

Acknowledgments

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Nomenclature

d	= diameter of pipe	[m]
l	= length of pipe	[m]
Δp	= pressure drop	[Pa]
Re	= Reynolds number	[—]
u	= average velocity of fluid	[m/s]

λ	= friction factor ($2\Delta p d / \rho u^2 l$)	[—]
ρ	= fluid density	[kg/m ³]

Literature Cited

- 1) Imahara, K., K. Nakamura, T. Komatsu and T. Nakagawa: *Nippon Kagaku Kaishi*, 1551 (1983).
- 2) Lee, W. K., R. C. Vaseleski and A. B. Metzner: *AIChE J.*, **20**, 128 (1974).
- 3) Nakamura, K.: *Kobunshi*, **34**, 86 (1985).
- 4) Virk, P. S.: *AIChE J.*, **21**, 625 (1975).
- 5) White, D. A.: *Nature*, **212**, 277 (1966).

PREPARATION OF A NEW HYDROGEL AND POROUS GLASS COMPOSITE MEMBRANE

KATSUTO OTAKE, TOMOYA TSUJI, MIKIO KONNO
AND SHOZABURO SAITO

Department of Molecular Chemistry and Engineering, Tohoku University, Sendai 980

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Introduction

Recently it has been learned that hydrogels, mixtures of crosslinked polymer networks having ionized groups and fluid media, undergo a discontinuous volume change with changes in environment such as temperature, pH or solvent composition.³⁾ This volume-phase transition is accompanied by changes in transport properties in the gels. Accordingly, the phase transition may be utilized in the creation of a new type of membrane with switching function.²⁾ However, the gels' mechanical weakness must be overcome before they can be utilized in membranes. This may be attained by making a composite membrane of a gel and other materials. Recently, Nishi and Kotaka synthesized a gel membrane made of poly(oxyethylene)/poly(acrylic acid) interpenetrating polymer networks.¹⁾ However, their method is restricted to polymer pairs which form an interpolymer complex.

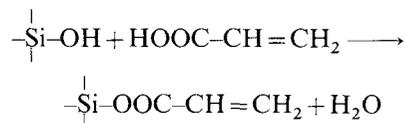
In this paper, we report a new method for synthesizing composite membranes that should be applicable to various polymer-gels. The permeability of one new type of composite membrane of polymer-gel and

porous glass is also described.

1. Experimental

The inorganic porous substance used was porous glass plate (Asahi Glass Co. Ltd., average pore size = 6900Å), and the gel employed was crosslinked acrylamide (Am)/acrylic acid (AA) random copolymer.

Prior to the preparation of the composite membrane, the glass surface was modified by the following dehydration condensation reaction of AA and hydroxyl groups on the surface:



To support the gel on the porous glass, radical polymerization was employed. The two monomers, Am and AA, were used together with a crosslinking reagent, *N,N'*-methylenebisacrylamide, and an initiation reagent, potassium persulfate. A prescribed amount of the chemicals was dissolved in water at a total monomer content of 10 wt% and an Am/AA mole ratio of 4 to 1. The porous glass was immersed in the aqueous monomer solution and saturated with it. Then polymerization was performed at 70°C for

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15 min. During polymerization, the gel formed was chemically fixed on the surface of the porous glass by reaction with the vinyl groups introduced by the surface modification.

All experiments were carried out at 25°C with the composite membrane prepared. The volume flux of aqueous acetone solutions was measured at various acetone concentrations. The pressure downstream of the membrane was maintained at atmospheric pressure and the pressure difference across the membrane ranged from 100 kPa to 1500 kPa. The compositions of the feed and the permeate solution were measured by gas chromatography.

The swelling behavior of the gel is thought to affect membrane permeability. However, since it was difficult to observe the swelling behavior of the gels in the composite membrane, bulk gel of the same composition as the membrane was prepared. The equilibrium swelling volume of the bulk gel in the aqueous acetone solutions was measured at 25°C, and the ratio of the swelling volume V to the initial volume V_0 of the gel, the swelling ratio V/V_0 , was determined.

Aqueous acetone solution containing poly(oxy-

Table 1.* Molecular weight and molecular weight distribution of POE

Reagent	M_n	M_w	M_w/M_n
POE- 2000	2149	2192	1.019
POE- 7000	7201	7283	1.011
POE-20000	23549	24516	1.041

* Measured by GPC.

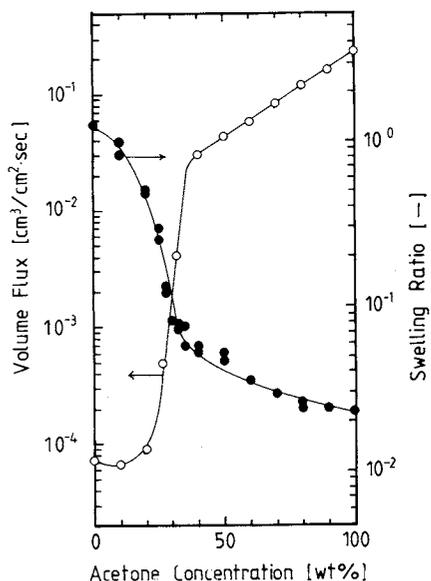


Fig. 1. Acetone concentration dependence of volume flux (open circles) of composite membrane at pressure difference 1500 kPa and swelling ratio (closed circles) of bulk gel. Experiments were performed at 25°C.

ethylene)s (POE) of three molecular weights, POE-2000, -7000 and -20,000, were used to examine the permeability further, also at 25°C. **Table 1** shows the properties of the POE. The compositions of the permeate solutions were measured by gel permeation chromatography (GPC) with refractive index unit.

2. Results and Discussion

Figure 1 shows the volume flux of the aqueous acetone solution through the membrane as a function of acetone concentration. In the same figure, the swelling ratio of the gel is also plotted. As the acetone concentration increased, the volume flux rapidly increased in the acetone concentration range around 30 wt%. This concentration range corresponds to that in which the swelling ratio of the bulk gels changed considerably, from the swollen state to the shrunken state. Thus the composite membrane shows low volume flux in the swollen state and a high volume flux in the shrunken state.

Over the entire range of acetone concentrations, the volume flux was proportional to the pressure difference across the membrane. In addition, the composition of the permeate solution was the same as that of the feed solution.

Figures 2a and **b** show the experimental results of the GPC curves of the feed and permeate solution. In **Fig. 2a**, when pure water was used as the solvent, POE-20000 could not be detected in the permeate solution. Furthermore, peak heights of POE-7000 and 2000 were reduced by less than one-half.

Figure 2b shows the results obtained with a 40 wt% acetone water solution solvent. The peak heights of the two POE solutions are about the same. This indicates that membrane permeability can be changed by solvent composition.

Figures 1 and **2** in this work exhibit a similarity to Nishi and Kotaka's observation on the dependence of the volume flux and the permeation characteristics on the swelling ratio.¹⁾

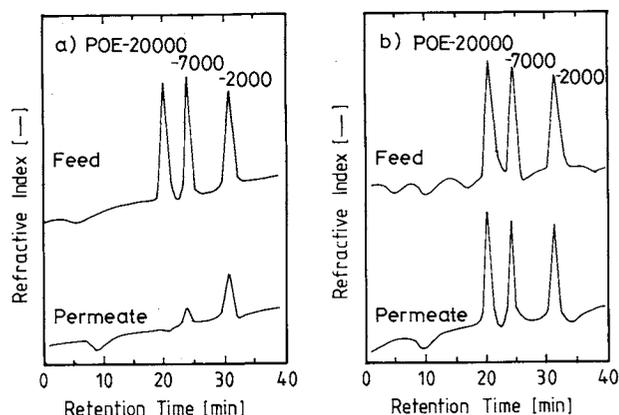


Fig. 2. GPC curves obtained with (a) pure water and (b) 40 wt% acetone water mixture at 25°C

Although the present work describes only one kind of hydrogel supported on porous glass, the preparation method proposed here would be applicable to other hydrogels with inorganic porous substances. In addition, mass transfer experiments with gel may be performed much more simply with this new type of membrane.

Literature Cited

- 1) Nishi, S. and T. Kotaka: *Macromolecules*, **18**, 1519 (1985); *idem.*, *ibid.*, **18**, 978 (1985).
- 2) Osada, Y. and Y. Takeuchi: *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 303 (1981).
- 3) Tanaka, T.: *Phys. Rev. Lett.*, **40**, 820 (1978).