Use of atomic force microscopy and solid-state NMR spectroscopy to characterize structure-property-performance correlation in high-flux reverse osmosis (RO) membranes

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Abstract

Morphology and relaxation studies were very effective in understanding of the reverse osmosis (RO) permeation for the high-flux reverse osmosis (RO) membranes which were the thin-film-composite (TFC) type based on aromatic polyamide of \textit{m}-phenylene diamine (MPD)/trimesoyl chloride (TMC). Microscopic morphology analyzed by atomic force microscopy (AFM) together with field-emission scanning electron microscopy (FE-SEM) and molecular relaxation characterized by solid-state \textsuperscript{1}H nuclear magnetic resonance (NMR) spectroscopy revealed an important factor crucially affecting the enhancement of RO permeability. The proton spin-lattice relaxation in the rotating frame for the aromatic polyamides in their wet state (i.e., saturated with D\textsubscript{2}O) has been shown to be sensitive to the water flux and played a significant role in enhancing the membrane permeability, regardless of the surface features. The aromatic polyamide possessing relatively shorter spin-lattice relaxation times in the rotating frame, \(T_1\), provided a TFC membrane with higher RO permeation, and vice versa. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aromatic polyamide high-flux thin-film-composite membranes; Atomic force microscopy; Field-emission scanning electron microscopy; Solid-state nuclear magnetic resonance spectroscopy; Spin-lattice relaxation in the rotating frame

1. Introduction

Over the last two decades, reverse osmosis (RO) thin-film-composite (TFC) membranes have found a variety of applications in water desalination, ultrapure water production, waste water treatment, and so on [1]. Recently, it becomes important to control the membrane performance and specialize it for the intended application. Various methods have been followed, and they generally belong to two approaches [2–9]. The first is to synthesize and develop new thin-film polymeric materials. The second usually involves two routes which are (i) surface modification by post-treatment with various chemicals and (ii) some modification of the polymer chains and hence control of the surface morphology by using additives during formation of the thin films. From the former approach, the improved properties of the resulting composite membranes have been achieved either by enhancing water flux accompanied with a loss of salt rejection, or vice versa. For the latter, a number of studies have been performed recently, and they have reported that...
the water flux increases significantly, up to an order of magnitude, without any loss in the salt rejection, and in some cases both the transport properties are simultaneously improved.

Most of the commercially successful TFC membranes possess an aromatic polyamide active layer, which is made via interfacial polymerization of m-phenylene diamine (MPD) in aqueous phase and trimesoyl chloride (TMC) in organic phase. From the standpoint of the performance efficiency, they are now required to have dramatically enhanced water permeability without sacrificing the salt separability. Recently, Saehan, Korea, supplied a series of MPD/TMC-based high-flux TFC membranes (SH-I, SH-II, SH-III). They are primarily targeted for the use in lower pressure applications. According to the manufacturer, the thin films of these membranes were fabricated by using some additives in the MPD aqueous solution or in the TMC organic solution when polymerized interfacially. One additive acted as a catalyst (1:2:4 in wt%) to increase the reactivity of TMC and another was a liquid surfactant which improved the wettability of MPD. Although the chemical structure and composition of the additives used were not publicly opened, they were believed to play a significant role in increasing the degree of polymerization and controlling the amine diffusion rate into the polyamide interface. This must bring about modification in the surface morphology and variation in the polymer chains forming thin films, compared to the bare MPD/TMC TFC membrane.

While a wide array of techniques to enhance the water flux of the TFC membranes have been developed in the laboratory and several high-flux TFC membranes have already been found on the market, relatively few studies aimed at understanding the behavior and mechanism of permeability enhancements. Recognizing that the membrane surface governs selective separation of the solute and passage of the solvent, it is important to characterize the morphological variations of the TFC membranes, in conjunction with flux enhancement. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) provide the most direct means to investigate and analyze the morphological structure of the TFC membranes [3,10]. In the previous work [11], a close relation between permeation flux and surface roughness in the TFC membranes has been found. Despite that the RO performance primarily depends on the nature of the thin-film polymers, little has been attempted to correlate the improved performance with the changes in the inherent material property of the thin-film polymers particularly in their “wet” or solvent-swollen state. This is mainly because (i) the thin-film polymer is crosslinked, hence insoluble, thereby causing sampling problems for the application of the conventional characterization techniques and (ii) there are a very limited number of techniques that allow a direct study of wet membranes. The solid-state nuclear magnetic resonance (NMR) spectroscopy is one of relatively few techniques which can overcome the characterization difficulties associated with the above (i) and (ii), and may provide a material property useful for basic understanding of the membrane permeation. The relaxation and molecular motion as an inherent material property must have some influence on the passage of the diffused-in solvent (water) across the thin film layer, which becomes a dominant factor to govern the permeation flux and its enhancement. Spin-lattice relaxation times of proton in the rotating frame, $T_1$, have been found to be a useful parameters in accessing low-frequency (tens of kHz) molecular motion of solid polymers [12].

This study is concerned with the high-flux TFC membranes based on the modification of MPD/TMC, which is induced by the additives during interfacial polymerization. The natural MPD/TMC prepared in the laboratory is also included as a reference. Details of the surface morphology are revealed by AFM and high-resolution field-emission (FE) SEM. The relaxation and molecular motion of the thin-film polymers wet with fully deuterated solvent (D$_2$O) are characterized by solid-state $^1$H NMR spectroscopy. Eventually, the structure-property-performance relationships for the TFC membranes are found, which would contribute to the basic understanding of the permeability enhancement and the designing of new TFC membranes with advanced performance.

2. Experimental

2.1. Membranes and polymers

A homologous series of high-flux TFC RO membranes, SH-I, SH-II, SH-III, were provided from
Table 1
Reverse osmosis (RO) characteristics of all the thin-film-composite membranes

<table>
<thead>
<tr>
<th>Thin-film-composite membranes</th>
<th>Reverse osmosis characteristicsa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water flux (gfd)</td>
</tr>
<tr>
<td>MPD/TMC</td>
<td>28</td>
</tr>
<tr>
<td>SH-I</td>
<td>28.4</td>
</tr>
<tr>
<td>SH-II</td>
<td>37.2</td>
</tr>
<tr>
<td>SH-III</td>
<td>45.4</td>
</tr>
</tbody>
</table>

a Tested in the laboratory; all the results were obtained with 0.2% NaCl in deionized water and at the operating pressure of 225 psi and the temperature of 25°C.

was appropriate for imaging the samples of low moduli, such as polymer that could be easily damaged by the tip. As the tip was scanned over the surface, the vibration amplitude of cantilever changed in response to force gradients that varied with the tip-to-sample spacing. An image representing surface topography was obtained by monitoring these changes in vibration amplitude. To obtain the highest lateral resolution, an image was taken with 512×512 pixels. Scanning was performed in 0.6–1 Hz rate, where the scan rate of 1 Hz indicated that one line of data was collected per second. In non-contact mode, scan rates from about 0.5–16 Hz could be usually used, depending on the scan conditions. For the SEM observation, the membrane samples were cut into appropriate sizes and the surfaces were coated with silver by a sputter-coating machine.

2.3. Solid-state NMR spectroscopy

The NMR experiments were performed with a Bruker MSL-200 spectrometer (4.7 Tesla for $^1$H). Before the experiments, the solid polymer samples were saturated with the fully deuterated solvent, D$_2$O. The proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured at 333 K and 353 K by analyzing the magnetization decay after $^1$H 90°–τ pulse sequence, Fig. 1. A $^1$H 90° pulse width of 7.0 μs was employed, and the repetition time for the net magnetization to be completely relaxed was 5–6 $T_1$. Typically, 20–25 different τ values were used and FIDs were integrated in order to characterize the individual decay curves. Relaxation times were obtained as slopes of semilogarithmic plots of magnetization intensity versus various τ’s.

3. Results and discussion

Figs. 2 and 3 show AFM surface images with a projection area of 10 μm×10 μm for MPD/TMC, SH-
Fig. 2. AFM surface images of MPD/TMC membrane (a), and SH-I membrane (b).
Fig. 3. AFM surface images of SH-II membrane (a), and SH-III membrane (b).
I, SH-II, SH-III TFC membranes, respectively. The bar at the left side of the each image represents the vertical deviations in the sample with the white regions being the highest and the black regions the lowest. The AFM permits the measurements of distance variations in the surface of the membranes with a

Fig. 4. Vertical height profiles of all the membranes taken from the line traversing the individual AFM images: MPD/TMC (a), SH-I (b), SH-II (c), and SH-III (d).
line traversing the image as shown in each figure. This results in the vertical height profiles. Fig. 4 compares the vertical height profiles along the horizontal line of 10 μm for all the membranes. They are shown to differ in their surface line roughness, based on the vertical deviation with respect to the scale of the ordinate and the numbers of peaks and valleys in the specified displacement (i.e., between 0 and 0 in the figure) along the abscissa. The MPD/TMC has a greater number of peaks and valleys in the given distance than the rest while the SH-III possesses the greatest distance between peaks and valleys among the four membranes. These observations are well demonstrated and in agreement with the FE-SEM micrographs (Figs. 5–8), where the similar surface features were exhibited but brighter and sharper images were delivered compared to those of AFM.

AFM image statistics for the entire projection area is possible, where the maximum peak-to-valley distance, \( R_{p-v} \), average roughness, \( R_{avg} \), root-mean-squared roughness, \( R_{rms} \), and surface area are usually determined. \( R_{p-v} \) is the difference in height between the highest and the lowest points within the selected area. \( R_{avg} \) is the mean roughness of the surface relative to the center plane that is imaginary flat floating at the mean height and is determined by the average deviation of the data points referenced to the average value of the data within the area:

\[
R_{avg} = \frac{1}{S} \int_{a}^{b} \int_{0}^{b} |f(x,y) - z_0| \, dx \, dy
\]  

(1)

Where \( S \) is the specified area, \( f(x,y) \) is the height in the specified area, \( a \) and \( b \) are the length of two sides of the
area, and \( z_0 \) is the mean height (i.e., average value of the heights) in the area. \( z_0 \) is given by

\[
z_0 = \frac{1}{S} \int_0^a \int_0^b f(x,y) \, dx \, dy
\]

(2)

\( R_{\text{rms}} \) is defined by

\[
R_{\text{rms}} = \left[ \frac{1}{S} \int_0^a \int_0^b \{f(x,y) - z_0\}^2 \, dx \, dy \right]^{1/2}
\]

(3)

It is noted that because \( R_{\text{rms}} \) contains squared terms, large deviations from the mean height are weighted more heavily than they are in \( R_{\text{avg}} \), and vice versa. The surface area within the projection area are measured approximately by adding all the area of the triangles formed through connecting a data point to two of its nearest corresponding neighbors. The quantitative analyses of the surface roughness were performed with three to five replication images for the individual membranes, and their arithmetic means are presented in Table 2. In the previous studies, there has been established an obvious correlation of the surface roughness and surface area with the water permeability of the TFC membranes. Namely, the permeation flux increases in proportion to increasing surface roughness and enlarging surface area. From Table 2, however, it is rather difficult to relate the water flux with the surface roughness and surface area. MPD/TMC has relatively higher surface area but lower water flux than SH-I and SH-II although their surface roughness is almost identical. The difference in the surface roughness and area between SH-I and SH-II is not prominent to explain the increase of water flux in SH-II relative to SH-I. These imply that the surface microscopic structure is no longer the only major

Fig. 7. FE-SEM micrographs of SH-II membrane surface at (a) 20 000×, and (b) 50 000×.

Fig. 8. FE-SEM micrographs of SH-III membrane surface at (a) 20 000×, and (b) 50 000×.
factor responsible for the RO transport behavior, and a more fundamental understanding on the nature of the thin-film polymers is required.

Fig. 9 is the semilogarithmic plots of the magnetization intensity as a function of delay time for MPD/TMC aromatic polyamide wet in D2O at 333 K, respectively. The magnetization decays are characterized by an exponential function:

\[ M(\tau) = M_0 \exp(-\tau/T_{1p}) \]  

The exponential decays are biphasic and the data are fitted by a non-linear least-squares fit based on the following equation:

\[ M(\tau) = M_{0,A} \exp(-\tau/T_{1p,A}) + M_{0,B} \exp(-\tau/T_{1p,B}) \]  

The slow decay phase, i.e., B, is ascribed to the protons which have been formed by exchange of deuterium in D2O with hydrogen in the polymer, whereas the component A is contributed from the polymer. This was confirmed by the dry samples where a single exponential decay is shown. The \( T_{1p} \) relaxation times are simply determined from the individual A component, and those values at 353 K can be

### Table 2

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Maximum peak-to-valley distance, ( R_{p-v} ) (( \mu \text{m} ))</th>
<th>Surface roughness (( \mu \text{m} ))</th>
<th>Surface area (( \mu \text{m}^2 ))</th>
<th>Water flux (gfd)a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average, ( R_{\text{avg}} )</td>
<td>Root-mean-square, ( R_{\text{rms}} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPD/TMC</td>
<td>0.46</td>
<td>0.042</td>
<td>0.053</td>
<td>171.2</td>
</tr>
<tr>
<td>SH-I</td>
<td>0.40</td>
<td>0.040</td>
<td>0.050</td>
<td>147.4</td>
</tr>
<tr>
<td>SH-II</td>
<td>0.46</td>
<td>0.043</td>
<td>0.054</td>
<td>148.8</td>
</tr>
<tr>
<td>SH-III</td>
<td>0.78</td>
<td>0.084</td>
<td>0.104</td>
<td>180.9</td>
</tr>
</tbody>
</table>

*Tested in the laboratory; all the results were obtained with 0.2% NaCl in deionized water and at the operating pressure of 225 psi and the temperature of 25°C.*

Fig. 9. Semilogarithmic plot of magnetization decay for MPD/TMC in D2O at 333 K.
similarly determined; they are summarized in Table 3. Although not shown, the \( T_1 \)'s of other aromatic polyamides (SH-I, SH-II, SH-III) are determined in the similar way as done in Fig. 9 and are listed in Table 3. As seen in the table, the $T_1$ values become shorter in the order MPD/TMC, SH-I, SH-II, SH-III. $T_1$ is related to the correlation time, $\tau_c$ [12], which defines the length of time that the molecule can be considered to be in a particular state of motion:

$$1/T_1 \propto B_1^2 \{(\tau_c/(1 + 4\omega_1^2\tau_c^2)}\}
$$

where $\omega_1$ is the resonance frequency (rad/s) in $B_1$ magnetic field. For the rigid, crosslinked polymers, their molecular motion near room temperature is usually in so called “slow motion region” where $\omega_1\tau_c > 1$, and $T_1$ is proportional to $\tau_c$. Thus, the solid molecules with longer $\tau_c$ are in slower molecular motion and in general, $\tau_c^{rg} > \tau_c^{mb}$, hence $T_1^{rg} > T_1^{mb}$ follows [13], where the superscripts rg and mb relatively denote the rigid and mobile materials, respectively. Therefore, the ordering of $T_1$ in Table 3 indicates an increase of the mobility from MPD/TMC to SH-III. Comparing the $T_1$ values with the RO permeation flux, there is an obvious correlation between them; the shorter the $T_1$, relaxation time, the higher the water flux, and vice versa. That is, the water diffusion across the thin-film polyamide layer elevated as the local chain motion became relatively released in the order from MPD/TMC to SH-III. Inversely, freezing the polymer chain retarded the water diffusion, which resulted in lowering the water flux. Therefore, the $T_1$ relaxation and hence chain mobility was found to play a crucial role in governing the RO permeability of the polyamides, regardless of the membrane surface microstructure.

### Table 3

$T_1$ relaxation times of aromatic polyamides wet with $\text{D}_2\text{O}$

<table>
<thead>
<tr>
<th>Aromatic polyamide</th>
<th>$T_1$ (ms)</th>
<th>Membrane water flux $^a$ (gfd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>333 K</td>
<td>353 K</td>
</tr>
<tr>
<td>MPD/TMC</td>
<td>20.0</td>
<td>16.0</td>
</tr>
<tr>
<td>SH-I</td>
<td>13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>SH-II</td>
<td>9.1</td>
<td>–</td>
</tr>
<tr>
<td>SH-III</td>
<td>6.1</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^a$ Tested in the laboratory; all the results were obtained with 0.2% NaCl in deionized water and at the operating pressure of 225 psi and the temperature of 25 °C.

### 4. Conclusions

The present paper intended to correlate the surface morphology, the relaxation properties, and the membrane performance of the commercially available high-flux RO TFC membranes, which would contribute toward further advances in designing of new membranes of technological interest.

Combined results of AFM surface analysis and FE-SEM surface observation revealed that as was in the case of SH-III, both higher surface roughness and surface area of the membrane were favorable to the higher water flux (see Table 2). In the case of the surface roughness kept similar as in MPD/TMC, SH-I, SH-II, however, the surface area alone was no longer related to the relative increase in the water permeability. Solid-state $^1\text{H}$ NMR relaxation measurements for the individual aromatic polyamides were performed after saturating them with $\text{D}_2\text{O}$. It was concluded that relaxation and mobility of the aromatic polyamides forming thin films played an important role in controlling the RO permeability, irrespective of the surface morphological features. The shorter $T_1$'s of aromatic polyamides reflected the thin films of more mobile chains, which participated in elevating the water diffusion through the thin layer and allowing higher water flux.

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### References


