NOTES

Separation of H_2 and CO through Poly(sulfone-amide) Membranes IV. Effects of Extraction of Cast Solvent and Following Thermal Treatment

Yoshimitsu SAKAGUCHI, Masaya TOKAI, Hiroshi KAWADA, and Yasuo KATO

Toyobo Research Center, Toyobo Co., Ltd., 1–1 Katata 2-chome, Ohtsu 520–02, Japan

The authors have studied hydrogen separation membranes made from aromatic polyamide containing sulfone linkages in the main chain [this polymer is called poly(sulfone-amide)]. In previous papers,[1,2] some relationships between H_2/CO permselectivity and polymer structure were found in this system.

In the case of stiff-chain glassy polymers including poly(sulfone-amide)s, separation of small molecules such as hydrogen from larger molecules such as carbon monoxide through the membrane is mainly affected by the packing character of the polymer chains, which determines the diffusivity of the gas molecules. Investigations for the relationships between gas-permeation character and polymer structure in aromatic polymers have been actively published in recent years.[3-9] In the poly-(sulfone-amide) membranes, it was found that the permeability ratio of H_2 relative to CO (P_{H_2}/P_{CO}) is controlled by the balance between the stiffness induced by the concentration of amide linkages in the backbone and the crookedness enhanced with the introduction of m-catenation into the main chains. Recently, the same effect, that is, m-catenation makes the diffusion of gases through a glassy-polymer

membrane slower compared with p-catenation, has been reported in several papers.[10-15]
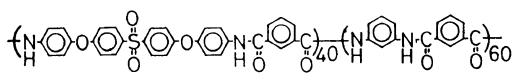
Another factor influencing the gas permeability in a membrane is how to prepare the membrane including after-treatment such as thermal treatment. In a previous paper,[16] we reported about the rearrangement of the polymer chains accompanied by the removal of cast solvent under thermal treatment. The thermal treatment of slightly dried membrane at higher temperature brought densification more effectively.

In this paper, effects of extraction of the cast solvent from the membrane by a non-solvent were studied. Influence of the following thermal treatment was also investigated.

EXPERIMENTAL

Preparation of Polymer

The poly(sulfone-amide) derived from iso-phthaloyl dichloride and the mixed diamine which consisted of bis[4-(4-aminophenoxy)-phenyl] sulfone and m-phenylenediamine (4 : 6) (4SMI-60, Structure 1) was prepared by low-temperature polycondensation as described in the previous paper.[1]

$$\left\{ N \bigcirc O \bigcirc \overset{\overset{O}{\overset{\|}{S}}}{\underset{\|}{O}} \bigcirc O \bigcirc N\text{-}C \bigcirc C \right\}_{40} \left\{ N \bigcirc N\text{-}C \bigcirc C \right\}_{60}$$

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Preparation of Membranes

4SMI-60 (4 g) was dissolved in 20 ml of *N*-methyl-2-pyrrolidone (NMP). The solution was filtered and the filtrate was cast on a polypropylene film at room temperature. By evaporating the NMP at 80°C for an hour, the membrane of 10—20 μm thickness was obtained; this membrane will be called as-cast membrane hereafter. Extraction of the NMP was carried out by immersing the as-cast membrane into acetone for 17 h. The thermal treatment was carried out by keeping the membrane at various temperature under reduced pressure (*ca.* 0.5 mmHg) for 17 h.

Permeability Measurement

Permeabilities of H_2 and CO were measured with the same way described in the previous paper.[16]

Permeation of a gas through a glassy polymer is usually explained by the dual-mode theory.[17] In this study, the permeability coefficient was determined from the steady-state permeation rate at a constant pressure of upstream gas (1 atm), and the apparent diffusion coefficient of CO was determined using the time-lag method.[18] The apparent diffusion coefficient (D_{app}) was calculated by the following equation,

$$D_{app} = \frac{l^2}{6L}$$

where L is the time lag and l, the thickness of the membrane.

Analysis of Membrane

Reduced viscosity, density, amount of the residual solvent, and dynamic viscoelastic property were measured as described in the previous paper.[16] Thermomechanical analysis (TMA) was carried out on the films with a

Shimadzu TMA-30. Change in the length of samples, 1 mm wide and 5 mm long, was recorded with the elongation mode under a load of 200 mg at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

Gas permeable membranes are usually prepared by the cast of polymer solution and the following thermal treatment. This thermal treatment brings about removal of the cast solvent and heat set of the polymer chains. In order to remove the cast solvent from a membrane, it is also applicable to immerse a slightly dried membrane into a non-solvent for the polymer.

For this purpose, the as-cast membrane of poly(sulfone-amide) (4SMI-60), which was dried at 80°C for an hour after the cast, was immersed in acetone for 17 h. Acetone mixes with NMP easily and does not induce swelling of the poly(sulfone-amide) membrane. Therefore, it is a effective non-solvent to extract the NMP from the membrane. The amount of residual NMP decreased from *ca.* 15 wt% to 3.5 wt% by this extraction. Then, the thermal treatment under reduced pressure was carried out. Effects of the NMP extraction by acetone and the following thermal treatment on gas permeabilities and some other properties are summarized in Table I.

P_{H_2}/P_{CO} of the membrane after the extraction was 92 and similar to that of the membrane thermally treated at 150°C for 17 h without extraction, which was 89.[16] The densities and residual NMP contents were also similar in these two membranes: 1.328 and 3.5% for the extracted membrane; 1.326 and 3.5% for the thermally treated membrane. From these results, it might be considered that the removal of the cast solvent, regardless of extraction or thermal treatment, induced a similar densification of the polymer structure.

The thermal treatment of the extracted membrane, however, gave opposite results

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Table I. Effects of the extraction of cast solvent and the following thermal treatment
on the properties of the poly(sulfone-amide) membrane

Thermal treatment temperature	$P_{H_2}{}^a$	$P_{CO}{}^a$	P_{H_2}/P_{CO}	Density[b]	Residual[c] NMP
				$g\,dl^{-1}$	%
r.t.	3.6×10^{-10}	3.9×10^{-12}	92	1.328	3.5
200°C	4.4×10^{-10}	5.0×10^{-12}	88	1.335	0.3
220°C	4.5×10^{-10}	5.5×10^{-12}	82	1.335	0.2

[a] $cm^3\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$, measured at 30°C.
[b] Measured at 30°C with a density gradient column.
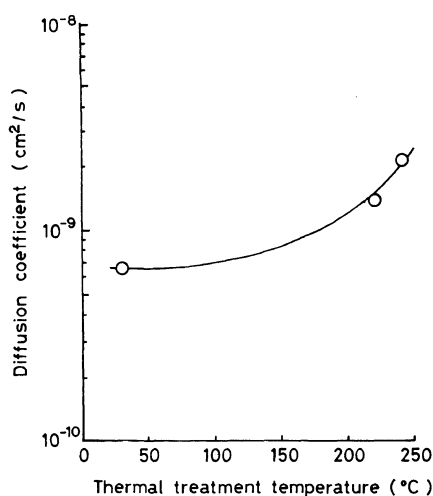[c] Determined by thermogravimetric analysis.

Figure 1. Effect of thermal treatment on the apparent diffusion coefficient of CO for the Poly(sulfone-amide) membrane extracted by acetone.

Figure 2. Temperature dependence of $\tan \delta$ for the poly(sulfone-amide) membrane: A, as-cast; B, immersed in acetone for 17 h; C, thermally treated at 200°C for 17 h after the extraction.

from the thermal treatment of the as-cast membrane. As shown in Table I, P_{H_2}/P_{CO} of the extracted membrane decreased in some degree by the following thermal treatment. On the other hand, the thermal treatment of the as-cast membrane increased P_{H_2}/P_{CO} with increasing temperature of the thermal treatment as described in the previous paper.[16] This increase was mainly attributed to the decrease of diffusion coefficient for CO ($D_{app,CO}$) as a result of the densification of the membrane structure. In the case of extracted membrane, $D_{app,CO}$ increased with the thermal treatment as illustrated in Figure 1. Though the extraction
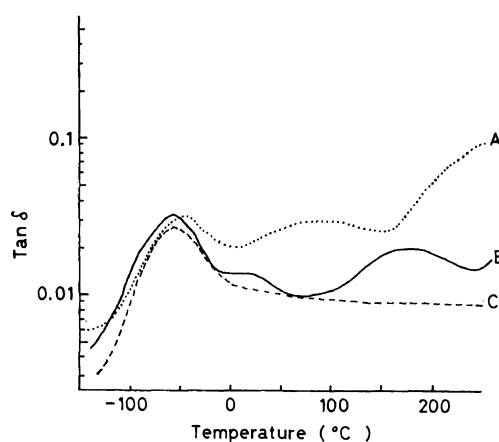
step caused some densification by removing the NMP, the following thermal treatment reduced the compactness instead of increasing the degree of packing.

To understand the structure difference between the thermally treated membranes with and without the extraction, the following characterization was carried out.

Figure 2 shows $\tan \delta$ profiles of the extracted membrane with the following thermal treatment. The $\tan \delta$ peaks between the peak around $-50°C$ and the glass transition (263°C) give some information about the effect of thermal treatment. In the case of the thermal treatment of the as-cast membrane, increasing the
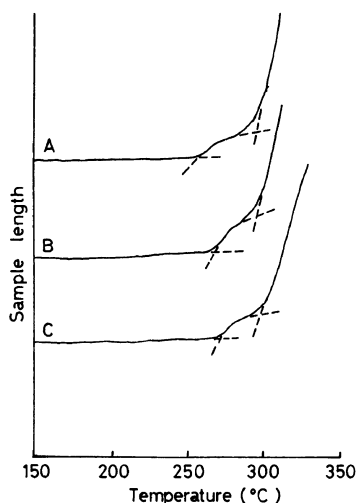
Figure 3. Effect of thermal treatment on TMA curves of the poly(sulfone-amide) membrane extracted by acetone. The thermal treatment temperature: A, 30°C; B, 200°C; C, 220°C.

temperature of thermal treatment shifted the peak between these two major transitions to higher temperature region and finally this peak disappeared. Similarly, the corresponding transitions for the extracted membrane disappeared with thermal treatment. Increase of the density with thermal treatment for the extracted membrane (Table I) was also similar to that for the as-cast membrane. No remarkable difference in heat-set was detected from these macroscopic views.

Some difference in microscopic aspect for these two systems is explained with the results of TMA measurement. As illustrated in Figure 3, the extracted membranes showed two-step elongation on TMA. The first elongation temperature depended on the thermal treatment temperature to some extent, and the second one appeared at the almost same temperature. As reported previously,[16] the membranes without extraction shrunk at first and then elongated on TMA. This shrinking temperature increased with increasing temperature of the thermal treatment.

This shrinking phenomenon suggests that the membrane has residual stress in it, and

more densification is possible with further thermal treatment at higher temperature. The extraction itself induced *ca.* 10% shrinkage of a length of the membrane and removed most of the cast solvent. Therefore, it is considered that there was no shrinkage on TMA because the stress in the membrane had already been removed at the stage of the extraction.

In the case of the as-cast membrane, the residual solvent in the membrane makes the polymer chains rearrange easily at relatively lower temperature. At the same time, the residual stress seems to contribute to a uniform densification effectively. As the extracted membrane does not have such effects, the densification is probably not uniform in the membrane and increased the defects which accelerate the diffusivity of gas molecules. As a result, P_{H_2} and P_{CO} increased, and P_{H_2}/P_{CO} decreased with the thermal treatment.

As discussed above, it was ascertained that the residual solvent plays a important role to determine the membrane structure in the course of its removal.

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