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Study of thermal annealing on Matrimid® fiber performance in pervaporation of acetic acid and water mixtures

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Abstract

Unlike the case for low-sorbing gas molecules such as N_2 and O_2, Matrimid® hollow fibers swell significantly in acetic acid (HAc) and water mixtures. Acetic acid was found to plasticize the polymer and facilitate the passage of the 'slow' molecule, acetic acid, while not affecting the 'fast' molecule, water, as significantly. The membrane selectivity of water over HAc inevitably decreased with increasing HAc content in the feed for the standard membrane. Sub-T_g (glass transition temperature) thermal annealing was used to stabilize large bore size defect-free Matrimid® hollow fibers by suppressing the HAc-induced plasticization. The resulting membrane selectivity was increased up to 95 using a 520 μm outer diameter/325 μm inner diameter and 20 cm long defect-free annealed fiber with acceptable water flux (1.6 kg/m^2 h) for 20 wt% HAc concentration feed streams at 101.5 °C. Micro-fluorescence spectra provide strong support for the notion that thermal annealing can reduce the free volume and promote the formation of charge transfer complexes. As a consequence, the improved rigidity of the polymer chains increases the polymer discrimination of shape and size for penetrants, although no chemical reaction occurs with thermal annealing.

Keywords: Plasticization; Thermal annealing; Free volume

1. Introduction

Pervaporation separations are attractive due to their low energy and capital costs, but lower selectivity with aggressive organic solvents that can cause severe plasticization, limits widespread adoption of this membrane technology. Our previous work [1,2] illustrates this issue with regard to HAc interactions with Matrimid® hollow fibers. Although research is on-going for developing new polymers to improve the membrane performance, an alternative route to enhancing the selectivity of the currently available membranes can be achieved by a thermal annealing method.

The Matrimid® hollow fibers used in this work were spun by the 'dry-jet, wet-quench' spinning method [3]. Due to rapid vitrification in the air gap, the formed outer selective skin layer of a hollow fiber is in a thermodynamic non-equilibrium state and has 'excess' un-relaxed free volume. Once this fiber experiences aggressive solvents like acetic acid, the polymer chains can be swelled and dilated, resulting in a low membrane selectivity of water over HAc.

A membrane can be thermally annealed at an elevated temperature to improve its performance. Kawakami et al. [4] annealed 6FDA-m-DDS dense film membranes at 150, 200, and 250 °C, and found that the packing density and the fluorescence intensity of this polyimide increased sharply with the increased curing temperature. An increase in inter-molecular and/or intra-molecular interactions by a charge transfer complex was proposed. Krol et al. [5] investigated the gas separation of propane/propylene using the polyimide Matrimid® 5218 with different heat treatment environments. They observed that the densification of the fiber morphology occurred due to heat treatment and mild heat treatment appeared to be effective in suppressing the propylene-induced plasticization. Barsema et al. [6] examined the intermediate structures between annealing and carbonization when exposing the polyimide membranes at different heating temperatures between 300 and 525 °C. Gas permeation measurements with He, N_2, O_2, CO_2, and C_3H_6 indicated that the structure became more dense at temperatures below the T_g of the polymer, while the formation of charge transfer complexes took place above the T_g. When compared with the untreated membranes, all heat treated membranes showed good resistance to plasticization by C_3H_6. Bos et al. [7] stabilized the Matrimid membranes by heat

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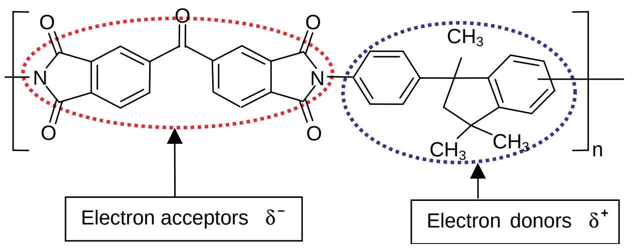

Fig. 1. Chemical structure of Matrimid® showing electron acceptive and donative groups [12–14].

treatment at 350 °C to suppress the CO_2-induced plasticization. Chemical crosslinking was believed to have occurred since the heat treated film did not dissolve in the original casting solvent any more. Wind et al. [8–10] found that both thermal annealing and covalent cross-linking of the polyimide films could reduce swelling to prevent large increases in the CO_2 diffusion coefficient at high feed pressures. The CO_2 permeability and polymer free volume strongly depended on the annealing temperature. Hibshman et al. [11] investigated the annealing effects on the polyimide–organosilicate hybrid membranes. The transport properties of these hybrid membranes were evaluated using pure gases such as He, N_2, O_2, CO_2, and CH_4. However, thermal annealing has not been investigated in depth in liquid separation to suppress the swelling effects from aggressive organic solvents in contrast to gas separation.

In this work, Matrimid® hollow fibers were treated at high temperatures but still below T_g (305–315 °C) to improve the membrane performance. The chemical structure of Matrimid® is shown in Fig. 1. It contains alternating electron donor and electron acceptor, which correspond to the phenylene group and aromatic imide group, respectively [12–14]. If enough mobility can be obtained through heat treatment, the aromatic imide group and phenylene group in different polymer chains will approach each other closely enough to allow π-electron interaction, which leads to the formation of charge transfer complexes. This behavior increases the packing density of the polymer chains and decreases the free volume in the outer selective skin layer. Thus, mobility of the polymer chains is dramatically restricted so that the rigid configuration formed among the adjacent polymer chains provides high size and shape discrimination between penetrants and suppresses the penetrants-induced plasticization.

2. Background

In a hollow fiber-based pervaporation process, the permeance of component i $(\mathcal{P}/\ell)_{\mathrm{i}}$ is defined as the flux (Q_{i}) normalized by the partial pressure difference (Δp_{i}) between the upstream and downstream membrane faces, viz.

$$\left(\frac{\mathcal{P}}{\ell}\right)_{\mathrm{i}} = \frac{Q_{\mathrm{i}}}{\Delta p_{\mathrm{i}}} \tag{1}$$

where $\mathcal{P}$ represents the permeability of component i and ℓ represents the thickness of the outer separation layer. The partial pressure difference is given by

$$\Delta p_{\mathrm{i}} = y'_{\mathrm{i}} p_{\mathrm{feed}} - y_{\mathrm{i}} p_{\mathrm{permeate}} \tag{2}$$

where p_{feed} and p_{permeate} represent the vapor pressures on the feed and permeate sides, respectively. y'_{i} and y_{i} are the respective mole fraction of component i on the feed and permeate sides.

Unlike gas separation, the partial pressure of component i in the feed vapor has to be correlated with the feed liquid by the vapor–liquid equilibrium equation as below:

$$y'_{\mathrm{i}} p_{\mathrm{feed}} = \gamma_{\mathrm{i}} x_{\mathrm{i}} p_{\mathrm{i}}^{*} \tag{3}$$

where γ_{i} is the activity coefficient for component i at the operating temperature, x_{i} is the mole fraction of component i in the feed liquid, and p_{i}^{*} is the saturated pressure of component i at the operating temperature.

The effective pervaporation separation factor, $\beta_{\mathrm{i/j}}$, is defined as the ratio of components in the permeate vapor over the ratio of components in the feed liquid as follows:

$$\beta_{\mathrm{i/j}} = \frac{y_{\mathrm{i}}/y_{\mathrm{j}}}{x_{\mathrm{i}}/x_{\mathrm{j}}} \tag{4}$$

where x_{i} and x_{j} are the mass or mole fractions of components i and j in the feed liquid, and y_{i} and y_{j} are the mass or mole fractions of components i and j in the permeate vapor.

As the ratio of the mass or mole fractions for components i and j on the permeate side is equal to the ratio of the corresponding flux across the membrane wall, the effective separation factor $\beta_{\mathrm{i/j}}$ can be further derived as follows:

$$\begin{aligned}\beta_{\mathrm{i/j}} &= \frac{y_{\mathrm{i}}/y_{\mathrm{j}}}{x_{\mathrm{i}}/x_{\mathrm{j}}} = \frac{(\mathcal{P}/\ell)_{\mathrm{i}}\Delta p_{\mathrm{i}}}{(\mathcal{P}/\ell)_{\mathrm{j}}\Delta p_{\mathrm{j}}(x_{\mathrm{i}}/x_{\mathrm{j}})} \\ &= \frac{(\mathcal{P}/\ell)_{\mathrm{i}}\left(y'_{\mathrm{i}}p_{\mathrm{feed}} - y_{\mathrm{i}}p_{\mathrm{permeate}}\right)}{(\mathcal{P}/\ell)_{\mathrm{j}}\left(y'_{\mathrm{j}}p_{\mathrm{feed}} - y_{\mathrm{j}}p_{\mathrm{permeate}}\right)(x_{\mathrm{i}}/x_{\mathrm{j}})}\end{aligned} \tag{5}$$

Ideally p_{permeate} can be assumed zero under vacuum permeation conditions if the bore pressure change is negligible [2]; thus, Eq. (5) can be expressed with a convenient form, viz.,

$$\begin{aligned}\beta_{\mathrm{i/j}} &= \frac{(\mathcal{P}/\ell)_{\mathrm{i}}(y'_{\mathrm{i}}P_{\mathrm{feed}})}{(\mathcal{P}/\ell)_{\mathrm{j}}(y'_{\mathrm{j}}P_{\mathrm{feed}})(x_{\mathrm{i}}/x_{\mathrm{j}})} = \frac{(\mathcal{P}/\ell)_{\mathrm{i}}(\gamma_{\mathrm{i}}x_{\mathrm{i}}p_{\mathrm{i}}^{*})}{(\mathcal{P}/\ell)_{\mathrm{j}}(\gamma_{\mathrm{j}}x_{\mathrm{j}}p_{\mathrm{j}}^{*})(x_{\mathrm{i}}/x_{\mathrm{j}})} \\ &= \underbrace{\left[\frac{(\mathcal{P}/\ell)_{\mathrm{i}}}{(\mathcal{P}/\ell)_{\mathrm{j}}}\right]}_{\alpha_{\mathrm{mem}}}\underbrace{\left[\frac{\gamma_{\mathrm{i}}p_{\mathrm{i}}^{*}}{\gamma_{\mathrm{j}}p_{\mathrm{j}}^{*}}\right]}_{\alpha_{\mathrm{evap}}}\end{aligned} \tag{6}$$

The symbols of α_{evap} and α_{mem} represent the evaporation factor and membrane selectivity, respectively. The value of α_{evap} focuses on the operating condition, while α_{mem} characterizes the identity of membrane materials. The effective separation factor with negligible downstream pressure can be simplified as

$$\beta_{\mathrm{i/j}} = \alpha_{\mathrm{mem}}\alpha_{\mathrm{evap}} \tag{7}$$

Although the overall separation factor is complicated, the membrane selectivity α_{mem} in pervaporation is actually the same as that in gas separation [15], i.e.

$$\alpha_{\mathrm{mem}} = \frac{(\mathcal{P}/\ell)_{\mathrm{i}}}{(\mathcal{P}/\ell)_{\mathrm{j}}} \tag{8}$$

3. Experiments

3.1. Pervaporation tests

Fabrication of a single-fiber pervaporation module, pervaporation setup and procedures for acetic acid and water mixtures, and permeate analysis were described in our previous work [1,2].

3.2. Defect-free hollow fiber spinning

Non-solvent induced phase separation is used to spin large bore size defect-free asymmetric Matrimid® hollow fiber membranes. The detailed spinning approach can be found in the literature [3]. The cartoon picture of an asymmetric hollow fiber is illustrated in Fig. 2, and Table 1 shows the spinning conditions and pure gas permeation results for the hollow fibers used in this work.

3.3. Thermal annealing procedures

A temperature-controlled vacuum oven is used to conduct heat treatment of the fibers. First, the oven is heated at the required temperature for 3 h and kept under vacuum until the environment reaches the steady state. The hollow fibers are then placed into the oven immediately. After the desired time period for heat treatment, the fibers are taken out of the oven and placed on a Kimwipe® at room temperature for 1 h. The pervaporation module can then be assembled using these thermally annealed fibers for pervaporation tests. Due to limitations in our experimental setup, the highest annealing temperature can not exceed 220 °C.

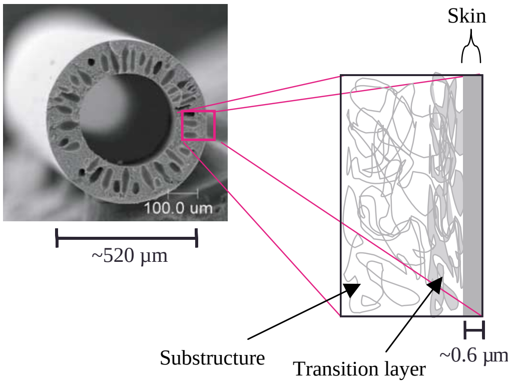

Fig. 2. Cartoon picture of asymmetric hollow fiber membranes.

Table 1
Spinning conditions and pure gas permeation results for the hollow fibers used in this work

Spinning conditions	
Air gap (cm)	12
Take-up rate (m/min)	13
Dope extrusion rate (ml/h)	180
Bore fluid extrusion rate (ml/h)	100
Pure gas permeation results	
Outer diameter (µm)	520
Inner diameter (µm)	325
O_2 (GPU)	3.37
He (GPU)	44
Selectivity	6.9
Selectivity	90

3.4. Spectroscopy technology

Spectroscopy uses the interaction of energy with a sample to perform an analysis. A spectroscopy spectrum contains considerable information such as atomic and molecular energy levels, molecular geometries, chemical bonds, interactions of molecules, and related processes. FTIR (Bruker Tensor 27 with TGA–IR) and ^{1}H NMR (Varian 300 MHZ spectrometer) are used to probe the membrane structure in this work due to their rapid and efficient features.

Jin et al. [12] investigated the fluorescence spectrum of a benzophenone-type aromatic polyimide, i.e. PI(BTDA/DPM), as shown in Fig. 3. The wavelength of 300 nm was used to excite the PI film and fluorescence was observed at 500 nm. Compared to the model compound of BTDA, in which the phosphorescence peaks appeared at 440 and 480 nm, the authors claimed that the 500 nm fluorescence peak was attributed to the formation of charge transfer complexes. The authors also proposed that both intra- and inter-molecular charge transfer complexes existed in this benzophenone-type polyimide with aromatic diamine based upon UV absorption spectra.

Fluorescence technology is used in this project to investigate morphology changes of the polymer chains and formation of charge transfer complexes for virgin and annealed fibers because of its sensitivity to the micro-environment. The model of micro-fluorescence used to analyze fiber samples is SEE #1000 with 50× objective.

4. Results and discussion

A model 20 wt% HAc/H_2O mixture was used as a feed solution for pervaporation tests at 101.5 °C unless it was specially mentioned. The outer diameter and length of sample fibers used in pervaporation were 520 µm and 20 cm, respectively. The effects of annealing variables on the fiber performance were investigated.

4.1. Heating temperature

Based upon hollow fiber spinning procedures [3], the nascent fibers must be placed into a vacuum oven at 110 °C for 1 h to remove the residual solvents. The thermal treatment temperature for the fibers should be higher than 110 °C. The temperatures 150, 180, and 220 °C were selected to perform heat treatment in vacuum for 1 h. Once these fibers were thermally annealed, the pervaporation modules were prepared

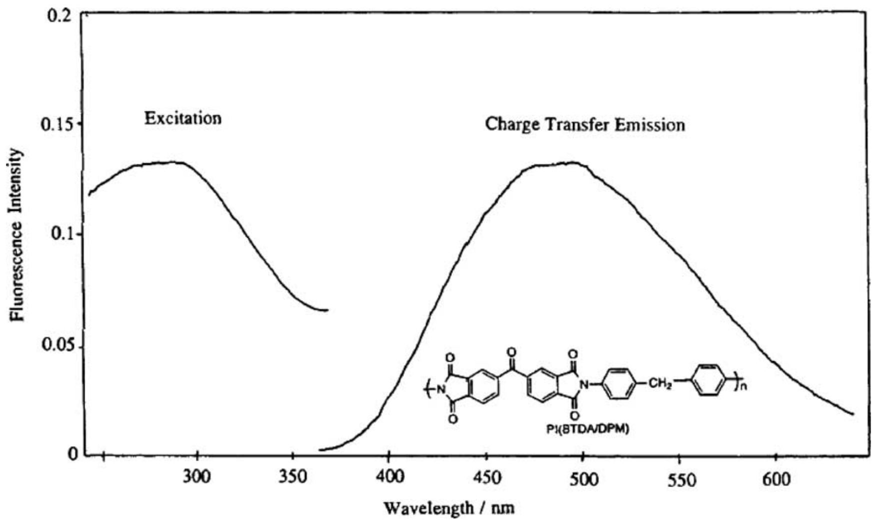

Fig. 3. Fluorescence spectrum of a benzophenone-type aromatic polyimide PI (BTDA/DPM) film [12].

using these fibers with different annealing temperatures. In addition, a new module was made of a virgin fiber without any further heat treatment as a reference. Pervaporation tests were conducted at 101.5 °C using 20% HAc concentration feeds. Figs. 4 and 5 show the permeance and selectivity of these four modules, respectively.

The fiber with heat treatment at 220 °C exhibits a significant enhancement in the membrane selectivity. The decreased free volume and altered free volume distribution due to heat treatment hinder the HAc transport much more dramatically than water. Therefore, the membrane selectivity is improved while the permeances of both penetrants are reduced. Meanwhile, this heating temperature enables the polymer chains to obtain enough mobility to allow charge transfer complexes being formed. This improves the rigidity of the polymer chains and suppresses the swelling effects from acetic acid. The fiber can maintain very good membrane selectivity ($\alpha \sim 95$) and be tested for up to 9 days. The fibers that were heated at 150 and 180 °C behave similar to the virgin fiber. The membrane selectivities are quite close in these three modules. This indicates that heat treatment at 150 and 180 °C does not provide enough energy to enhance noticeable shape and size discrimination ability of the polymer. Heating temperature must be optimized high enough but below T_g to keep the polymer in the glassy state. Table 2 shows the comparison of water flux, HAc flux, and membrane selectivity between a virgin hollow fiber and an annealed hollow fiber.

4.2. Spectroscopy results for annealed hollow fibers

Since a significant increase of the membrane selectivity has been observed with annealed fibers, it is desirable to investigate whether chemical reaction occurs with thermal annealing. It was observed that these annealed fibers can be dissolved in solvents such as NMP and CH_2Cl_2 easily. The FTIR spectrum of Matrimid® obtained at room temperature is given in Fig. 6 and corresponds well with the Matrimid spectra obtained by other investigators [16,17]. The spectra of the untreated and treated Matrimid® fibers are almost identical. This suggests that heat treatment in this work is not intense enough to cause any chemical crosslinking, while still sufficient to improve the membrane selectivity.

The ^{1}H NMR measurement was conducted on the Matrimid® fibers with and without heat treatment. Clearly all the spectra are almost identical regardless of thermal annealing, as shown in Fig. 7. This NMR study further validates that no chemical reaction occurs with thermal annealing.

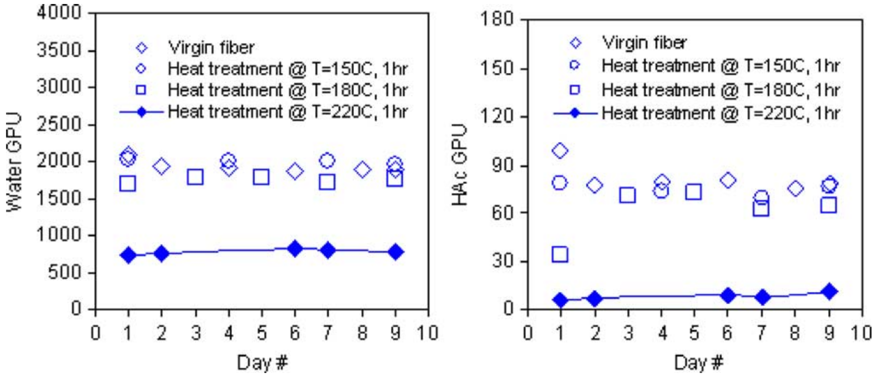

Fig. 4. Effects of heating temperature on water and acetic acid permeances.

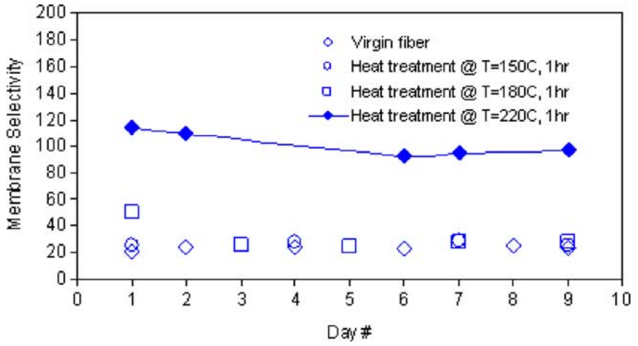

Fig. 5. Effects of heating temperature on the membrane selectivity α_{mem}.

Table 2
Comparison of separation results between a virgin hollow fiber and an annealed hollow fiber [1], outer diameter: 520 μm, bore size: 325 μm

Feed: 20 wt% HAc/H_2O mixture	Hollow fiber without heat treatment	Hollow fiber with heat treatment at $T=220$ °C, 1 h
Water flux (kg/m^2 h)	4.98	1.65
HAc flux (kg/m^2 h)	0.036	0.0033
Selectivity $\alpha_{H_2O/HAc}$	25	95

As stated above, fluorescence behavior is sensitive to the micro-environmental change with the molecular interaction [18] and is reliable and convenient to study the formation of charge transfer complexes and densification of polymer chains [12]. All the fibers for fluorescence measurements were prepared with the same methodology and evaluated using identical instrumental parameters so that the comparison is meaningful. The variation is only the 'annealing' temperature for each fiber. Fig. 8 shows micro-fluorescence emission spectra for the fibers cured at different temperatures.

When excited at the wavelength of 365 nm, the fluorescence emission spectra bands were observed at about 548 nm for all of the fibers. The emission intensity increased with an increase in the heating temperature. This supports the fact that charge transfer complexes are most likely formed in the Matrimid® fiber. In contrast to the polymer of PI(BTDA/DPM) in Jin's paper (Fig. 3), the three alkyl groups in Matrimid® promote charge transfer complexes more stable and stay at the lower energy level, so it is not surprising that the wavelength of Matrimid® fluorescence emission spectrum is longer than that of PI(BTDA/DPM). Of course, absorption spectroscopy could be a more valuable tool to validate the formation of charge transfer complexes, whereas scatting effects might be a perturbing factor on the micro-fluorescence measurement. However, it is difficult to obtain the absorption spectra in this work due to the limitation of the fiber size.

Experimentally, it is not easy to unambiguously distinguish between intra-molecular charge transfer complexes and inter-molecular charge transfer complexes in the Matrimid® fiber, since both are concurrently formed. However, the increased fluorescence intensity is an apparent indication that inter-molecular interactions between parallel planar structures become dominant and the inter-molecular packing density is increased with thermal annealing [4]. In other words, thermal annealing appears to help the polymer chains relax and rearrange between adjacent coplanar molecules, which decreases the chain interstitial space accordingly and produces strong inter-molecular charge transfer complexes. Thus the fluorescence emission is significantly increased with an increase in the thermal annealing temperature. The configuration of aromatic polyimide benzene rings and formation of charge transfer complexes in the Matrimid® fibers presumably suppress the mobility of polymer chains and provide high size and shape discrimination between penetrants. Fig. 9 shows the hypothetical electron acceptor and donor, and possible intra- and inter- charge transfer complexes formed for Matrimid®.

Sub-T_g transition temperatures in polyimides have been discussed by Hsiao et al. [19] based upon dynamic mechanical analysis (DMA). The β relaxation occurred in a wide range up to 200 °C, depending on the specific chemical structure of each polyimide. The glass transition temperature ($T_g > 300$ °C), which corresponded to the α relaxation process, was higher

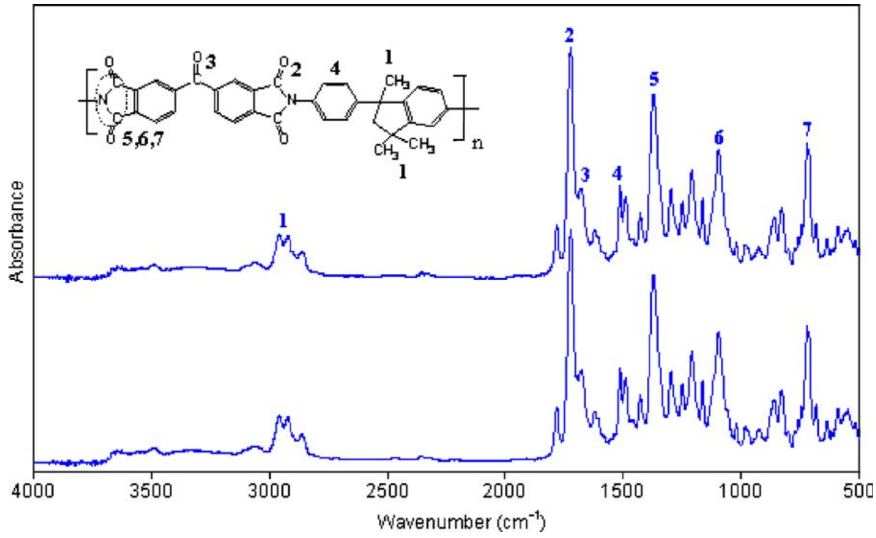

Fig. 6. Chemical structure of Matrimid® and FTIR absorption spectra for virgin and annealed fibers at room temperature.

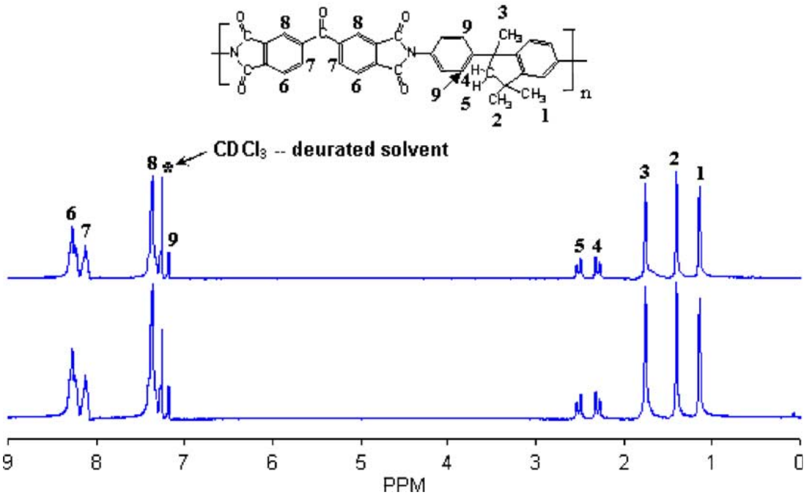

Fig. 7. Chemical structure of Matrimid® and ^{1}H NMR absorption spectra for virgin and annealed fibers at room temperature.

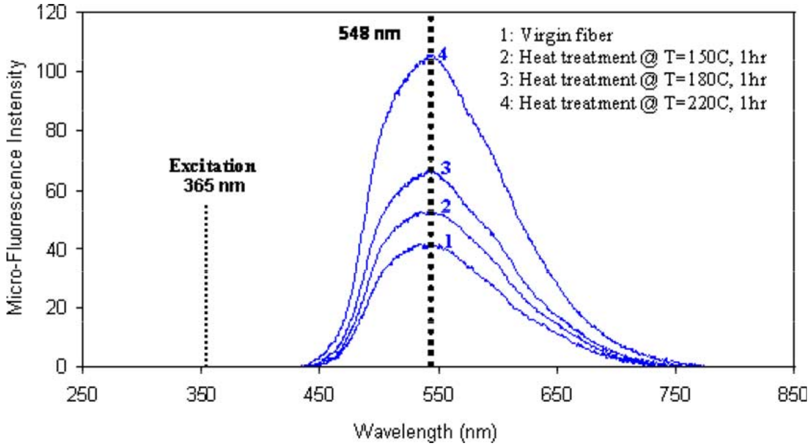

Fig. 8. Variations of micro-fluorescence emission spectra for the fibers cured at different temperatures.

than the β transition temperature. The authors claimed that sub-T_g relaxation process at the β transition temperature was related to the local or segmental motions in polymer chains, which was quite close to the explanation in our paper. Their DMA results, although the chemical structure of Matrimid® is not same as other polyimides, support the hypothesis that the β transition temperature of around 220 °C may exist in Matrimid®; however, this is beyond the scope of the current study to pursue.

4.3. Heating time

In addition to the heating temperature, the duration of heat treatment is another important variable that is worth investigating. Long time heat treatment is not practical; conversely the formation of charge transfer complexes might fail if the annealing time is too short. One, 5, and 12 h were selected to 'anneal' the fibers at 220 °C in vacuum. Another module made of a virgin fiber was used as a reference. The micro-fluorescence emission spectra are shown in Fig. 10.

As excited at the wavelength of 365 nm, the fluorescence emission peaks were observed at about 548 nm for all of the fibers. The emission intensity increased dramatically with annealed fibers. However, only small enhancement of emission intensity was observed for the longer annealing times. This indicates that 1 h thermal annealing is enough to form stable charge transfer complexes in the outer skin layer of a hollow

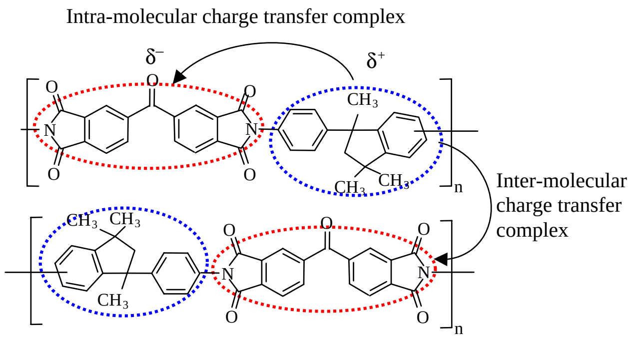

Fig. 9. Possible intra- and inter- molecular charge transfer complexes for Matrimid®.

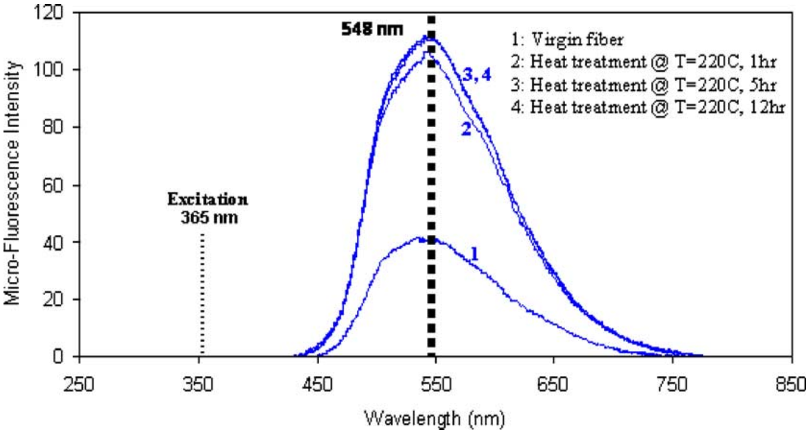

Fig. 10. Variations of micro-fluorescence emission spectra for the fibers cured at different times.

fiber, which results in the higher selectivity towards larger molecule transport. Further improvement of membrane selectivity appears to be unlikely, even with long time annealing. The permeation results of virgin and annealed fibers for different annealing times are illustrated in Fig. 11.

Both water permeance and membrane selectivity decrease when annealing time increases to 5 and 12 h in contrast to the fiber with 1 h heat treatment. The morphology change of polymer chains in the outer skin layer of hollow fibers should be similar for these three annealing times based upon micro-fluorescence spectra. However, the substrate layer and macrovoids underneath the outer skin of a hollow fiber might collapse because of long time curing. This causes the densification of the substrate and influences transport properties of the ‘fast’ gas molecule more significantly than for the less permeable component; therefore two separate effects caused by thermal annealing alter water and HAc transport through the membrane. Sufficient annealing time is helpful to form charge transfer complexes and decrease the free volume in the outer selective layer, and this can increase the membrane selectivity and decrease the water flux. On the other hand, additional substrate resistance arising from over-annealing can affect water much more than acetic acid, resulting in both decreased permeance and selectivity. This argument can be supported by pure gas permeation tests. The fibers with the same heat treatment procedure were tested using N_2, O_2, and He at 35 °C, as shown in Table 3.

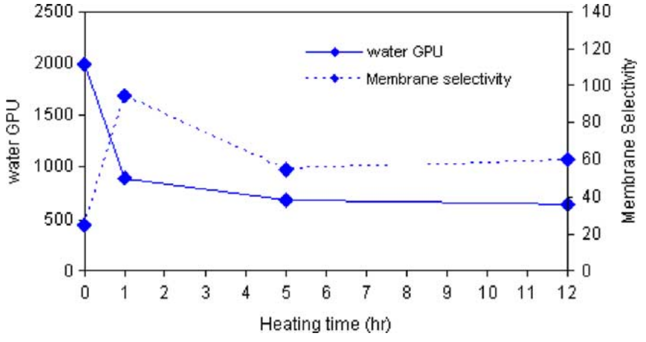

Fig. 11. Effects of annealing times on water permeance and membrane selectivity.

The annealed fibers demonstrate the lower permeance because of the free volume loss and formation of charge transfer complexes in the outer selective layer. The passage of the ‘fast’ gases, such as O_2 and He, through the 5 or 12 h-annealed fiber is affected much more than that of the 1 h-annealed fiber. The additional substrate resistance arising from the longer thermal treatment time is believed to hinder fast gases more significantly and thereby lower the selectivity of and α_{O_2/N_2} and α_{He/N_2}.

The membrane selectivities of HAc/H_2O mixtures are still improved to some degree with over-heated fibers, in contrast to the selectivity of 30 for a virgin fiber. Nevertheless, the heat treatment time has to be optimized to minimize the substrate resistance and maximize the intensity of charge transfer complexes in the selective layer. One-hour curing time appears sufficient, since it drives the membrane selectivity up to 95 for a model 20 wt% HAc/H_2O solution feed.

4.4. Heating environment

Vacuum equipment is usually involved in the annealing step in most open literatures [8–11]. If vacuum can be avoided in heat treatment of hollow fibers, while maintaining similar fiber performance, annealing will be very attractive for industrial application. In this section, the hollow fibers were thermally cured in air and vacuum at 220 °C for 1 h separately. Thereafter, two modules were prepared using air-annealed and vacuum-annealed fibers for pervaporation tests with

Table 3
Pure gas permeation results for hollow fibers with different annealing times

Fibers Identification (OD ~ 520 μm) (length ~ 20 cm)	O_2 (GPU)	He (GPU)	Selectivity $\alpha O_2/N_2$	Selectivity $\alpha H_e/N_2$
Virgin fiber	3.37	44	6.9	90
Thermally annealed fiber at 220 °C, 1 h	1.67	23	6.4	88
Thermally annealed fiber at 220 °C, 5 h	1.15	14	5.5	62
Thermally annealed fiber at 220 °C, 12 h	1.14	13	5.0	59

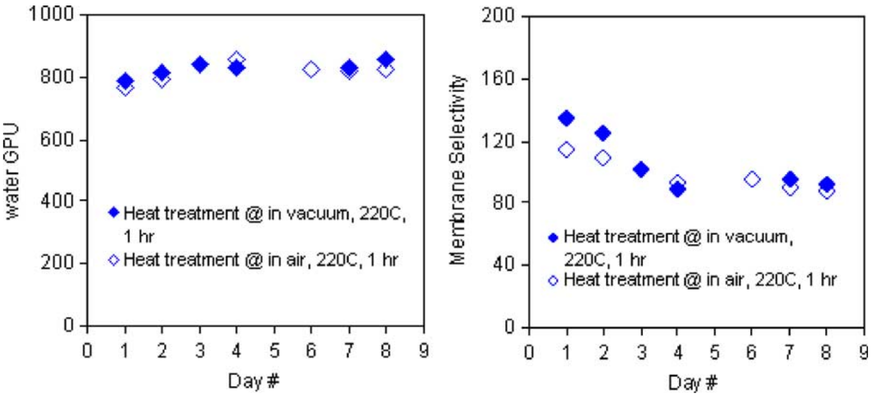

Fig. 12. Effects of heating environments on water permeance and membrane selectivity.

20 wt% HAc/H_2O mixture feeds. Fig. 12 shows the separation results.

As it can be seen, the water permeance and membrane selectivity are very close for both air and vacuum annealed fibers. This indicates O_2 (in air) does not affect the rearrangement of polymer chains and modification of interstitial chain space. Some differences exist for the membrane selectivity between air-annealed and vacuum-annealed fibers in the initial two days, but still in an acceptable error range. It should be noted that even a small change of the free volume distribution can cause different separation results.

The air- and vacuum- annealed fibers can be easily dissolved in solvents such as NMP and CH_2Cl_2. The same FTIR spectra as Fig. 6 were obtained for virgin, air annealed, and vacuum annealed fibers. This indicates that no chemical reaction occurs with air or vacuum heating. Heat treatment in this work is not intense enough to cause any chemical crosslinking, but is still sufficient to improve the fiber performance. In addition, heat treatment can be completed in air instead of vacuum condition.

4.5. Thermal annealing for 50 wt% HAc concentration feeds

The thermally annealed fibers exhibit a significant enhancement of the separation factor with a model 20 wt% acetic acid–water mixture. To our best knowledge, the highest acetic acid concentration in an aqueous solution that has been reported is about 10 wt% [20,21] using polyimide hollow fiber membranes. Therefore, it is interesting to investigate whether heat treatment works with higher HAc concentration feeds as well. A model 50 wt% HAc/H_2O solution was used as a feed for pervaporation tests at the temperature of 103.5 °C.

The fibers were heat-treated at 220 °C in vacuum for 1 and 12 h, respectively. Thereafter, two modules were prepared to conduct pervaporation tests with model 50 wt% HAc/H_2O mixture feeds. As a reference, a module made of a virgin fiber was used to perform the same test. Fig. 13 shows the permeation and selectivity results for these three modules.

Throughout the 14 day test, the membrane selectivity of the annealed fibers was about 10. Two competing factors can affect the fiber performance in this case. First, the loss of free volume and formation of charge transfer complexes in the outer skin layer due to heat treatment. Second, swelling effects arising from high acetic acid concentration feeds also impact fiber performance. It is clearly shown that heat treatment improves the rigidity of the polymer chains that can suppress the HAc-induced plasticization; however, this suppression is not sufficient to avoid the decrease of the membrane selectivity in high HAc concentration feeds over extended periods of time. That is, a strong interaction between high HAc concentration feeds and the polymer can activate polymer chain segments and may change the free volume and its distribution

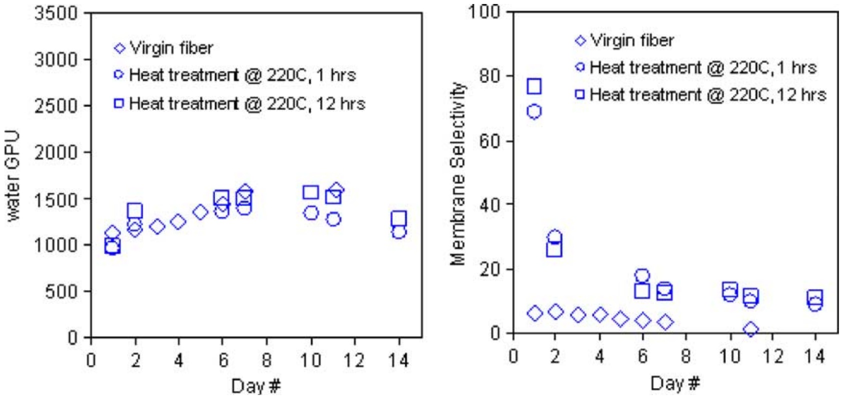

Fig. 13. Effects of heating time on water permeance and membrane selectivity with model 50 wt% HAc/H_2O mixture feeds.

significantly. The HAc-induced swelling in a virgin fiber is more drastic because almost no selectivity is shown on day #11.

It has also been observed that no large difference exists for the fibers with heat treatments of 1 or 12 h. This indicates that the HAc-induced plasticization dominates with the high HAc concentration feed and charge transfer complexes from thermal annealing are not intense enough to suppress the HAc-induced plasticization. Even with annealed hollow fibers, the skin layer can be dramatically swelled when exposed to 50 wt% HAc concentration solutions. In an extreme case, nonselective permeation might control the transport of both penetrants, if the free volume is increased drastically by the HAc-induced swelling stress. Thus, the membrane selectivity inevitably drops down close to one.

5. Conclusion

Thermal annealing applied to Matrimid® hollow fibers significantly improves the membrane selectivity of acetic acid and water mixtures. A membrane selectivity of 95 is achieved with acceptable water flux of 1.6 kg/m^2 h for 20 wt% HAc/H_2O feeds using 520 μm outer diameter and 20 cm long hollow fibers. The loss of free volume and formation of charge transfer complexes arising from heat treatment increase size- and shape-discrimination of the polymer for water and acetic acid molecules. The hindrance to the segmental mobility among the polymer chain segments in annealed membranes suppresses the HAc-induced swelling. Only the morphology of the polymer matrix changes but no chemical reaction occurs with thermal annealing.

Heating variables are investigated and optimized for the fiber structure used in this work. The temperature of 220 °C and heating time of 1 h are good for a model 20 wt% HAc feed for the currently optimized fiber morphology, because overheating generates excess substrate resistance. Thermal annealing does not work effectively to maintain selectivity with high HAc concentration feeds. This indicates that heat treatment is capable of suppressing the HAc-induced plasticization, but not sufficiently intensive in more aggressive environments such as a 50 wt% HAc concentration feed.

Thermal annealing might be applied to other pervaporation hollow fiber membranes, provided that the chemical structure of a membrane material is feasible to form charge transfer complexes. Fluorescence spectroscopy has proved very helpful for first calibration of charge transfer complexes and packing density of the polymer chains.

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