

## CuO-Filled Aminomethylated Polysulfone Hybrid Membranes for Deep Desulfurization

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**ABSTRACT:** CuO-filled aminomethylated polysulfone hybrid membranes were prepared for sulfur removal from gasoline. The as-prepared membranes were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The separation performance of the hybrid membranes was evaluated by pervaporation (PV) separation of *n*-heptane/thiophene binary mixture. CuO-filling leads to a decrease in permeation flux. The sulfur-enrichment factor increased first and then decreased with increasing CuO loading, and it is worth noting that there is a rebound in enrichment factor above 8 wt % CuO loading. Influencing factors such as nitrogen content, feed temperature, sulfur content, and various hydrocarbons on membrane PV performance were also evaluated. Permeation flux of  $23.9 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  and sulfur-enrichment factor of 3.9 can be achieved at 4 wt % CuO loading in PV of *n*-heptane/thiophene binary mixture with  $1500 \mu\text{g}\cdot\text{g}^{-1}$  sulfur content. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3718–3725, 2013

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### INTRODUCTION

Pervaporation (PV) is an efficient separation technology and considered as a prospective membrane process in purification of liquid mixtures. The potential applicability of PV has been widely studied in recent years for separation of azeotropic, close-boiling, and isomeric mixtures.<sup>1</sup> One application of the PV process is the gasoline desulfurization. The enhanced removal of sulfur from fuel such as gasoline and diesel has become very important in the petroleum-refining industry because of more stringent environmental quality requirements for sulfur pollution from oil products. Gasoline, which is the research subject under discussion, is a complex mixture consisting of hundreds of organic compounds. Fluid catalytic cracking (FCC) gasoline, which accounts for 30–40 wt % or more of the total gasoline pool, is by far the most significant sulfur contributor, especially in China.<sup>2</sup> Thiophene species are the primary sulfur compounds of FCC gasoline, which account for about 60–80 wt % of total sulfur content.<sup>3</sup> Therefore, removal of thiophene from hydrocarbons is the key of gasoline desulfurization.

Several research groups have investigated the removal of sulfur from hydrocarbons in model compounds of gasoline.<sup>4</sup> For instance, an enrichment factor of 3.31 in combination with a

flux of  $33.3 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  was achieved with polyethylene glycol (PEG) membranes in separation of a binary thiophene (1200 ppm)/*n*-hexane mixture at 358 K and a permeate pressure of 1.3 mbar.<sup>5</sup> And polydimethylsiloxane (PDMS) composite membranes yielded an enrichment factor of 4.4 and a flux of about  $15.6 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  in separation of thiophene/*n*-octane mixtures at 304 K.<sup>6</sup>

The membrane is the core component for deep desulfurization of FCC gasoline. The chemical properties and the physical structure of the membrane material both affect its performance considerably.<sup>7</sup> In the past, various membrane materials have been studied with the aim of separating the thiophene/*n*-heptane mixture. The most commonly used materials are PDMS,<sup>8–10</sup> polyurethane (PU),<sup>11,12</sup> polyvinyl pyrrolidone (PVP),<sup>13,14</sup> and PEG.<sup>5,15</sup> The drawbacks of these membranes for PV are their low mechanical strength and high swelling. The deficit in mechanical strength means that the membrane needs a porous thick membrane as the support layer. The high swelling often leads to a peeling of the active membrane from the support layer. High swelling may also deteriorate the selectivity of the membrane and accelerate chemical degradation at high temperatures and pressures.<sup>1</sup> A series of modifications such as cross-linking and blending were applied to avoid these

defects.<sup>15,16</sup> However, these methods cannot take into account both the permeation flux and separation factor.

To refrain from the deficiency, polymers with aromatic groups are currently being studied. Most researchers focus on the synthesis of new aromatic polymers such as polyimide [PI (6FDA-MDA)] and PI (Matrimid 5218).<sup>17,18</sup> However, most aromatic polymers are hydrophobic which usually have worse PV performance than hydrophilic polymers for gasoline desulfurization.<sup>1</sup> Modification of aromatic polymers used for gasoline desulfurization is thus of great importance. Polysulfones (PSFs) are well known as excellent thermal and solvent-resistant materials, and have better mechanical strength.<sup>19</sup> However, PSFs are hydrophobic polymers, therefore, modification of PSF to make it hydrophilic is essential in the preparation of PSF-based membranes for desulfurization. In addition, we get the inspiration from adsorption in which researchers found the existence of strong  $\pi$ -complexation between  $\text{Ag}^+/\text{Cu}^{2+}$  and C=C in thiophene or substituted thiophene.<sup>20</sup> So, it is expected that the addition of inorganic particles to membranes would increase the permeability because of the disruption of polymer packing and lead to faster diffusion of penetrates in the membranes. Qi<sup>21</sup> prepared the  $\text{Ag}^+$  filled membrane with considering the interaction between the filler and thiophene. This would enhance the sorption of thiophene in the mixed matrix membrane and improve the sulfur removal-efficiency in PV desulfurization.

In this work, aminomethyl (a hydrophilic group) was introduced into a PSF membrane by an aminomethylation reaction. Cupric oxide (CuO) particles were taken as the filler for preparation of the CuO-filled aminomethylated polysulfone (AMPSF) hybrid membranes. The thiophene/hydrocarbon binary mixture was used as feed to evaluate PV desulfurization of the CuO-filled AMPSF membranes. Influencing factors such as nitrogen content, feed temperature, sulfur content, and various hydrocarbons were evaluated experimentally.

## EXPERIMENTAL

### Materials

PSF and chloromethyl methyl ether were purchased from Xuzhou Engineering Plastics Plant and Shanghai Yumei Chemical Co., Ltd, respectively. Dichloromethane, *N,N*-dimethylacetamide (DMAC), *n*-heptane, *n*-hexane, *n*-octane, cyclohexane, and toluene were purchased from the Sinopharm Chemical Reagent Co., Ltd. Zinc chloride, CuO, phthalimide, sodium hydride, hydrazine hydrate, and thiophene as the sulfur specie were purchased from Aladdin Reagent Company. All these were of analytical reagent grade and used without further purification.

### Synthesis of Aminomethylated PSF

Twenty gram of dried PSF was dissolved in 200 mL of dichloromethane at 25°C. Twenty gram of chloromethyl methyl ether used as the chloromethylation reagent and 1.5 g of zinc chloride used as the catalyst were added to the PSF solution. The resulting solution was heated slowly to 40°C for 6 h. When the chloromethylation reaction was completed, the

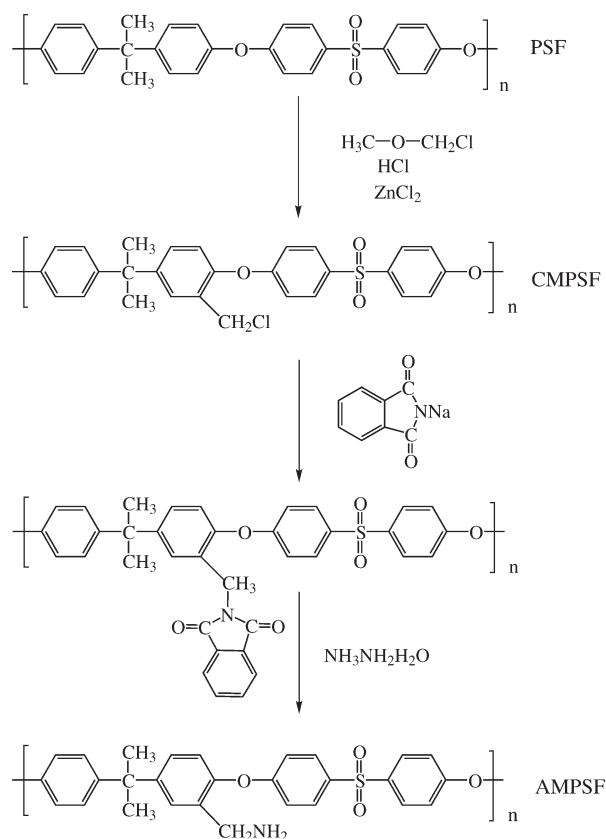


Figure 1. Schematic of synthesis of aminomethylated PSF.

solution was cooled to room temperature and then poured into more than 300 mL of cold methanol under strong stirring to yield a precipitate. The precipitate was washed with hot distilled water and dried at 65°C for 10 h. The dried precipitate was cut into small pieces and dissolved in DMAC. The solution was then poured into a large volume of distilled water with stirring at 75°C to get another precipitate. This precipitate was filtered, further washed with distilled water, and dried at 65°C to yield purified chloromethyl polysulfone (CMPSF).

Two gram of phthalimide and 0.3 g of sodium hydride were dissolved into 25 mL of DMAC at 25°C to make a mixture. 2.5 g of dried CMPSF was dissolved into 25 mL of DMAC, and then poured into the above mixture to take amidation reaction at 80°C for 12 h. The product was precipitated by methanol, filtered, washed by distilled water, and dried at 65°C to get an intermediate product. 2.5 g of the dried intermediate reacted with 0.4 mL of hydrazine hydrate in 50 mL of DMAC at 70°C for 10 h to produce a raw AMPSF. The product was precipitated by methanol, filtered, washed by distilled water, and dried at 35°C to yield AMPSF. The process for the synthesis is shown in Figure 1. AMPSF with various nitrogen contents could be prepared by controlling the reaction temperature and the reaction time. The nitrogen content can be measured by the Kedar Shrestha nitrogen determination method.

### Membrane Preparation

One gram of AMPSF was dissolved in 20 mL of DMAC at room temperature with stirring for 12 h to form a 5 wt % AMPSF homogeneous solution. The solution, after stirring for 12 h at room temperature, was filtered to remove impurity. The filtrate was further kept under vacuum at room temperature for 24 h to remove air bubbles. The CuO particles were then added into the solution to form a suspension. The resulting suspension was ultrasonicated for 10 min to promote the dispersion of CuO particles. The final solution was cast onto a glass plate and then placed in an oven at 110°C for 2 h to form dried membrane. All the membrane samples were stored in a dust-free and dry environment before use. The active layer has a thickness of about 20  $\mu\text{m}$ .

### PV Experiments

The PV cell contains an effective membrane area of 12.56  $\text{cm}^2$ . The feed solution with 1500  $\mu\text{g}\cdot\text{g}^{-1}$  sulfur content was continuously circulated from a feed tank to the feed side of the membrane by a pump. The pressure on the permeate side was less than 800 Pa. The permeate was collected in liquid nitrogen trap and the total sulfur content of the feed and the permeate samples was analyzed by gas chromatography (GC-950).

The permeation flux ( $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ),  $J$ , at a steady state is obtained by

$$J = \frac{M}{A \times t} \quad (1)$$

where  $M$  is the weight of permeate during the experimental time interval  $t$  at steady state and  $A$  is the effective membrane area.

The sulfur enrichment factor,  $E$ , is defined as

$$E = \frac{C_p}{C_f} \quad (2)$$

where,  $C_f$  and  $C_p$  are the total sulfur content in the feed and the permeate, respectively.

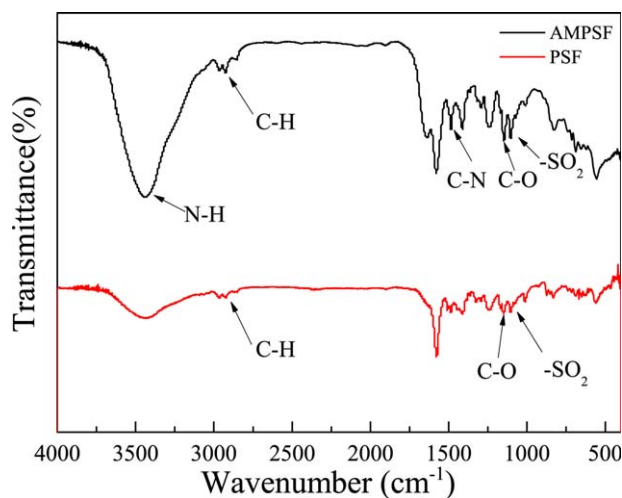
### Membrane Characterization

The hydrophobicity of the as-prepared membranes was characterized using a contact angle meter (SL200B, SOLON TECH, Shanghai, China) at  $26 \pm 1^\circ\text{C}$  with  $67 \pm 2\%$  relative humidity. FTIR spectra of the PSF and AMPSF membranes were scanned using Nicolet-330. Environmental scanning electron microscopy (ESEM, XL30ESEM-TMP, Philips, the Netherlands) was used to characterize the surface of the membranes. Crystal structure characterization was carried out using X-ray diffraction (XRD, Panalytical X'pert Philip, the Netherlands) with Cu-K $\alpha$  radiation. The diffraction was operated at 40 kV and 30 mA in a  $2\theta$  range of  $5\text{--}60^\circ$ , using a step size of  $0.0167^\circ$  and a counting time of 10 s per step.

## RESULTS AND DISCUSSION

### FTIR Analysis

Figure 2 shows the FTIR spectra of the PSF and AMPSF polymers. The spectrum of the pristine PSF shows three broad peaks at wave numbers in the region 2950–3050, 1200–1300, and 1050–1150  $\text{cm}^{-1}$ , indicating the presence of  $-\text{CH}_3$ , C–O, and



**Figure 2.** FTIR spectra of PSF and AMPSF. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$-\text{SO}_2$ , respectively. From the FTIR spectra of the AMPSF, the appearance of new peaks at the region  $3400\text{--}3500\text{ cm}^{-1}$  is because of the formation of  $-\text{NH}_2$  in the absence of moisture. This verifies the successful formation of AMPSF.

### SEM Analysis

SEM characterization of the unfilled and CuO-filled AMPSF membranes was carried out to investigate the dispersion of CuO particles in the polymeric phase. From Figure 3(a), it can be seen that the surface of the unfilled membrane is smooth, dense, and defectless. Figure 3(b) shows the surface of the hybrid membrane with 8 wt % CuO loading in which CuO particles are uniformly dispersed in the AMPSF matrix. There are not any nanogaps between the polymer and the nanoparticles, as confirmed by PV below. The SEM image of the hybrid membranes with 8 wt % CuO loading after PV for 24 h is shown in Figure 3(c). There were no obvious changes in the surface of the membrane before and after PV. The evenly distributed CuO particles have good stability and do not destroy the membrane.

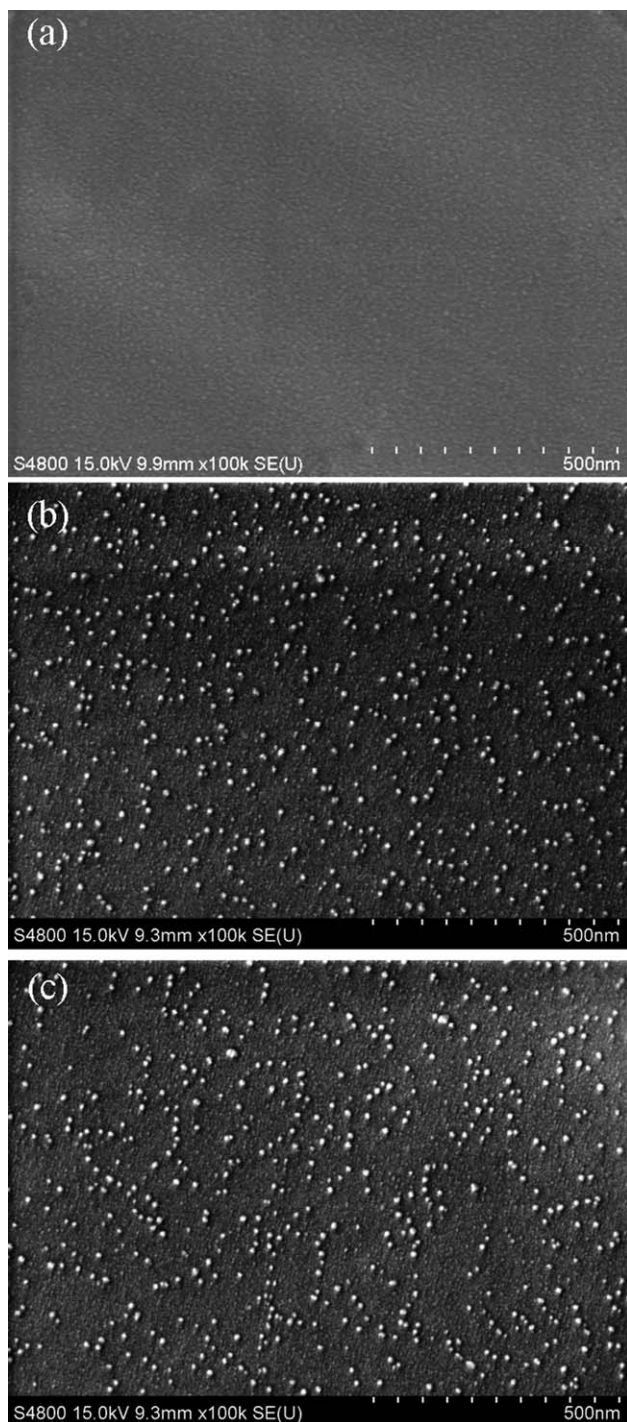
### XRD Analysis

The XRD spectra of the hybrid membranes with various CuO loadings are shown in Figure 4. From the spectra, both the unfilled and filled membranes have a wide peak at  $2\theta \approx 15\text{--}20^\circ$  and a sharp peak at  $2\theta \approx 13^\circ$ , indicating that the aminomethyl PSF is a semicrystalline polymer. Except the unfilled membrane, all the other membranes have two distinct sharp peaks at  $2\theta \approx 35\text{--}40^\circ$ , indicating the existence of inorganic crystal particles in the membranes. The intensity of the sharp peaks is found to increase with increasing CuO loading. One can thus conclude that the inorganic crystal is CuO particles. The increase in the peak intensity also suggests an increase in the degree of crystallinity.

### PV Performance

FCC gasoline is a mixture consisting of hundreds of compounds. It is hard to carry out detailed investigations for all gasoline components. For reasons of practicality, typical binary mixtures are used as feed. Once a promising membrane material is identified, our model gasoline mixture is used to investigate

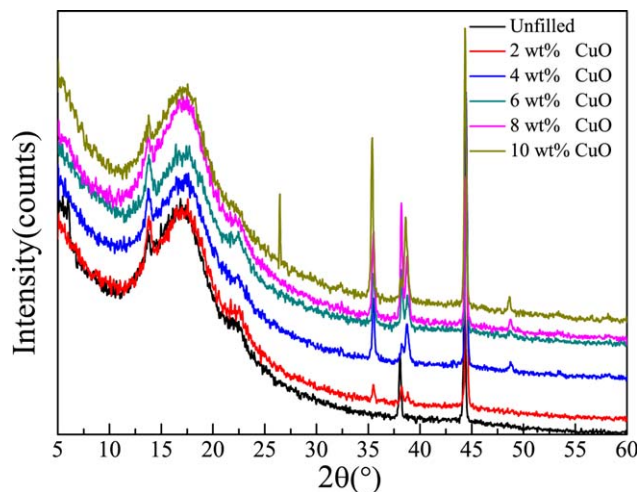




**Figure 3.** Surface morphologies (a) unfilled membrane, (b) 8 wt % CuO-filled membrane before and (c) after PV for 24 h.

the membrane performance. In this study, thiophene/*n*-heptane binary mixture was chosen and various hydrocarbons were also investigated.

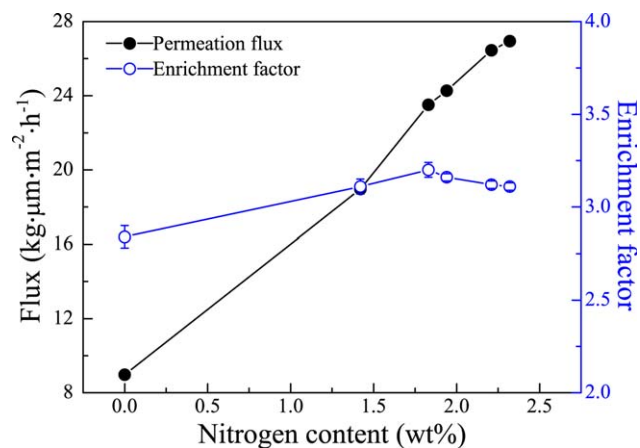
The effect of CuO loading in the membranes was evaluated. Actually, it is hard to evaluate a PV process just by examining flux or separation factor alone without considering related operating parameters. Therefore, other factors such as nitrogen



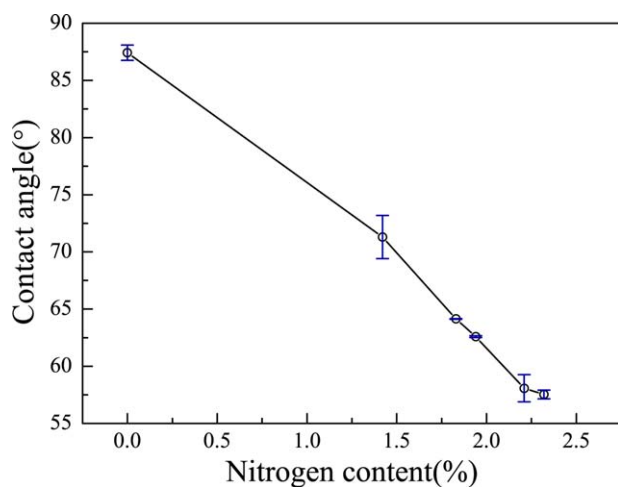
**Figure 4.** XRD spectra of the CuO-filled membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

content, feed temperature, various hydrocarbons, and sulfur content were studied experimentally.

**Effect of Nitrogen Content.** Considering that nitrogen has a high affinity for thiophene, the effect of nitrogen content on PV (Figure 5) and contact angle (Figure 6) was investigated in order to get the optimal nitrogen content. It can be seen that the hydrophilicity of the membrane increased with increasing nitrogen content. Higher hydrophilic membrane has a higher affinity for thiophene that is more hydrophilic than hydrocarbons. The permeation flux and the sulfur-enrichment factor both increased with increasing nitrogen content. This can be explained by the solution-diffusion mechanism.<sup>22</sup> It is probably that the aminomethylation of the PSF membrane enhanced both diffusion selectivity and sorption selectivity. When the nitrogen content reached about 2 wt %, a slight decrease in the enrichment factor was observed with increasing nitrogen content further. This is because the higher sorption capacity would lead to an increase in swelling and thus a decrease in diffusion



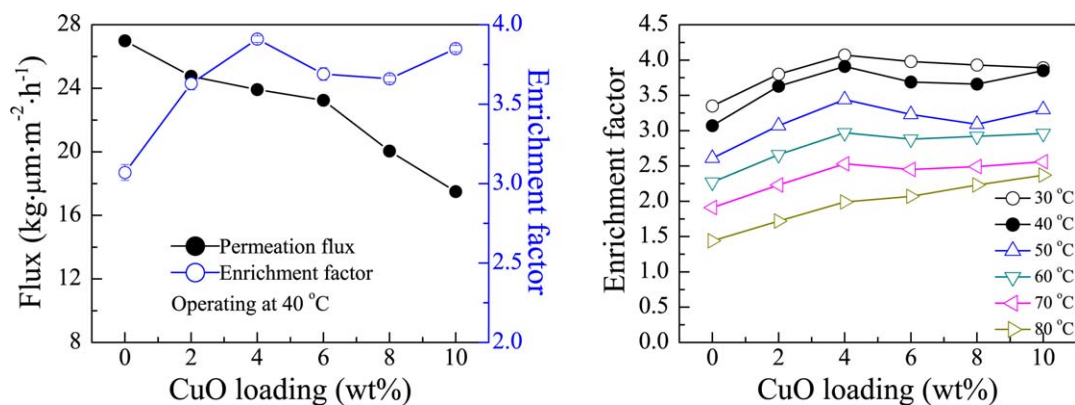
**Figure 5.** The effect of nitrogen content on permeation flux and sulfur-enrichment factor (membrane with 4 wt % CuO loading at 40°C). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** The effect of nitrogen content on contact angle. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

selectivity. From this phenomenon, the modified PSF with about 2 wt % nitrogen content was chosen to prepare membrane for desulfurization.

**Effects of CuO Loading.** In order to realize the transport mechanisms and to get the optimal CuO loading in the hybrid membrane, the effect of CuO loading on permeation flux and enrichment factor was investigated, as shown in Figure 7. The CuO loading varied in the range of 0–10 wt %. It is observed from Figure 7(a) that the permeation flux decreased with increasing CuO loading. It can be explained by the tortuosity effect. The filled CuO particles are completely impermeable for the permeant molecules. Thereby, the diffusion of the penetrants is no longer free, but hindered. The penetrants have to go through longer diffusion pathways around the filled CuO particles and the diffusivities of the penetrants decrease consequently.<sup>21</sup> It can be seen that with increasing CuO loading, enrichment factor (the maximum error below 5%) first increased and then decreased. When the CuO loading reached 8 wt %, enrichment factor increased again. Two contributing factors should be responsible for the results. One is the swelling of the membranes and the other is that there is a strong



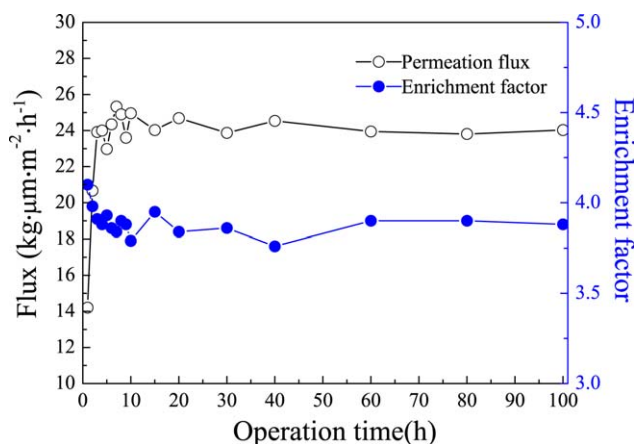
**Figure 7.** The effect of CuO content on permeation flux and sulfur-enrichment factor. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$\pi$ -complexation between  $\text{Cu}^{2+}$  and thiophene by C=C double bonds. The  $\pi$ -complexation between  $\text{Cu}^{2+}$  and C=C double bonds is a reversible reaction, so the CuO particles can continually adsorb and desorb thiophene molecules by means of sulfur content gradient between the feed side and the permeate side. This is probably because swelling and  $\pi$ -complexation have opposite effects on the enrichment factor. Therefore, the enrichment factor would be the combined result from the swelling and  $\pi$ -complexation. The sulfur-enrichment factor would first increase because of the enhanced sorption capacity of thiophene and then decrease when the diffusion hindrance becomes dominant and the swelling weakens the difference of diffusivity between hydrocarbon and thiophene with increasing CuO loading in the membranes. The swelling of membrane was constrained seriously leading to a constant diffusivity with increasing CuO loading progressively. In this case, increasing CuO loading only enhanced sorption capacity of sulfur compound without causing difference in diffusivity between hydrocarbon and thiophene, so the  $\pi$ -complexation played an important role and the enrichment factor increased again. The results were similar with the conclusion for  $\text{Ag}_2\text{O}/\text{PDMS}$  membranes.<sup>21</sup>

The effect of CuO loading on enrichment factor under different feed temperatures was investigated, as shown in Figure 7(b). With increasing feed temperature, the effect of CuO loading on enrichment factor weakened. This is because the time for achieving swelling equilibrium is shortened by increasing feed temperature, and the degree of swelling is more closely related to the feed temperature than CuO loading.

Considering the practical application, the stability of membranes is an important aspect. In this study, PV was conducted for 100 h to test the stability of the membrane with 4 wt % CuO loading, as shown in Figure 8. The PV of the membrane reached steady within 5 h, and changed slightly afterwards.

**Effects of Feed Temperature.** Figure 9 shows the effect of feed temperature on permeation flux and enrichment factor. The permeation flux increased with increasing feed temperature [Figure 9(a)]. This is because the mobility of the permeant molecules increased with increasing feed temperature. Furthermore, with increasing feed temperature, the flexibility of



**Figure 8.** The effect of operation time on PV performance (membrane with 4 wt % CuO loading). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

polymer chains increased leading to an enlargement in available free volume of the polymer matrix for diffusion. All these factors lead to an increase in the permeation flux. It can be seen that enrichment factor decreased with increasing feed temperature. This is because a larger available free volume weakened the difference of sorption and diffusion between sulfur and hydrocarbon, resulting in a decrease in sulfur-enrichment factor.

The effect of feed temperature on permeation flux was investigated, as shown in Figure 9(b). The permeation flux increased with increasing feed temperature. At the same temperature, the permeation flux reduced with increasing CuO loading. In addition, the decrease in permeation flux with increasing CuO loading is greater at higher temperatures than at lower temperatures. This is because the swelling of the membrane is higher at higher temperatures. As a result, the tortuosity effect will be enhanced with increasing CuO loading.

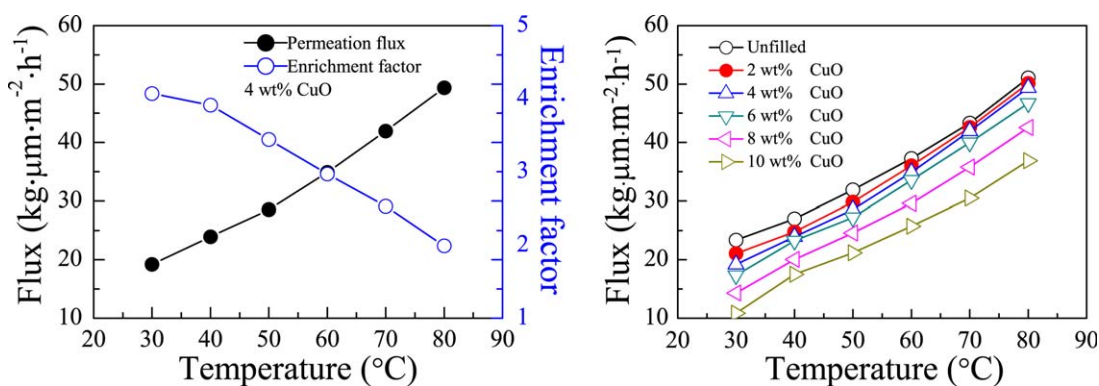
**Effects of Sulfur Content.** The effect of feed sulfur content on permeation flux and enrichment factor was also investigated. Normally, with increasing feed sulfur content would result in a sharp increase in permeation flux and a sharp decrease in sulfur-enrichment factor because of the extensive swelling of the membrane.<sup>7,16</sup> However, sulfur content exhibited a slight influ-

ence on PV performance above  $1500 \mu\text{g}\cdot\text{g}^{-1}$  sulfur content (Figure 10). It is because the incorporation of CuO depresses the swelling of the hybrid membranes. When the sulfur content has come to  $1500 \mu\text{g}\cdot\text{g}^{-1}$ , the swelling of the membrane reached equilibrium. In this case, the sulfur concentration on the membrane surface was saturated leading to a steady PV performance.

**Effects of Various Hydrocarbons.** FCC gasoline is a rather complex mixture consisting of hundreds of compounds. In this work, various hydrocarbons such as alkane of different number of carbons, cycloalkanes, and aromatics were investigated. The PV performances of binary mixtures of various hydrocarbons with  $1500 \mu\text{g}\cdot\text{g}^{-1}$  sulfur content at  $40^\circ\text{C}$  are listed in Table I.

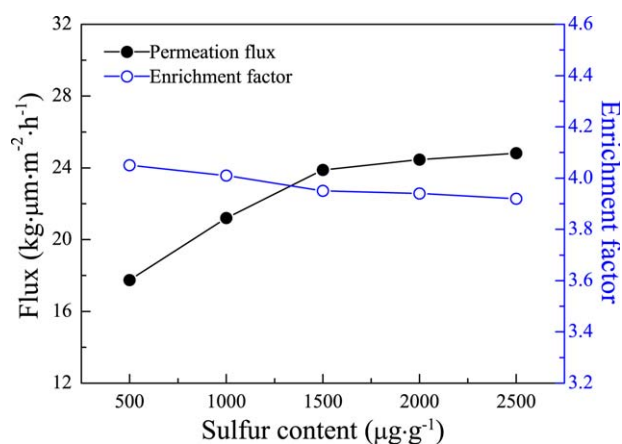
It can be seen that the permeation flux for alkane/thiophene mixture decreased and the sulfur-enrichment increased with increasing carbon number in the alkanes. According to the solution–diffusion mechanism, the difference in solubility and diffusivity of individual components is responsible for PV separation performance. Numerous researchers have reported that an increase in penetrant size will lead to a decrease in diffusivity.<sup>8,17</sup> However, larger permeant molecules tend to have a larger solubility because of the higher degree of plasticization of the polymer.<sup>23</sup> From the experimental results, we can conclude that with increasing alkane chain length, the effect caused by increased solubility is offset by the decreased diffusivity. As a result, the permeation flux decreased with increasing carbon number. Considering the sulfur compound being thiophene, so the hydrocarbon was mainly responsible for the decreased flux, as a result, the enrichment factor increased.

When cyclohexane/thiophene binary mixture was used as feed, the smallest permeation flux and largest enrichment factor were achieved. The reason maybe that cyclohexane has larger size, which is unfavorable to diffusion leading to smaller permeation flux, and the fixed sulfur compound and sulfur content were necessarily led to a larger enrichment factor. However, for toluene/thiophene binary mixture, the largest permeation flux and smallest enrichment factor were observed. This is probably that toluene is a typical aromatic component which can stimulate the swelling of a polymer membrane with which it is in contact.<sup>24</sup> The swelling can result in an enlargement of pore space in a membrane and an increase in the diffusion of feed



**Figure 9.** The effect of temperature on PV performance. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 10.** The effect of sulfur content on permeation flux and sulfur-enrichment factor (membrane with 4 wt % CuO loading at 40°C). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

molecules. This finally results in an increase in permeation flux and a decrease in enrichment factor.

**Performance Comparison of the Hybrid Membrane and Other Reported Membrane Materials.** It is interesting to compare the PV performance of the hybrid membrane with the other membranes reported in the literature. The performances of some pervaporative desulfurization studies are listed in Table II.

From Table II, PUU membrane showed higher sulfur-enrichment factor than other membranes reported, however, the permeation flux below  $0.1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  made it unsuitable for practical application. On the other hand, compared to other membranes, PI-*block*-PEG membrane had higher flux but small enrichment factor. From the permeation flux and enrichment factor measured under various feed and operating conditions, it is clearly hard to obtain the optimal PV performance from the membrane shown in Table II. This is because operational temperature and feed sulfur content are different. PV performance in this work has improved in terms of lower feed temperature of 40°C. Clearly filled membranes have excellent PV performance.

## CONCLUSIONS

CuO/AMPSF hybrid membranes were successfully prepared for PV desulfurization. Characterization and PV of the membranes under various conditions were conducted. FTIR characterization verifies successful aminomethylation. SEM characterization indicates that CuO particles are uniformly dispersed into the polymeric phase and well compatible with the AMPSF matrix. XRD characterization verifies the existence of CuO particles and shows the crystal structure of the hybrid membrane with various CuO loadings. High sulfur-enrichment factor (3.9) and the permeation flux ( $23.9 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) can be achieved using the hybrid membranes. This is because of the  $\pi$ -complexation

**Table I.** PV Performances of Various Hydrocarbons Feed with  $1500 \mu\text{g}\cdot\text{g}^{-1}$  Sulfur Content at 40°C

No.	1	2	3	4	5
Model feed component	<i>n</i> -Heptane/thiophene	<i>n</i> -Hexane/thiophene	<i>n</i> -Octane/thiophene	Cyclohexane/thiophene	Toluene/thiophene
Permeation flux ( $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )	23.9	26.6	19.0	15.8	32.4
Sulfur-enrichment factor	3.9	3.4	5.9	6.4	2.7

**Table II.** The PV Performances of Some Reported Membrane Materials

No.	Membranes	Feed/temperature (°C)	Sulfur content ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Flux ( $\text{kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )	Flux ( $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )	<i>E</i>	Reference
1	AMPSF	<i>n</i> -Heptane/thiophene (40)	1500	26.95	1.35	3.11	This work
2	CuO-AMPSF	<i>n</i> -Heptane/thiophene (40)	1500	23.92	1.20	3.91	This work
3	PUU	Refinery naphtha (70)	439		0.085	5.12	[18]
4	PDMS	<i>n</i> -Octane/thiophene (30)	3700	15.6		4.4	[6]
5	Ag <sub>2</sub> O-PDMS	<i>n</i> -Octane/thiophene (50)	2630	42.75		4.46	[21]
6	PEG	FCC gasoline (110)	1227		1.63	3.05	[5]
7	CuY-PEG	FCC gasoline (110)	1190		3.19	2.95	[2]
8	PI	<i>n</i> -Heptane/thiophene (77)	1028		1.68	3.12	[17]
9	PI- <i>b</i> -PEG	<i>n</i> -Heptane/thiophene (60)	1000	283		1.7	[25]

Ag<sub>2</sub>O-PDMS, Ag<sub>2</sub>O-filled polydimethyl siloxane; AMPSF, aminomethylated polysulfone; CuO-AMPSF, CuO-filled aminomethylated polysulfone; CuY-PEG, CuY zeolite-filled polyethylene glycol; PDMS, polydimethyl siloxane; PEG, polyethylene glycol; PI, polyimide; PI-*b*-PEG, polyimide-*block*-polyethylene glycol; PUU, polyurea/urethane.

between  $\text{Cu}^+$  and  $\text{C}=\text{C}$ . The performance within 100 h indicates a good stability of the membranes. The effects of operating conditions and various hydrocarbons on PV performance were also investigated, and the results were similar to those found in the literature. In brief, the novel hybrid membranes showed better results for the sulfur removal. The related investigations will provide helpful suggestions for the newly emerging membrane desulfurization technology.

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