

# Porous Membrane of Polydimethylsiloxane by Hydrosilylation Cure: Characteristics of Membranes Having Pores Formed by Hydrogen Foams

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## SYNOPSIS

Porous polydimethylsiloxane (PDMS) membranes were prepared by catalytic hydrosilylation cure of a silicone compound containing a vinyl group and a SiH group in the presence of additives such as water, ethanol, ethylene glycol, and 2-methoxyethanol. The pores were formed in the membrane as a result of hydrogen foams produced by the reaction between the SiH group and the OH group of the additive during the cure. The cure reaction, hydrogen generation, and properties of the porous membranes that resulted were examined as a function of the additive concentration in the compound at various cure temperatures. As application of the membrane, the ultrafiltration properties were determined. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polydimethylsiloxane (PDMS) has unique characteristics<sup>1</sup> such as elastomeric behavior, gas permeability, biocompatibility, thermal stability, and excellent hydrophobic and electrical properties. The vulcanizate is applied to numerous industry uses.<sup>1</sup> It is well known that PDMS containing an unsaturated vinyl group and a SiH group is cured by hydrosilylation in the presence of catalysis (usually a platinum derivative)<sup>1,2</sup> in accordance with the equation in Scheme 1. Because the cure reaction occurs easily, the development in the synthesis of silicone rubbers<sup>3</sup> and various industries for water repelling<sup>4</sup> and encapsulation<sup>5,6</sup> of electric parts has been made.

In the encapsulation field, PDMS elastomer<sup>7</sup> having many pores is prepared by hydrosilylation cure. The porous structure of the elastomer results from hydrogen foams produced during the cure, since water added to the compound reacts with the SiH

group of PDMS according to the equation in Scheme 2: R = H. We are interested in the porous elastomer for application to the membrane processes because of, thus far, no report on porous PDMS membrane.

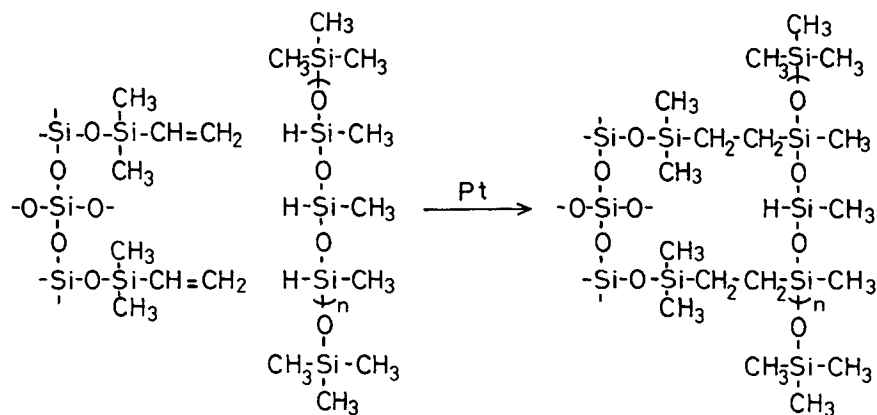
In this work, we prepared PDMS having a vinyl group and a SiH group and applied it to the preparation of porous PDMS membrane by hydrosilylation cure in the presence of additives (R = H, —C<sub>2</sub>H<sub>5</sub>, —CH<sub>2</sub>CH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>, and —CH<sub>2</sub>CH<sub>2</sub>—) having an OH group. The effect of the additive on the pore formation in PDMS membranes was examined by measuring the cure time, hydrogen generation, SEM photographs, and ultrafiltration properties.

## EXPERIMENTAL

### Materials

PDMS membranes were formed by hydrosilylation cure (Scheme 1) between PDMS (1) having a vinyl group (0.22 mmol/g) and PDMS (2) having a SiH group (16 mmol/g) in the presence of platinum catalyst. To obtain high mechanical strength of the cured PDMS membrane, we prepared PDMS (1)

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scheme 1

having a Q resin structure designated in conventional silicone nomenclature<sup>1</sup>: Q: SiO<sub>2</sub>. PDMS (1) having both Q resin units and vinyl groups was prepared from tetraethoxysilane, dimethylvinylethoxysilane, and chlorotrimethoxysilane (1 : 0.012 : 0.8 mol %) according to the literature.<sup>8</sup> The solventless resin prepared was mixed with 20 wt % of SiO<sub>2</sub> filler (density: 2.65, average diameter: 3.1 μm) and platinum catalyst prepared from a H<sub>2</sub>PtCl<sub>6</sub>-methanol solution. PDMS (2) having a SiH group, poly(methyl hydrogen siloxane), was made by ring-opening polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane in acidic catalyst at 80°C as reported elsewhere.<sup>9</sup> The properties of the PDMS compound and the formulation are listed in Table I. The amount of the catalyst in the compound is 20 parts per million of Pt based on the total weight of PDMS (1) and (2).

### Membrane Preparation

For processing membrane preparation, materials were compounded, degassed *in vacuo*, cast on Teflon sheets with a pair of 150 μm thick spacers, and then

cured at 30°C for 2 h. To obtain satisfactory physical properties of membranes, the weight ratio of PDMS (1) to PDMS (2) was fixed at 10 : 1. The properties of the elastomer at 2.5 mm thickness and 10 mm width are as follows: hardness, 40; strength, 30 kg/cm<sup>2</sup>; and elongation, 100%.

Fourier-transfer IR spectra via the attenuated total reflection method (FTIR-ATR spectra) were taken at a 45° angle to the incident light with a Shimadzu 8100 spectrometer.

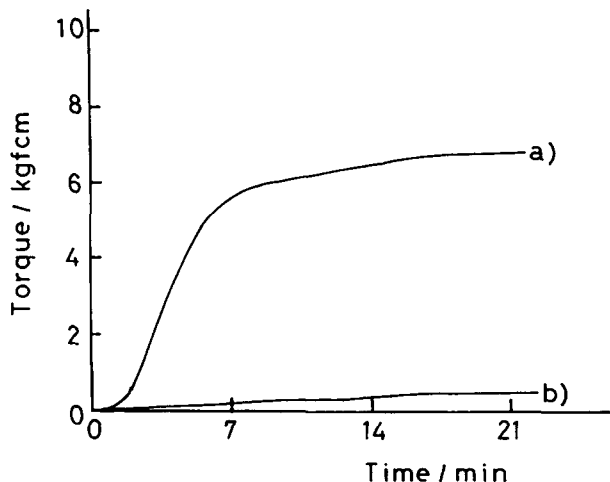
### Permeation Measurements

The membranes of 43 mm effective diameter were used for permeation experiments under the applied pressure of 760 mm H<sub>2</sub>O and a stirring rate at 200 rpm using an Amicon-type 8050 cell. The ultrafiltration rate of water and 0.1 wt % of aqueous solution of poly(ethylene glycol) (PEG) (MW = 2 × 10<sup>6</sup>) was calculated from the flow rate of the eluted solution and was expressed by volume flux per unit area of the membrane and unit time (m<sup>3</sup>/m<sup>2</sup> s). The experimentally obtained rejection, *R*, of PEG is defined as  $R = (1 - A_a/A_b) \times 100$ , where *A<sub>a</sub>* and

**Table I** Formulation and Properties of PDMS Compounds

Type	Content (mmol/g)	Viscosity (cp)	Part (ppm)	
PDMS (1)	Vinyl	0.22	7 × 10 <sup>4</sup>	100
PDMS (2)	SiH	16.00	15	10
SiO <sub>2</sub>	Filler	—	—	20
Pt cat. <sup>a</sup>	Catalyst	—	—	0.002

<sup>a</sup> Methanol solution of chloroplatinic acid was used.



**Figure 1** Typical torque curve (a) of PDMS compound without additive. Cure temperature: 30°C. Curve (b) is reference data without the compound.

$A_b$  denote the area of the elution curve of HPLC for the solute measured before and after the permeation, respectively.

## RESULTS AND DISCUSSION

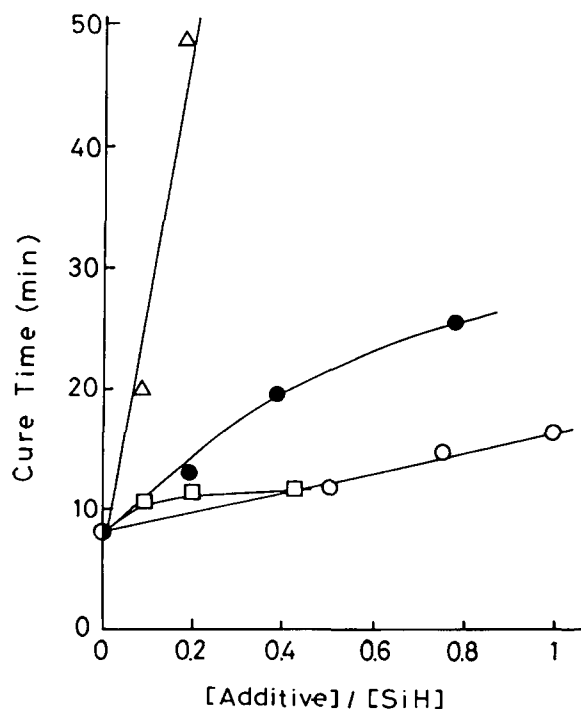
### Hydrosilylation Cure and Hydrogen Production

Figure 1 shows the typical torque curve of the PDMS compound at 30°C. The value of the torque increased with time and became constant at longer than about 8 min. However, in the presence of an additive such as water, we could not obtain the torque curve because the hydrogen formation in the measurement cell interferes with the measurement. Therefore, we qualitatively estimated cure time of PDMS compounds by use of tack free time; the value is defined as the time for the compound surface to become free from tack when the compound is cast on the glass substrate in about 500  $\mu\text{m}$  thickness. To confirm this, the value without additives was compared with the data of the torque curve. Figure 2 shows the cure time of the compounds at various mol ratios,  $[\text{additive}]/[\text{SiH}]$ , of the additive to SiH group of PDMS (2) in the compound. The value without the additive is almost equal to that (about 8 min) for the torque experiment (Fig. 1). This shows that the value estimated from the tack free time is reasonable to estimate the cure. The values of the cure time in Figure 2 increase with an increase in the additive concentration in the compound. However, for 2-methoxyethanol addition at greater than  $[\text{additive}]/$

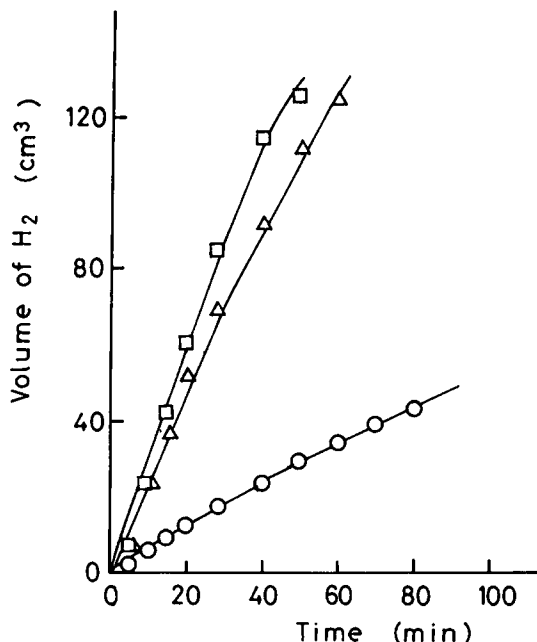
$[\text{SiH}] = 2.5$ , unfortunately, no membrane formation occurred.

Also, Figure 2 compares the cure time for compounds having water, ethylene glycol, ethanol, and 2-methoxyethanol. In the presence of these additives, the cure time becomes long relative to that of the compound without the additives. It is thought that the addition of the hydroxy compounds results from consumption of the curing sites such as the SiH group; hydrogen generation occurs in accordance with the equation in Scheme 2. The cure of the compound containing 2-methoxyethanol is much slower than those with ethanol, ethylene glycol, and water. Here, in the compound having 10 g of PDMS (1), 1 g of PDMS (2), and 0.1 g of the additive, the mol ratio of the additive to the SiH group for 2-methoxyethanol, ethylene glycol, ethanol, and water is 0.082, 0.071, 0.20, and 0.35, respectively. Although the content of 2-methoxyethanol in the compound is lower than those of ethanol and water, the cure for the former compound is much slower than that for the latter ones. It appears likely that the addition of 2-methoxyethanol inhibits the cure reaction.

We measured amounts of the hydrogen generated



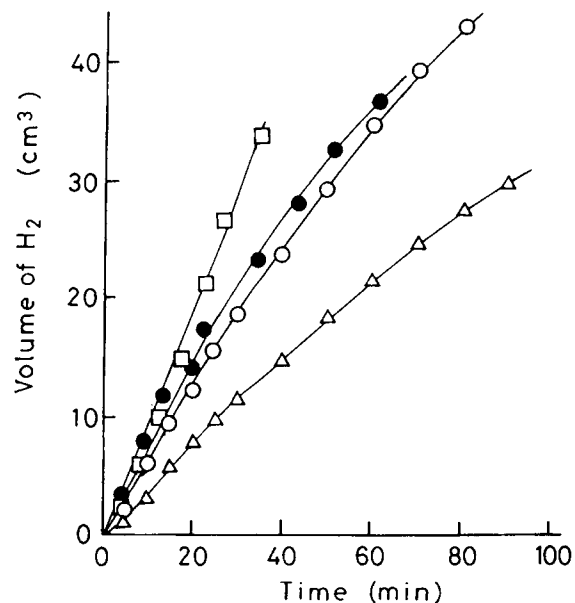
**Figure 2** Cure time of PDMS compound having (○) water, (□) ethylene glycol, (●) ethanol, and (△) 2-methoxyethanol at various  $[\text{additive}]/[\text{SiH}]$  ratios. Cure temperature: 30°C.



**Figure 3** Volume of  $H_2$  generation at various times for PDMS compounds having water. Weight ratio of the compound content: (□) PDMS (1) : PDMS (2) : water = 10 : 1 : 1, (Δ) 10 : 1 : 0.5, and (○) 10 : 1 : 0.1.

at various times after mixing of PDMS (1) and PDMS (2) by use of a simple method as follows: 10 g of PDMS (1) and PDMS (2) mixed was placed in 50 mL of glass vessel equipped with Pyrex glass tube having a 6 mm  $\phi$  inner diameter in which there is soapsuds. When hydrogen gas was produced in the vessel, the position of the soapsuds in the tube moves with time. The volume of hydrogen generation in the vessel was measured from the position change. Figure 3 shows volume of hydrogen generated at various  $[H_2O]/[SiH]$  ratios. The amounts of hydrogen gas linearly increased with time after the mixing of PDMS (1) and PDMS (2). The increase of the additive concentration in the compound results in the high rate of the hydrogen generation.

Figure 4 shows the amounts of the hydrogen generation for various additives. The rate of hydrogen generation for the compounds containing ethylene glycol, ethanol,  $H_2O$ , and 2-methoxyethanol decreased in that order. The highest rate of the hydrogen generation for ethylene glycol addition may



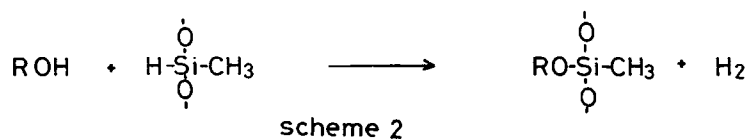
**Figure 4** Relationship between  $H_2$  generation and time: (○) water, (□) ethylene glycol, (●) ethanol, and (Δ) 2-methoxyethanol at various  $[additive]/[SiH]$  ratios. Cure temperature: 30°C.

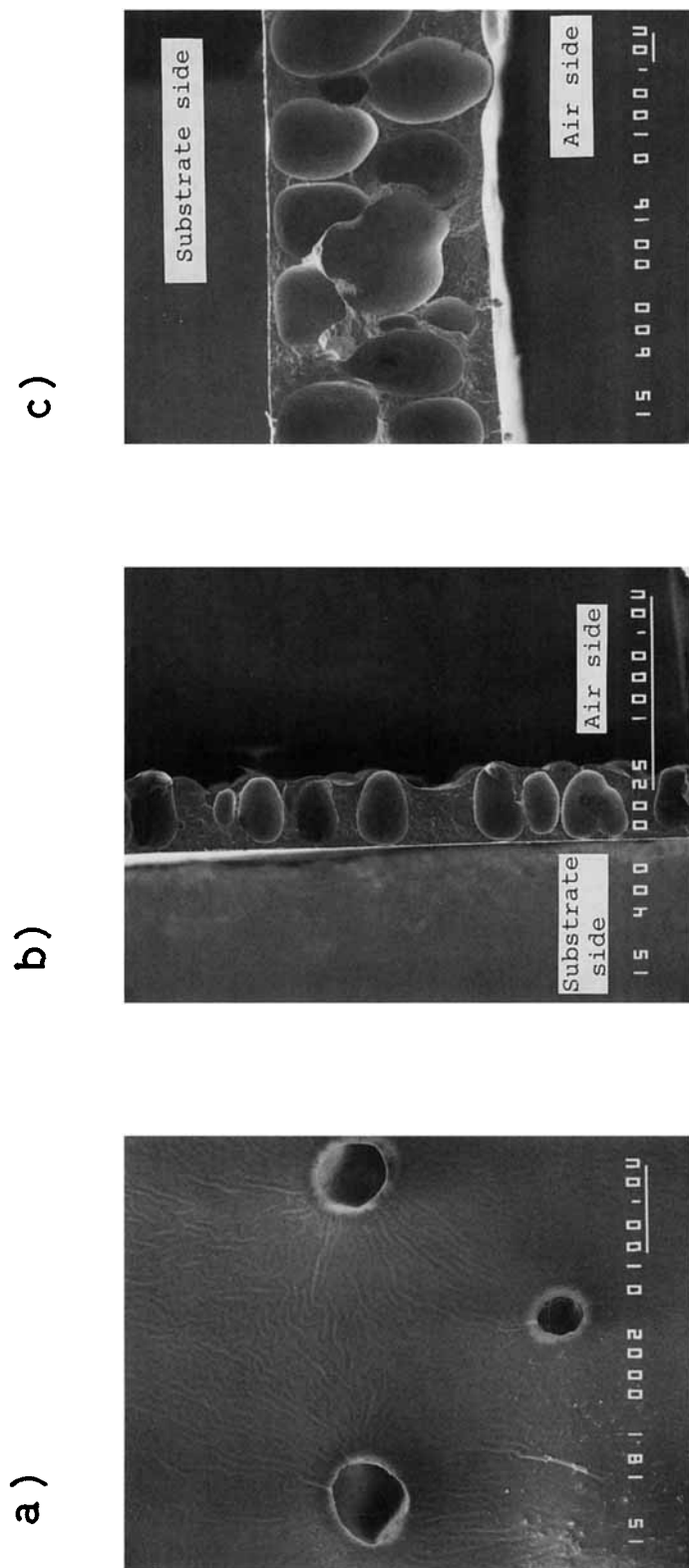
be due to two hydroxy groups in the molecule structure relative to ethanol and 2-methoxyethanol.

We confirmed the consumption of the SiH group of poly(methyl hydrogen siloxane) on the cured membrane using the FTIR method. The spectrum of the membrane without the additive contains the peak at  $2200\text{ cm}^{-1}$ , assigned to the SiH group.<sup>10</sup> But in the presence of water during the cure, the peak of the membrane disappeared. This result suggests that the consumption occurs by the reaction of hydrogen generation (Scheme 2).

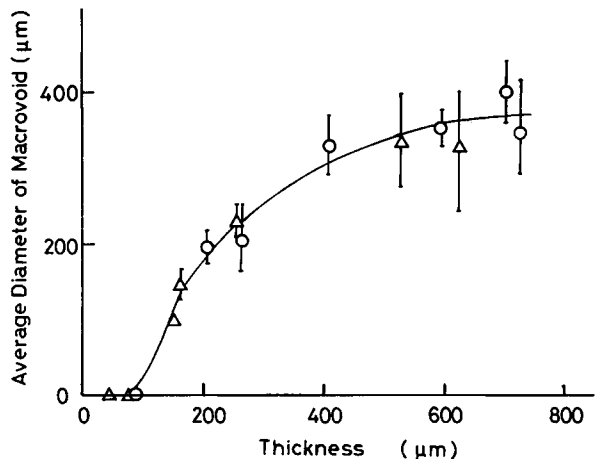
#### Formation of Porous Membrane

It was well known in silicone foam<sup>11</sup> that, according to Scheme 2, water in the elastomer results in the formation of many pores during the hydrosilylation cure. Figure 5(a) shows scanning electron microscopy (SEM) of surface for the PDMS membrane prepared from the compound at the weight ratio of PDMS (2) : water = 1 : 0.1. The surface on the air side contains many voids having about 150  $\mu\text{m}$  di-





**Figure 5** Scanning electron microscope of PDMS membranes: (a) air-side surface; (b, c) cross section of the membrane prepared from compound having water.

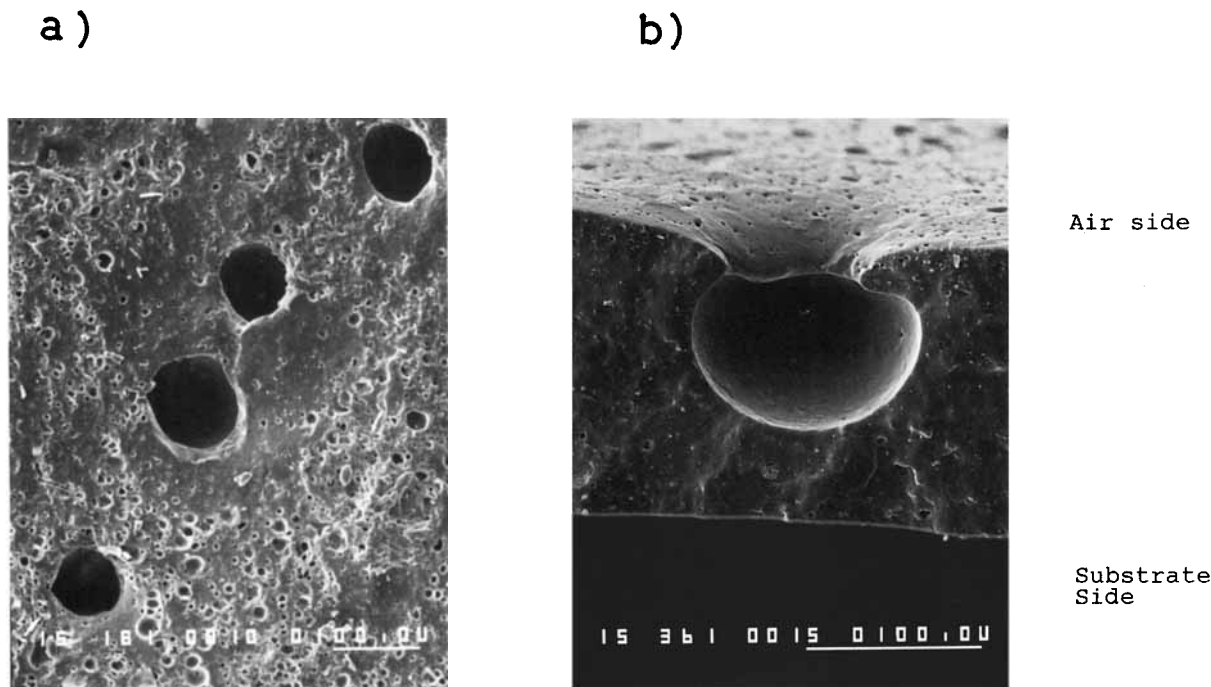


**Figure 6** Average diameter of macrovoids in the cross section of the membrane having various membrane thicknesses: (○) water; (△) 2-methoxyethanol.

ameter, whereas at the membrane opposite, these pores were not be observed at magnification 10,000X. As shown in Figure 5 (b), the membrane has a heterogeneous porous cross section in about 310–370 μm thickness. Substantially, the cross section consists of a macrovoid and a skin layer on the substrate side. In Figure 5 (c), the cross section of the membrane having about 720 μm thickness has many macrovoids in the range of about 300–400 μm di-

ameter. Clearly, the increase of the membrane thickness increases the number of the macrovoids in the cross section. Figure 6 shows the relationship between the average diameter of the macrovoids in the cross section and the thickness of the membranes. The size of the macrovoid becomes large with increasing thickness of the membrane in the range of 100–400 μm. At larger than 400 μm thickness, the diameter of the macrovoids was about 300–400 μm. On the other hand, at less than 100 μm thickness, there were no macrovoids in the cross section of the membranes.

Figure 7 (a) and (b) shows the surface and cross section of the membrane prepared by 2-methoxyethanol addition at PDMS (2) : additive = 1 : 0.1. In addition to the macrovoids having about 100 μm diameter, there are many small pores in the layer on the substrate side. However, the small pores were not observed in the photograph [Fig. 5 (a)] for the water addition. As mentioned, the addition of 2-methoxyethanol brought about the slow cure and low hydrogen generation relative to those of water addition. Thus, the formation of the small foams in the membrane is closely related in the cure condition. Alternatively, both the rates of cure and H<sub>2</sub> generation for water are so large that the resulting foams remained as a macrovoid in the membranes cured.



**Figure 7** SEM photographs of (a) air-side surface and (b) cross section of PDMS membrane prepared from the compound having 2-methoxyethanol.

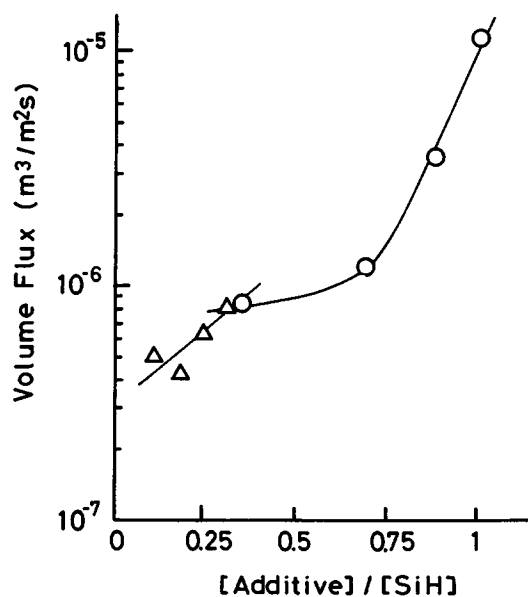
**Ultrafiltration Properties of Porous Membranes**

We evaluated the ultrafiltration behavior of porous membranes of about 120–150 μm thickness. Unfortunately, the membranes prepared from ethylene glycol addition could not be used for the permeation experiments, because of significant swelling in water.

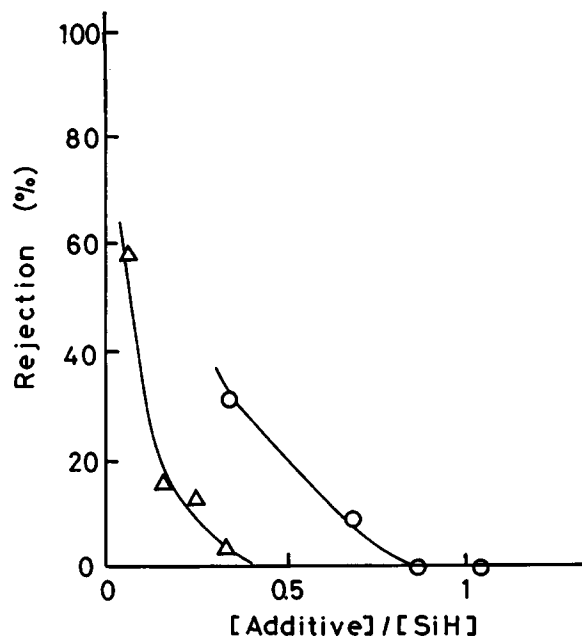
Figure 8 shows the volume flux of 0.1 wt % of PEG aqueous solution for membranes prepared at various ratios of [additive]/[SiH]. The value of the volume flux increased with increasing concentration of each additive. This suggests that the pore size of the membranes becomes large with increase of the additive concentration in the compound. As shown in Figure 3, the increases of water addition to the compound accelerated the hydrogen generation. In such cases, the acceleration of the hydrogen generation makes the pore size large.

In water addition at lower than 0.3 of the mol ratio, the volume flux was extremely low and permeation experiments could not be carried out; SEM observation suggested the homogeneous cross section of the membrane.

On the other hand, in the cases of ethanol addition, no permeation of water and PEG solution through the membrane was observed in the similar range of the mol ratio (Fig. 2). The SEM photograph of the membranes for ethanol addition showed a homogeneous cross section of the membrane. In this case, the viscosity of the compound containing



**Figure 8** Volume flux of 0.1 wt % aqueous solution of PEG for membranes prepared at various [additive]/[SiH] ratios: (○) water; (△) 2-methoxyethanol.



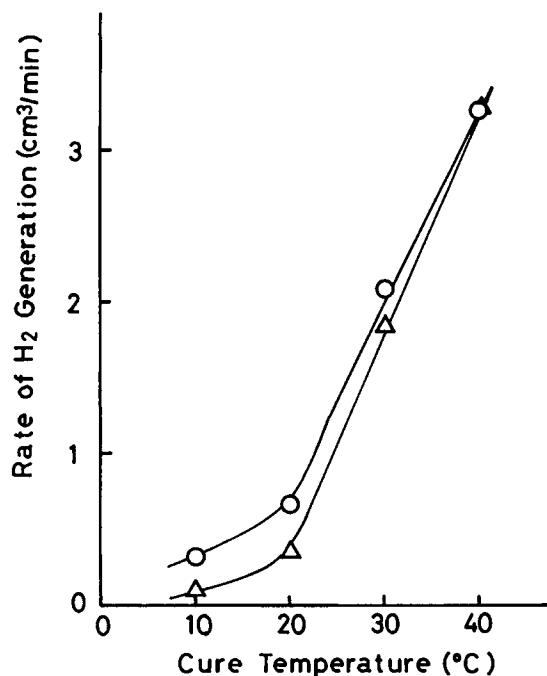
**Figure 9** Plots of rejection of PEG for PDMS membranes prepared at various [additive]/[SiH] ratios: (○) water; (△) 2-methoxyethanol. The concentration of PEG (molecular weight:  $2 \times 10^6$ ) in feed solution is 0.1 wt %.

ethanol is extremely low relative to that of the compound with water, because of good miscibility of the PDMS compound with ethanol. Thus, the diffusion of hydrogen foams in the uncured compound may be much faster than those of the other additives. As a result, the number of foams remained in the uncured membrane is small.

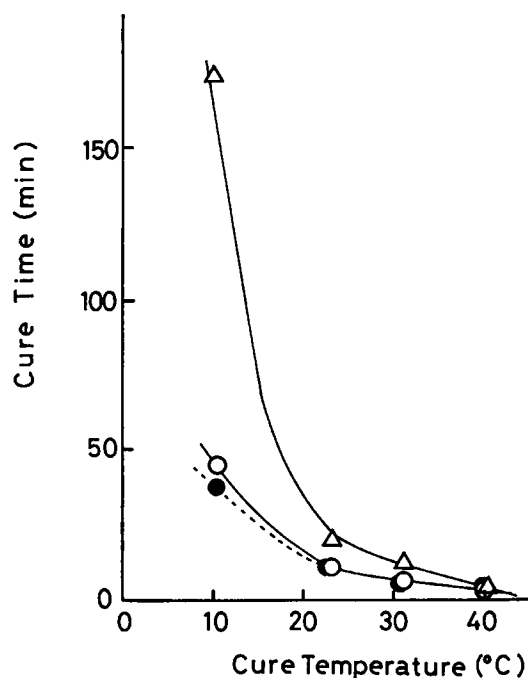
Figure 9 shows the rejection of PEG (MW =  $2 \times 10^6$ ) for porous membranes prepared from the compound with water and 2-methoxyethanol addition. The value of the rejection decreased with increase of the mol ratio. The molecular size of PEG of  $2 \times 10^6$  molecular weight is about  $6 \times 10^{-8}$  m (Ref. 12) and the size of PEG is much smaller than that of the round macrovoids observed by the SEM photograph of the membranes. The rejection of the PEG molecule by the membranes may result from the size of the skin layer on the substrate side.

**Effect of Cure Temperature**

The cure rate and the hydrogen formation depends on the cure temperature, as shown in Figures 10 and 11; both rates of the cure and hydrogen generation increases with increase in the cure temperature. Figure 12 shows rejection of PEG at various cure temperatures. With increasing the cure temperature,



**Figure 10** H<sub>2</sub> generation rate at various cure temperatures. Additive; (O) water; ( $\Delta$ ) 2-methoxyethanol. The ratio of [additive]/[SiH] for water and 2-methoxyethanol is 0.35 and 0.082, respectively.

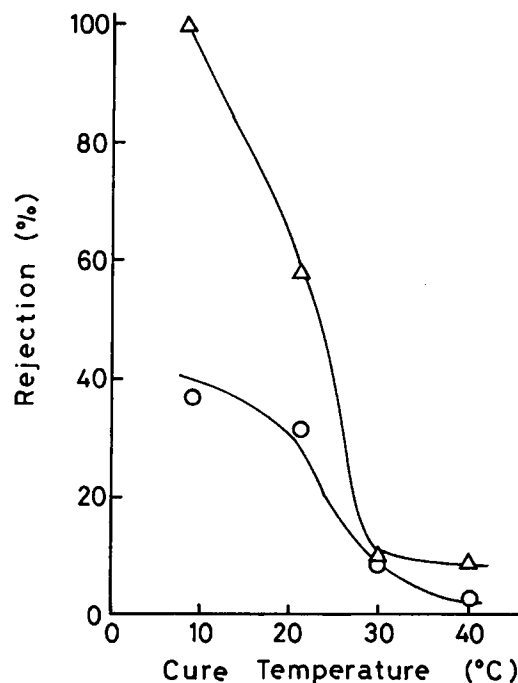


**Figure 11** Cure time of the PDMS compounds at various cure temperatures. Additive; (O) water; ( $\Delta$ ) 2-methoxyethanol. The ratio of [additive]/[SiH] is shown in the caption of Figure 10.

the rejection of PEG decreased, especially in the range of 10–30°C for 2-methoxyethanol addition. As mentioned above, the increases of the additive concentration in the compound brought about a late slow cure and high H<sub>2</sub> generation. The condition at 30°C leads to the formation of large macrovoids in the membranes and high permeation rate of the solute solution through the membranes. But, at 40°C, the H<sub>2</sub> generation and the cure time for the compound of 2-methoxyethanol addition are almost equal to those of water addition. Although the hydrosilylation cure easily occurs, the H<sub>2</sub> generation is significantly accelerated by the increase in the cure temperature and causes many macrovoids in the membrane. In such cases, the resulting macrovoids in the membrane is favorable for permeating the macromolecular solute.

## CONCLUSION

Porous PDMS membranes were prepared by the generation of hydrogen foams during the catalytic hydrosilylation cure of a silicone compound containing vinyl group and SiH group, when water and



**Figure 12** Plots of rejection of PEG via cure temperature of PDMS compound. Additive: (O) water; ( $\Delta$ ) 2-methoxyethanol. The ratio of [additive]/[SiH] is shown in the caption of Figure 10.



2-methoxyethanol is in the presence of the compound. The effect of the additive on the cure reaction and hydrogen generation was examined at various temperatures. The characteristics of porous PDMS membrane and the application to ultrafiltration were studied.

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