were in accordance with the conventional rule that the membrane permeation decreases with increasing evaporation time. According to the reports of Pinnau and Koros<sup>19</sup> and Kawakami et al.,<sup>20,21</sup> the outermost region of the membrane undergoes phase separation by spinodal decomposition during the evaporation process. The evaporation step before the immersion step strongly influences the surface skin-layer





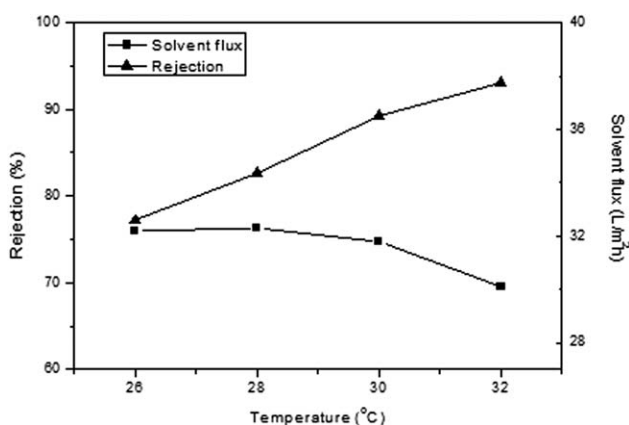
**Figure 6.** Effect of the solvent evaporation time on the membrane performance (PI concentration = 17 wt %, temperature = 32°C, RH = 40%).

thickness. Such a process is called *dry-phase separation*, during which an ultrathin skin layer is formed. Thus, increasing the evaporation time was expected to result in a thicker skin layer; this was mainly responsible for the low permeation flux.

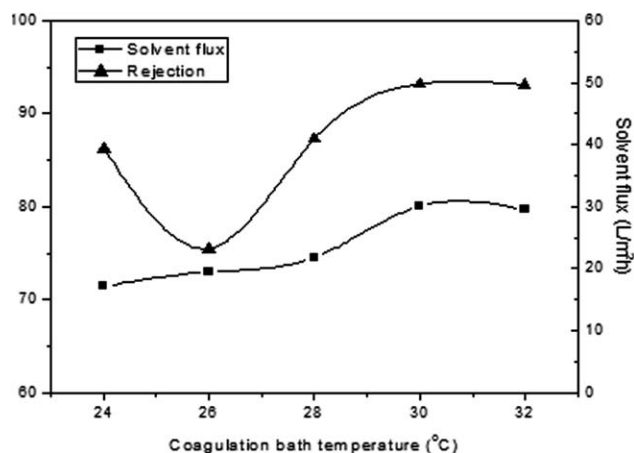
As shown in Figure 6, the rejection of the membrane first increased from 73.3 to 93.1% when the evaporation time increased from 45 to 50 s and finally decreased to 67.6% when the evaporation time continuously increased to 65 s. The change in lubricant rejection with increasing evaporation time was due to the competition of two influential factors, the evaporation of the solvent and the water absorption of the casting solution. When the evaporation time was lower than 50 s, the evaporation of the solvent was the major influence on the membrane surface layer, which was more inclined to form a denser membrane surface layer. Conversely, when the evaporation time was greater than 55 s, the water absorption became the main factor in the formation of larger pore membranes.

#### Effects of the Solvent Evaporation Temperature on the Separation Performance of the NF Membranes

To investigate the influence of the evaporation temperature on the membrane performance and morphology, evaporation temperatures of 26, 28, 30, and 32°C was applied to prepare NF



**Figure 7.** Effect of the solvent evaporation temperature on the membrane performance (PI concentration = 17 wt %, evaporation time = 50 s, RH = 40%).



**Figure 8.** Effect of the coagulation bath temperature on the membrane performance.

membranes at a RH of about 40%. After 50 s of solvent evaporation, the wet membrane was then immersed in the coagulation bath at a temperature of 30°C. The results of the solvent flux and lubricant rejection as a function of the evaporation temperature are presented in Figure 7.

As shown in Figure 7, the solvent flux decreased from 32.2 to 30.1 L m<sup>-2</sup> h<sup>-1</sup>, and the lubricants rejection increased continuously from 77.2 to 93.1% when the film-formation temperature increased from 26 to 32°C. The reason was that with increasing film-formation temperature, the solvent and volatile additives readily evaporated from the aggregate holes and the polymer surface layer; this resulted in a small hole, and a dense surface layer formed. Moreover, this layer inhibited the exchange rate of the solvent and nonsolvent during the phase-inversion process and thereby resulted in a lower solvent flux and a higher lubricant rejection. Because of the practical application of controllable cost and temperature, the evaporation temperature is usually room temperature.

#### Effects of the Coagulation Bath Temperature on the Separation Performance of the NF Membranes

The coagulation bath temperature, as both a thermodynamic factor and kinetic factor, is of major concern in the phase-inversion process,<sup>22,23</sup> which affects the membrane properties. The casting solution containing 17 wt % PI was cast onto a support fabric with the surrounding temperature of 32°C and a RH of 40%. After a 50-s evaporation period, the membrane was immersed in a coagulation bath of ethanol containing 5 wt % crosslinking agent DAH to remove the residual solvent under temperatures that were varied from 24 to 32°C. The results of the solvent flux and lubricant rejection as a function of the coagulation bath temperature are presented in Figure 8.

The results demonstrate that the lubricant rejection of the membrane first decreased from 86.2 to 75.5% when the coagulation bath temperature increased from 24 to 26°C and then increased to 93.1% at a coagulation bath temperature of 32°C. The solvent flux showed contrary trends. The flux increased from 17.1 to 30.1 L m<sup>-2</sup> h<sup>-1</sup> when the coagulation bath temperature increased from 24 to 30°C and then decreased to 29.5 L m<sup>-2</sup> h<sup>-1</sup> at a coagulation bath temperature of 32°C.

**Table I.** Effects of the Crosslinking Time on the Volume Swelling Rate of the PI NF Membranes

Crosslinking time (min)	Diameter before soaking (cm)	Diameter after soaking (cm)	Coefficient of cubical expansion (%)
0	4.0	4.22	$11.30 \pm 0.022$
10	4.0	4.17	$8.68 \pm 0.012$
30	4.0	4.15	$7.64 \pm 0.015$
60	4.0	4.15	$7.64 \pm 0.014$
70	4.0	4.21	$10.78 \pm 0.016$

A reasonable explanation for these observations must consider the effect of the rate of the demixing process on the morphology of the membranes. On the one hand, in the ternary phase diagram, the one-phase region expanded, and the liquid–liquid demixing region shrank at high coagulation bath temperatures. When phase separation occurred, the polymer concentration decreased in the polymer-rich phase but increased in the polymer-lean phase; this led to a loose membrane structure. On the other hand, at a high coagulation bath temperature, the diffusion rates of the solvent and nonsolvent molecules became fast, and the phase-inversion process was accelerated.<sup>24</sup> Therefore, the membrane fabricated at a high coagulation bath temperature probably exhibited a relatively thin skin layer and a high porosity; this was favorable for improving the solvent flux.

#### Effect of the Chemical Crosslinking Time on the Solvent Resistance of the PI NF Membrane

A series of PI homogeneous membranes were prepared and were modified with different crosslinking times. The effects of the crosslinking degree on the swelling of the PI homogeneous membrane in a butanone/toluene/lube oil mixture were studied through the variation of the film diameter, as shown in Table I. As shown in Table I, an increase in the crosslinking time led to a higher degree of crosslinking; this showed a marked improve-

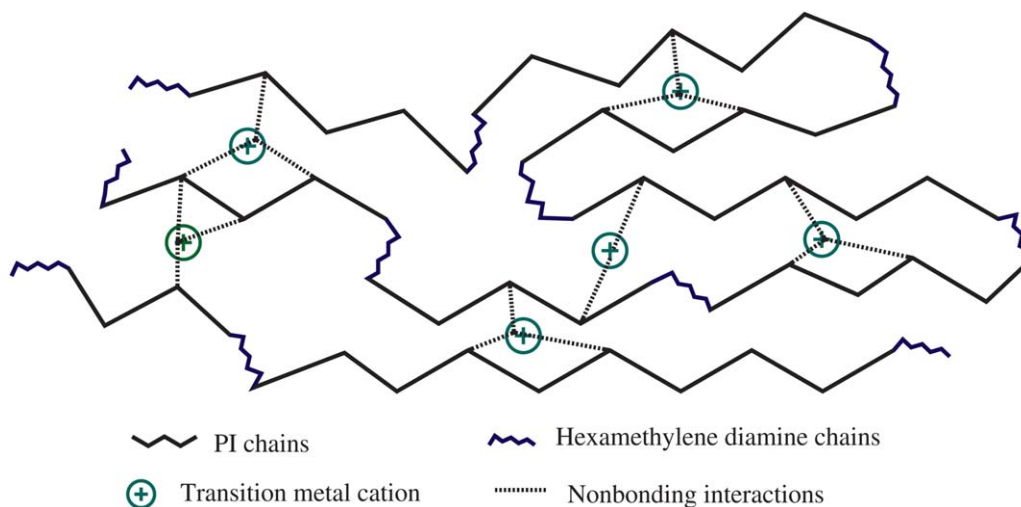
**Table II.** Effects of the Inorganic Salt on the Volume Swelling Rate of the PI NF Membranes

Sample	Diameter before soaking (cm)	Diameter after soaking (cm)	Coefficient of cubical expansion (%)
PI membrane without inorganic salt	4.0	4.48	$9.42 \pm 0.015$
PI membrane containing 5 wt % inorganic salt	4.0	4.15	$7.64 \pm 0.012$

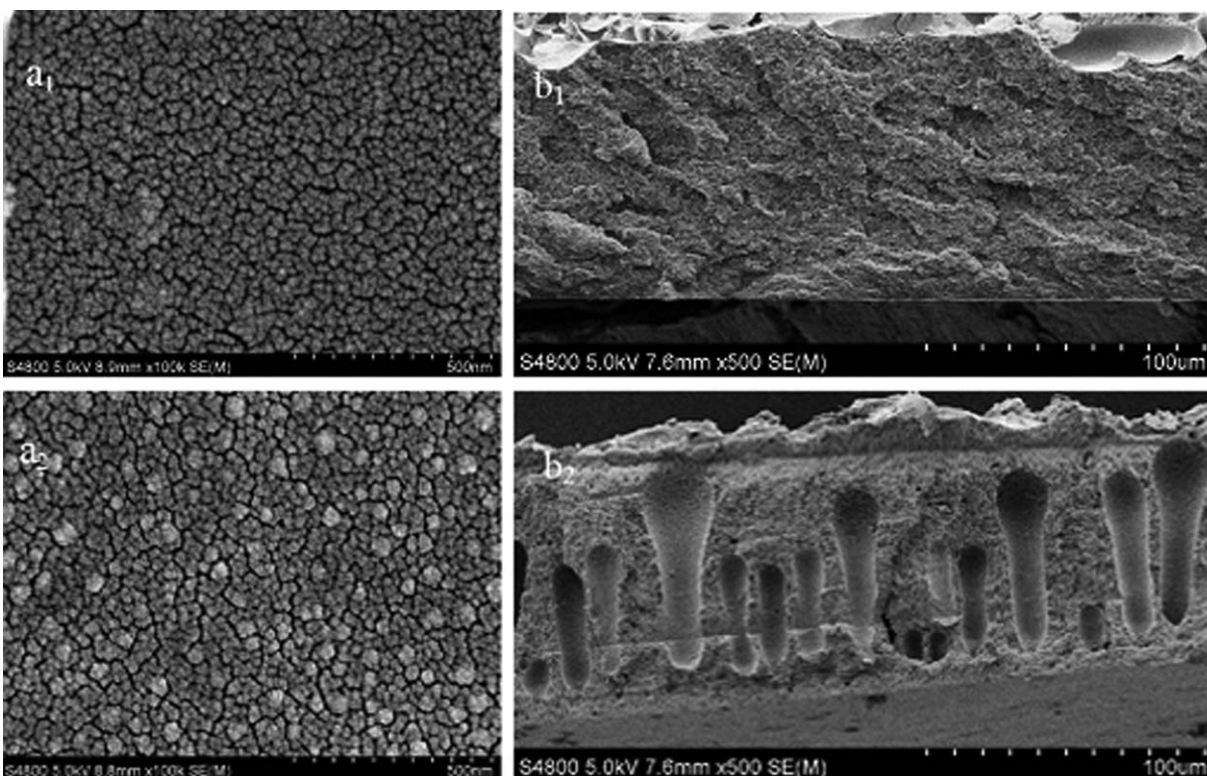
ment in the swelling ratio of the modified films compared to original membranes, which ranged from 11.3 to 7.64%. The possible reaction mechanism between the PI molecular chain and DAH and the crosslinked PI structure is shown in Figure 1, which shows that the amine groups from DAH reacted with the imide bonds from the PI chain to become a denser PI film when the film was immersed in the ethanol solution.<sup>25</sup> When the immersion time was increased, the PI chains crosslinked with each other and presented excellent solvent-resistance properties. From these results, it was clear that the method with DAH as a crosslinking agent had a large influence on the solvent resistance of the PI membranes via the linking of the PI molecular chains. After optimization of the membrane synthesis parameters, it was also expected that membranes could be obtained with fine swelling properties within certain modified times.

#### Effect of the Inorganic Salt $ZrCl_4$ on the Solvent Resistance of the PI NF Membranes

The addition of a fourth organic/inorganic component to the polymer/solvent/nonsolvent system is a well-known technique for enhancing the properties of membranes prepared by a phase-inversion process.<sup>26–28</sup> Inorganic salt additives are considered to



**Figure 9.** Structure of the PI/inorganic salt NF membrane after chemical crosslinking modification. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** (a<sub>1</sub>) Surface and (b<sub>1</sub>) cross-sectional SEM photographs of the PI membrane without the inorganic salt and (a<sub>2</sub>) surface and (b<sub>2</sub>) cross-sectional SEM photographs of the PI membrane containing 0.5 wt % inorganic salt.

change the solvent properties and the interaction among the macromolecule chains; this can improve the mechanical strength and chemical resistance.

The solvent resistance of the obtained membrane prepared by a 17 wt % PI casting solution containing 5% of the inorganic salt  $ZrCl_4$  is shown in Table II. As shown in Table II, the addition of inorganic salts can resist the membrane expansion to a certain extent, and this improves the solvent resistance of the membrane. The reason is that nonbonding interactions, such as complexation and van der Waal's forces, exist in the inorganic salts and the PI macromolecules. When the membrane is immersed in an organic solvent, additional energy is needed to overcome nonbonding interaction. The structure of the cross-linking PI membrane containing  $ZrCl_4$  is illustrated in Figure 8.

#### Effect of the Inorganic Salt $ZrCl_4$ on the PI NF Membrane Morphology

Inorganic salts additives as a pore-forming reagent can be used to increase the permeability of a porous membrane without reducing the rejection performance of the membrane.<sup>29</sup> In this study, the inorganic salt  $ZrCl_4$  as a novel additive was used to prepare PI NF membranes. SEM was used to study the morphology of the membranes. The surface and cross section of the PI membrane without and with the addition of inorganic salt are characterized in Figure 9.

As shown in Figure 10, we observed that the membranes prepared were symmetrical in morphology. The addition of inorganic salts was favorable to the formation of the pore

structure. The reason was that the addition of the inorganic salt made phase separation quicker; this offered more time for the coarsening of the polymer-poor phase and yielded larger pores. The lubricant rejection of the NF-membrane-free inorganic salt was only 30%, and the solvent flowed out immediately at a pressure of 2 MPa. Under the same preparation conditions, the lubricant rejection of the NF membrane containing 5 wt % inorganic salt was up to 93%, and the solvent flowed out after a stable time of 10 min at a pressure 4 MPa. The research of membrane performance also showed that the addition of inorganic salts could increase the membrane pressure resistance.

#### CONCLUSIONS

Before the installation of the membranes, the solvent dewaxing unit was simultaneously limited by refrigeration and solvent handling capacity in the dewaxed oil recovery section when a light neutral stock was run. It was limited by both the chilling train hydraulic capacity and filter surface area availability during the running of heavier stocks. In this study, the crosslinked PI membrane was prepared for solvent recovery from lube oil filtrates. The results indicate that the addition of the crosslinking reagent and inorganic salt not only enhanced the properties of solvent resistance and pressure resistance but was also in favor of the formation of finger pores, which improved the separation performance of the PI membrane. The long-term operational stability of the membrane indicated that the crosslinked PIs membrane offers a promising new method for solvent recovery from lube oil filtrates.

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## REFERENCES

1. Bhore, N.; Gould, R. M.; Jacob, S. M.; Staffield, P. O.; McNally, D.; Smiley, P. H.; Wildemuth, C. R. *Oil Gas J.* **1999**, *97*, 67.
2. Burdyny, T.; Struchtrup, H. *Energy* **2010**, *35*, 1884.
3. Hu, K.; Dickson, J. M. *J. Membr. Sci.* **2006**, *279*, 529.
4. Hilal, N.; Al-Zoubi, H.; Darwish, N. A.; Mohammad, A. W.; Arabi, M. A. *Desalination* **2004**, *170*, 281.
5. Strathmann, H. *AIChE J.* **2001**, *47*, 1077.
6. Soltanieh, M.; Matsuura, T.; Tabe-Mohammadi, A.; Feng, C. *Sep. Purif. Technol.* **2006**, *51*, 359.
7. White, L. S.; Nitsch, A. R. *J. Membr. Sci.* **2000**, *179*, 267.
8. Shao, L.; Liu, L.; Cheng, S. X.; Huang, Y. D.; Ma, J. *J. Membr. Sci.* **2008**, *312*, 174.
9. Vanherck, K.; Vankelecom, I.; Cano-Odena, A.; Koeckelberghs, G.; Dedroog, T. *J. Membr. Sci.* **2010**, *353*, 135.
10. Staudt-Bickel, C.; Koros, W. J. *J. Membr. Sci.* **1999**, *155*, 145.
11. Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. *Macromolecules* **2003**, *36*, 1882.
12. Wind, J. D.; Sirard, S. M.; Paul, D. R.; Green, P. F.; Johnston, K. P.; Koros, W. J. *Macromolecules* **2003**, *36*, 6433.
13. Chen, X. Y.; Rodrigue, D.; Kaliaguine, S. *Sep. Purif. Technol.* **2012**, *86*, 221.
14. Hu, Z.; Li, S.; Zhang, C. *J. Appl. Polym. Sci.* **2007**, *106*, 2494.
15. Ahmad, Z.; Sagheer, F. A.; Arbash, A. A.; Ali, A. A. M. *J. Non-Cryst. Solids* **2009**, *355*, 507.
16. Liu, Y.; Wang, R.; Chung, T. S. *J. Membr. Sci.* **2001**, *189*, 231.
17. Sun, H. X.; Liu, S. N.; Ge, B. S.; Xing, L.; Chen, H. L. *J. Membr. Sci.* **2007**, *295*, 2.
18. Wienk, I. M.; Boom, R. M.; Beerlage, M. A. M.; Bulte, A. M. W.; Smolders, C. A.; Strathmann, H. *J. Membr. Sci.* **1996**, *113*, 361.
19. Pinnau, I.; Koros, W. J. *J. Polym. Sci. Part B: Polym. Phys.* **1993**, *31*, 410.
20. Kawakami, H.; Mikawa, M.; Nagaoka, S. *J. Appl. Polym. Sci.* **1996**, *62*, 965.
21. Kawakami, H.; Mikawa, M.; Nagaoka, S. *J. Membr. Sci.* **1997**, *137*, 241.
22. Wang, Y.; Shi, B.; Li, X. *Polym. Eng. Sci.* **2013**, *53*, 1614.
23. Saljoughi, E.; Amirilargani, M.; Mohammadi, T. *Desalination* **2010**, *262*, 72.
24. Mousavi, S. M.; Saljoughi, E.; Ghasemipour, Z.; Hosseini, S. A. *Polym. Eng. Sci.* **2012**, *52*, 2196.
25. Shao, L.; Chung, T. S.; Goh, S. H.; Pramoda, K. P. *J. Membr. Sci.* **2004**, *238*, 153.
26. Mu, T.; Cong, Y.; Zhang, B. *J. Appl. Polym. Sci.* **2013**, *129*, 3582.
27. Yang, S.; Liu, Z. *J. Environ. Sci.* **2004**, *16*, 191.
28. Krieter, D. H.; Morgenroth, A.; Barasinski, A.; Lemke, H. D.; Schuster, O.; von Harten, B.; Wanner, C. *Nephrol. Dial. Transplant.* **2007**, *22*, 491.
29. Chou, W. L.; Yu, D. G.; Yang, M. C.; Jou, C. H. *Sep. Purif. Technol.* **2007**, *57*, 209.