NOTE

Structures and Gas Permeabilities of Poly(vinylidene Fluoride)/Oligodimethylsiloxane Blend Membranes

In a recent article, we reported preparation of the blend membranes composed of poly(vinyl chloride) (PVC) and oligodimethylsiloxane (ODMS), and gas permeabilities of the membranes for O_2 and N_2 were discussed with relation to the structure of 1–10 μm orders formed in the membranes.[1] The membranes were considered to be similar to the porous membranes made of PVC, of which pores are filled with ODMS, and the mechanism of the gas permeation was explained in relation to the similarity of the structures with the silicone–polysulfone membranes of the PRISM separator produced by Monsanto Co.[2] That is, the thin layers of PVC formed on the porous membranes determine the permeabilities of the membranes.

Although the vapor pressure of ODMS is not negligible, the stability of the PVC–ODMS membrane is considerably high. This might be attributed to the hydrogen-bond formation between the terminal OH groups of ODMS and chlorine atoms in the PVC. Thus, we intended to advance further investigation on the compatibility of ODMS with other halogen-containing polymers like poly(vinylidene fluoride) (PVDF). PVDF and ODMS blend system was tried to prepare films, and the relation between the structures in the membranes and gas permeabilities were investigated.

EXPERIMENTAL

Poly(vinylidene fluoride) (KF-1000, Kureha Chemical Industry Co. Ltd.) was used after purification by reprecipitation of DMF solution into methanol. Oilgodimethylsiloxane ($HO\text{-}(Si(CH_3)_2\text{-}O)_n H$, Petrarch Systems Inc.) having a degree of polymerization of approximately $n = 9$ was used without purification. Guaranteed grade of DMF (Tokyo Kasei) was used without further purification. Although ODMS is not miscible with DMF, a three-component system of PVDF–ODMS–DMF makes a homogeneous and transparent solution in a wide range of composition. PVDF (0.75–1.5 g) and ODMS (0–0.75 g) were dissolved in DMF (7 mL), and, after filtration with a G3 glass filter, the mixture solution was cast on a glass plate. The cast film was put in a desiccator with silica gel and kept 4 h under a reduced pressure of about 25 mm Hg to let DMF evaporate. All the membranes thus prepared are white and translucent except for the PVDF membrane containing no ODMS, and the phase separation in the blend membranes is suggested to occur during membrane formation.

After being stripped off from the glass plate, the membranes were dried for 24 h under vacuum at room temperature. The membranes were served for the measurements of gas permeability (Rikaseiki, K-315), scanning electron microscopy (Akashi, ALPHA-30), and Fourier transform infrared spectroscopy (Digilab, FTS-20C).

As the vapor pressure of ODMS at 20°C is not so low (about 0.7 mm Hg[1]), ODMS in the membrane is apt to vaporize while drying the membranes. Thus, the membranes were dissolved in deuterated DMF and the exact contents of ODMS were determined by the proton NMR (JEOL, JNM-MH-100) measurements. The results were summarized in Table I.

Measurements of glass transition temperatures of the blend membranes were carried out by using a differential scanning calorimeter (Perkin-Elmer, Model DSC-2). Approximately 20 mg of each sample was used, and a heating rate was 20°C/min.

RESULTS AND DISCUSSION

It has been reported that several crystalline phases α, β, γ, δ, and others, exist in PVDF and the relative volume fraction of each crystalline phase changes depending on the preparing conditions of the membranes.[3,4] For example, the PVDF membrane prepared by casting a

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TABLE I
ODMS Contents in the Blend Membranes

PVDF/ODMS mixed	PVDF/ODMS measured
9/1	96/4
8/2	92/8
7/3	83/17
6/4	75/25
5/5	95/5

PVDF–dimethylphosphoramide solution on a glass plate contains a significant amount of β-form crystals,[3] and the membrane made from a PVDF–chlorobenzene–dimethylformamide solution contains a large amount of α-form crystals.[4] The formation of these crystals has been confirmed by X-ray diffraction analysis[4-8] and the infrared spectrum measurements.[4,8-11] Figures 1 and 2 show the infrared spectra of the PVDF and the PVDF–ODMS blend membranes, respectively. The vibrational bands at 530, 615, 765, 796, 855, 875, and 975 cm^{-1} correspond to the α-form crystal and the vibration bands at 845 and 884 cm^{-1} are assigned to the β-form crystal, while the bands at 810 and 882 cm^{-1} are characteristic of the γ-form crystal.[3,8] The band at 510 cm^{-1} is characteristic of both the β- and γ-form crystals.[8] The infrared spectrum of Figure 1 indicates the existence of the β- and γ-form crystals as well as the α-form in the PVDF membrane.

Figure 2(a) shows the infrared spectrum of the membrane of PVDF/ODMS = 5/5, and 2(b) is that of ODMS only. The strong absorption band in a lower wave number range than 500 cm^{-1} is attributable to the ZnSe windows, which were used to support ODMS liquid. A strong peak at about 805 cm^{-1} is assigned to the Si–O stretching vibration. As the spectrum of Figure 2(a) is made up to the spectra of ODMS and PVDF, the difference spectrum was calculated by the computer equipped to the FTS-20C and was shown in Figure 2(c). All the peaks assigned to the β- and γ-form crystals are eliminated and only the peaks assigned to the α-form crystal remain, except for a small peak at 820 cm^{-1}. According to these results, we can conclude that only the α-form crystals exist in the blend membranes when the amount of ODMS is large.

Figure 3 shows the sections of respective blend membranes, and Figure 4 shows the whole section of the 5/5 blend membrane observed by a scanning electron microscopy. All the specimens were prepared by the freeze–fracture method and coated with Au to prevent electrical charging. These photographs show clearly that fibril-like structures are formed, and the volume fraction of the fibrils and their diameters become large with an increasing content of ODMS. In the case of

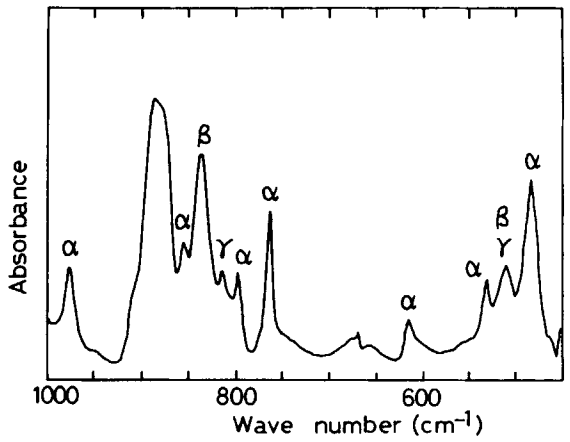


Fig. 1. Infrared spectrum of PVDF membrane. There appear peaks assigned to α-, β-, γ-form crystals.

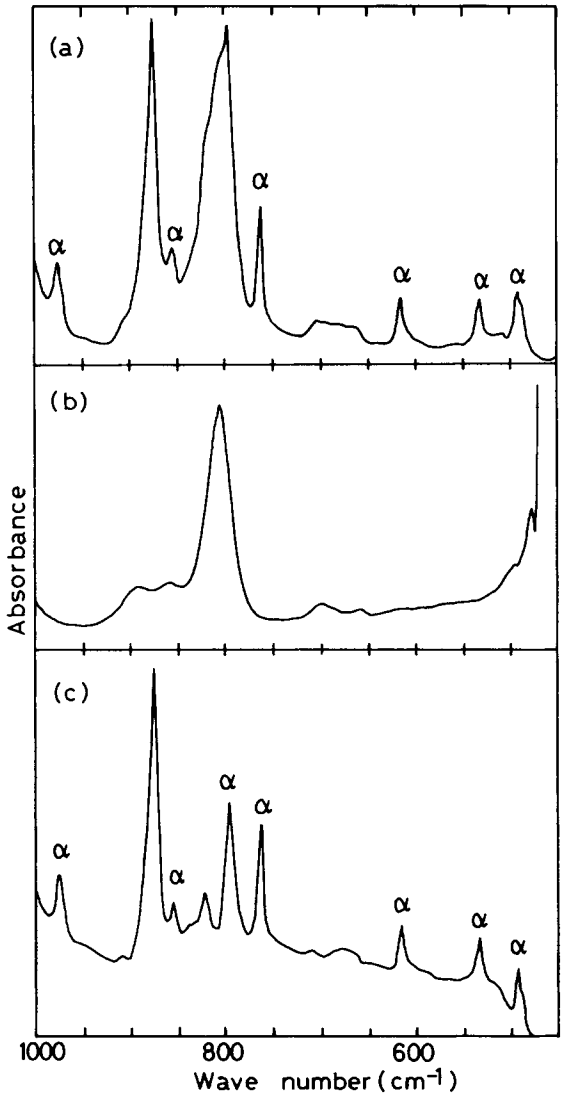
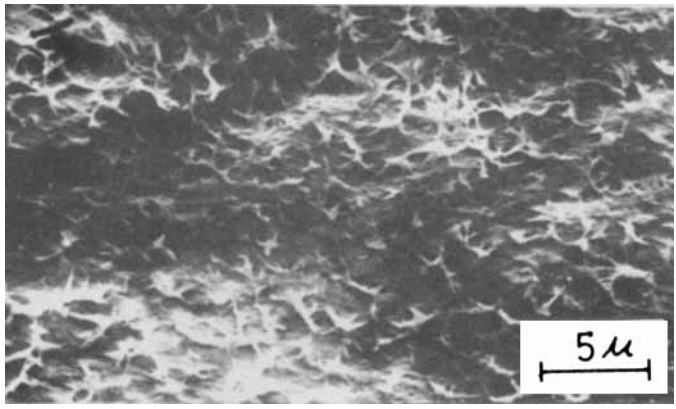


Fig. 2. Infrared spectra of (a) PVDF/ODMS blend membrane, (b) ODMS, and (c) difference spectrum (a) − (b). PVDF/ODMS = 5/5.

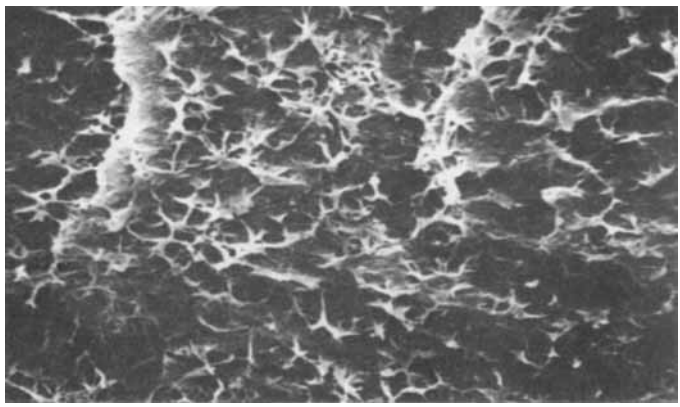
PVDF/ODMS = 5/5, the membrane is spongelike and completely occupied by the networks of the fibrils, as shown in Figures 3(F) and 4.

These membrane structures would reflect the behaviors of gas permeabilities. It would be expected for the membranes containing a considerable amount of ODMS that, for the gas permeation through the ODMS phase, filling the pores determines the gas permeation rate of membranes. This was confirmed by the gas permeation measurements, of which the results are shown in Table II and Figure 5. With an increasing content of ODMS, the separation factor decreases from the original value of 3.5 to about 2, which is nearly equal to the value of the silicone rubber membrane.

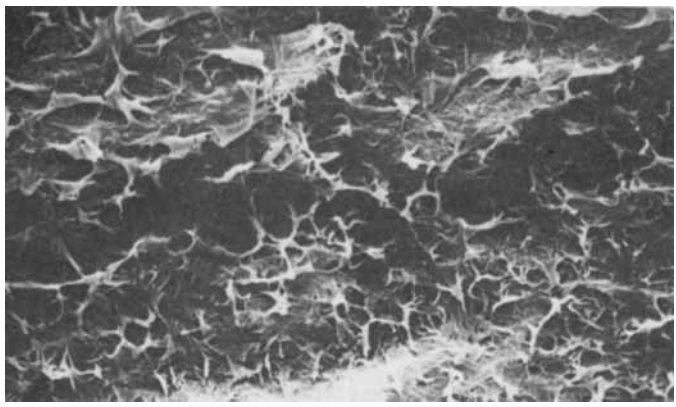
The glass transition was observed as a step change in the ordinate of the DSC curve and the glass transition temperature T_g was determined as the temperature at which the heat capacity changes by one-half of the total change associated with the transition. Data are listed in Table III. The T_g of PVDF reported already is about 233 K.[12] The DSC curves of the PVDF and 9/1



(A) PVDF

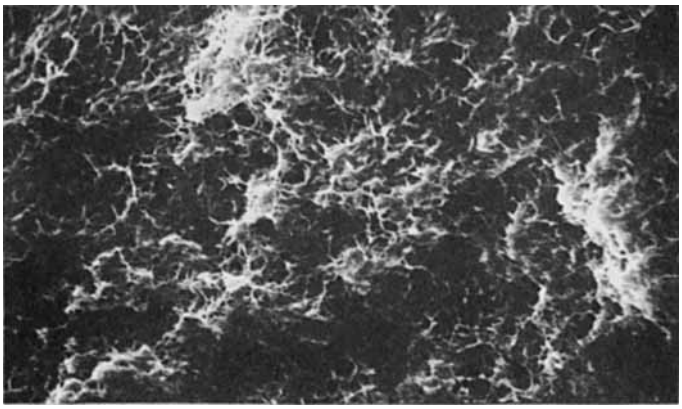


(B) PVDF/ODMS = 9/1

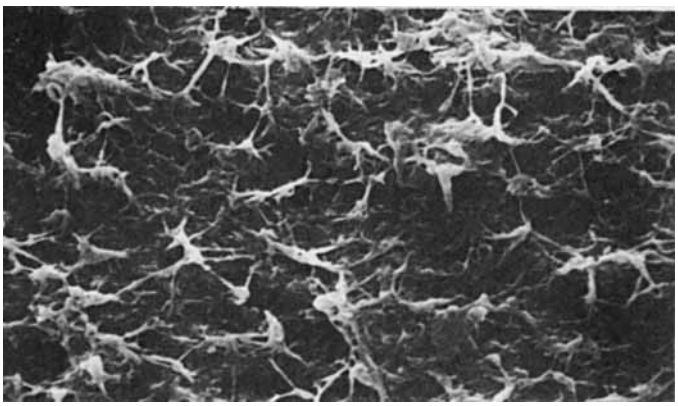


(C) PVDF/ODMS = 8/2

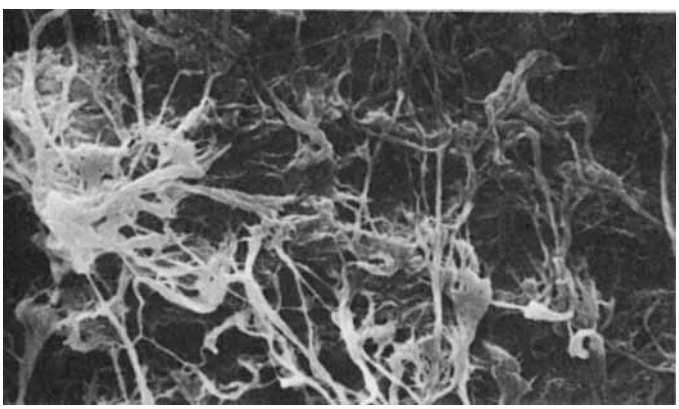
Fig. 3. Cross-sectional views of the PVDF/ODMS blend membranes by SEM (×3000).



(D) PVDF/ODMS=7/3



(E) PVDF/ODMS=6/4



(F) PVDF/ODMS=5/5

Fig. 3. (*Continued from previous page.*)

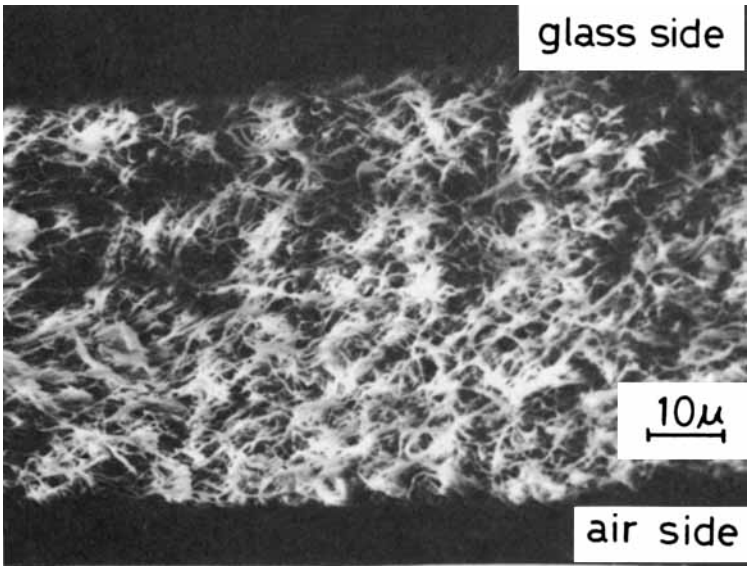


Fig. 4. Cross-sectional view of the membranes by SEM (×1000). PVDF/ODMS = 5/5.

TABLE II
Permeabilities for Oxygen and Nitrogen, and Separation Factors of PVDF/ODMS Blend Membranes at 25°C

PVDF/ODMS wt. ratio	Thickness (μm)	P_{O_2} [cm^3 (STP) cm/cm^2 s cm Hg]	P_{N_2} [cm^3 (STP) cm/cm^2 s cm Hg]	P_{O_2}/P_{N_2}
10/0	15	4.62×10^{-12}	1.34×10^{-12}	3.5
9/1	20	1.15×10^{-11}	3.41×10^{-12}	3.4
8/2	70	1.65×10^{-10}	7.13×10^{-11}	2.3
7/3	35	6.60×10^{-10}	3.16×10^{-10}	2.1
6/4	35	9.29×10^{-10}	4.48×10^{-10}	2.1
5/5	50	1.33×10^{-9}	6.40×10^{-10}	2.1

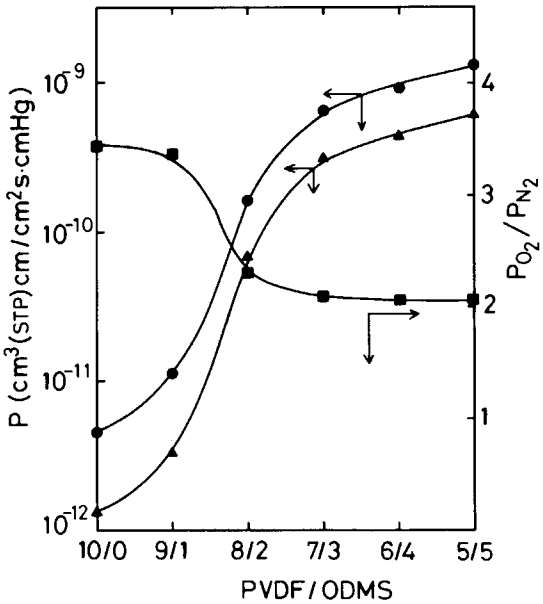


Fig. 5. Permeabilities for O_2 and N_2, and separation factors of the PVDF/ODMS membranes at 25°C. (-●-, -▲-, -■-) permeabilities for O_2 and N_2, and separation factor.

TABLE III
T_g of the Blend Membranes

PVDF/ODMS mixed	T_g (K)	Relative changes in the heat capacity
10/0	—	—
9/1	—	—
8/2	225	1
7/3	225	2
6/4	225	6
5/5	225	53

blend membranes have very small changes at about 245 K, but it seems difficult to conclude that those changes are responsible for glass transitions. On the other hand, the 8/2, 7/3, 6/4, and 5/5 blend membranes showed clear changes in their DSC curves at about 225 K, which were considered to be caused by glass transitions. The changes in the DSC curves at T_g become large and clear as the content of ODMS in the blend membrane increases, which implies an increasing tendency of the amorphous content with an increasing content of ODMS.

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