

The Effect of Hexane Treatment on the Permeation of Silicone-Coated Polyethersulfone Membranes*

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Synopsis

The polyethersulfone membranes were cast from casting solutions including poly(vinyl pyrrolidone) additive. The membranes were further dried, silicone-coated, and used for the permeation study with hydrogen and nitrogen gases. It has been found that solvent hexane which was included in the silicone rubber solution for surface coating increased the pore size on the membrane surface when poly(vinyl pyrrolidone) was present in the membrane. The above effect counteracted the pore size decrease by silicone coating, and, as a result, an H₂/N₂ permeability ratio of only 8.9 was achieved as compared with 28, which was obtained when the base polyethersulfone membrane was prepared from a casting solution without poly(vinyl pyrrolidone) additive.

INTRODUCTION

In contrast to most of the fundamental works on gas permeation, in which dense homogeneous membranes are used, all of commercially important membranes possess asymmetric structures. This is natural because the combination of high flux and sufficiently high separation factor for the components of gas mixtures can be achieved by the asymmetric membrane structure. It is well known that the performance of the membrane depends largely on the condition of the formation of such asymmetric structures. There is, however, only limited work in the literature in which the effect of membrane preparation variables on the membrane performance for the gas separation has been systematically studied.¹⁻⁷

The objective of this work is to clarify the cause and effect relationship between variables involved in the membrane preparation and the membrane performance. More specifically, this is one of a series of investigations which have been conducted to clarify the effect of the pore size of the polyethersulfone base membrane and the number of the silicone coatings on the performance of the silicone rubber coated polyethersulfone membrane for gas separation. In our previous work,⁸ we have found that the maximum in the permeation rate ratio of hydrogen/nitrogen gas system achieved by silicone-coated membranes increased with a decrease in the average pore size of the base polyethersulfone film. The natural consequence of the previous work, therefore, is to decrease the average pore size of the polyethersulfone membrane further to achieve an even higher maximum permeation rate ratio. It has to be noted that all poly-

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ethersulfone films used in the previous work were prepared from the casting solution including polyethersulfone polymer and dimethylsulfoxide solvent alone. From a separate investigation on the preparation of polyethersulfone ultrafiltration membranes, it has been known that the average pore radii of membranes prepared from casting solutions without any additives were larger than those of membranes prepared from casting solutions in which polyvinyl pyrrolidone was included as an additive.⁹ Therefore, we have attempted to make polyethersulfone ultrafiltration film with poly(vinyl pyrrolidone) additive with an expectation that a higher maximum hydrogen/nitrogen permeation rate ratio would be obtainable when the polyethersulfone films were dried and coated with silicone rubber. The result of the above investigation is presented in this paper.

EXPERIMENTAL

Materials used in this work is the same as those reported in the earlier paper.⁸ Curing agents I (tetraethyl orthosilicate) and II (dibutyltin dilaurate) were supplied by Aldrich Chemical Company Inc.

The method to prepare polyethersulfone membranes is the same as that reported in the earlier paper⁸ except poly(vinyl pyrrolidone) was included in the casting solution as a nonsolvent additive. The composition of the casting solution is given in Table I.

The method to prepare silicone-coated polyethersulfone membranes is the same as that reported in the earlier paper.⁸ In some experiments pure hexane solvent was used, instead of hexane solution including silicone and curing agents, in order to investigate the effect of hexane solvent during the coating procedure.

TABLE I
Composition of Film Casting Solutions and Pore Size Distribution of UF Membranes^a

Membranes	1	2	3	4
<u>Composition of film casting solutions</u>				
PES concn (wt %)	23	23	23	23
PVP concn (wt %)	0.77	2.31	6.52	9.77
<u>Pore size distribution^b</u>				
$\bar{R}_{b,1} \times 10^{10}$ m	39	38	24	28
$\sigma_1/\bar{R}_{b,1}$	0.10	0.22	> 0.49	> 0.49
$\bar{R}_{b,2} \times 10^{10}$ m	155	153	104	152
$\sigma_2/\bar{R}_{b,2}$	~ 0.07	0.17	0.47	0.48
h_2	0.85	0.55	0.15	0.045

^a Solvent, DMSO.

^b $\bar{R}_{b,1}$, $\bar{R}_{b,2}$ = average pore radii of the first and second distributions, respectively, σ_1 , σ_2 = standard deviations of the first and second distributions, respectively, h_2 = number of the second pore/the number of the first pore. Numerical values for the above parameters were obtained by the method described in Ref. 12 using transport equations based on the surface force-pore flow model.

The method of ultrafiltration experiments is the same as that reported in the earlier paper.^{8,10} Poly(ethylene glycol)s of different molecular weights were used as reference solutes.

The method of gas permeation experiment is the same as that reported in the earlier paper.^{8,11}

RESULTS AND DISCUSSION

The data in Table I include the pore size distribution on the surface of the ultrafiltration (UF) membrane. The pore size distribution was calculated based on the surface force-pore flow model¹² so that the given pore size distribution could best fit the experimental data on the separation of reference polyethylene glycol solutes. Table I indicates that there are two kinds of pores in each UF membrane, one in the range of $24\text{--}39 \times 10^{-10}$ m, called the first pore, and the other in the range of $104\text{--}155 \times 10^{-10}$ m, called the second pore. As the amount of poly(vinyl pyrrolidone) (PVP) in the casting solution increases, the ratio of the number of second pores to that of the first pores decreases, which lowers the average pore size on the membrane surface. Since there are few first pores in the UF membranes which are prepared from the casting solution without PVP additive,⁹ it is believed that the first pores arise only in the presence of PVP.

Figure 1 shows the results of gas permeation experiments with and without silicone coatings. Before the silicone coating the permeability (defined as permeation rate per unit pressure) decreases with an increase in the amount of PVP added to the membrane casting solution, indicating that the average pore size of the dry polyethersulfone membrane also decreases with an increase in the amount of PVP. The ratio of hydrogen permeability to that of nitrogen $\alpha_{\text{N}_2}^{\text{H}_2}$ is constantly 3.7, indicating the dominance of Knudsen flow, since the theoretical permeability ratio is $\sqrt{28/2} = 3.7$. After three coatings the highest permeation rate ratio $\alpha_{\text{N}_2}^{\text{H}_2}$ achieved was only 8.9, which was far below the maximum permeation rate of 28 obtained in our previous work.⁸ Therefore, the experimental results were against our expectation that we would be able to achieve a higher maximum permeation rate ratio by adding PVP into the casting solution and thus decreasing the average pore size of the base polyethersulfone membrane. Permeability data shown in Figure 1, however, reveal more of the film coating mechanism. With respect to membrane 1 (prepared from the casting solution with PVP content of 0.77%) the order in the hydrogen permeability is

before coating > after the 3rd coating

> after the 2nd coating > after the 1st coating

with respect to membrane 4 (prepared from the casting solution

with PVP content of 9.77%) the order is completely reversed

after the 1st coating > after the 2nd coating

> after the 3rd coating > before coating

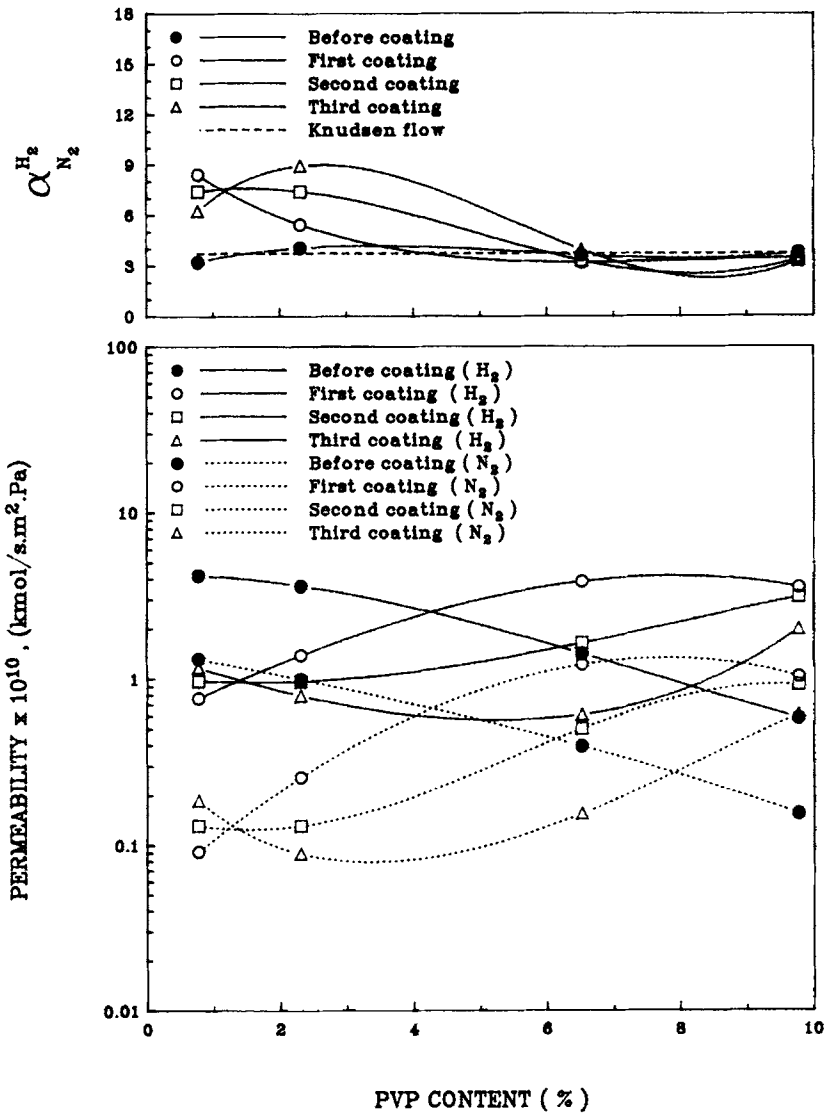


Fig. 1. Gas permeability data of dry polyethersulfone membranes with and without silicone coatings. Membranes, 1-4; operating pressure, 345 kPa g (= 50 psig); temperature, 23-25°C; effective film area, 10.2 cm².

Membranes 2 and 3 which were prepared from casting solutions with PVP contents of 2.31 and 6.52%, respectively, are intermediate in the permeability order. Considering that membrane 1 has the largest average pore radius with the largest number of the 2nd pore and membrane 4 has the smallest average pore radius with the smallest number of the 2nd pore, the above experimental observations can be explained when: The second pore governs the response of membrane 1 to the silicone coating and the first pore governs the response of membrane 4 to the silicone coating. Further, the second pore (larger pore) is quickly closed by the first coating and then gradually opened by the following

coatings, while the first pore (smaller pore) is quickly enlarged during the first coating and then gradually closed by the following coatings. Thus, the permeability data shown in Figure 1 is considered to be the result of the combination of the opening and closing of the first and second pores.

It is easy to understand that pores are closed by progressive silicone coatings, but the enlargement of the pore by the coating was totally unexpected. We have attributed this phenomenon to the effect of hexane solvent used in the coating procedure. In order to confirm the above assumption, four dry membranes 1h, 2h, 3h, and 4h were produced by drying UF membranes 1, 2, 3, and 4 and then tested for their permeabilities. The results are shown in Figure 2 as solid lines for He, H₂, and N₂ gases. Comparing permeability data before silicone coating in Figure 1 and before hexane treatment in Figure 2, the general tendency is the same, i.e., the permeability decreases with an increase in the PVP content in the casting solution. This is natural since dry 1h, 2h, 3h, and 4h membranes and dry 1, 2, 3, and 4 membranes were produced by drying wet membranes from UF membrane batch 1, 2, 3, and 4. Membranes 1h-4h were then subjected to exactly the same procedure as that of silicone coating except

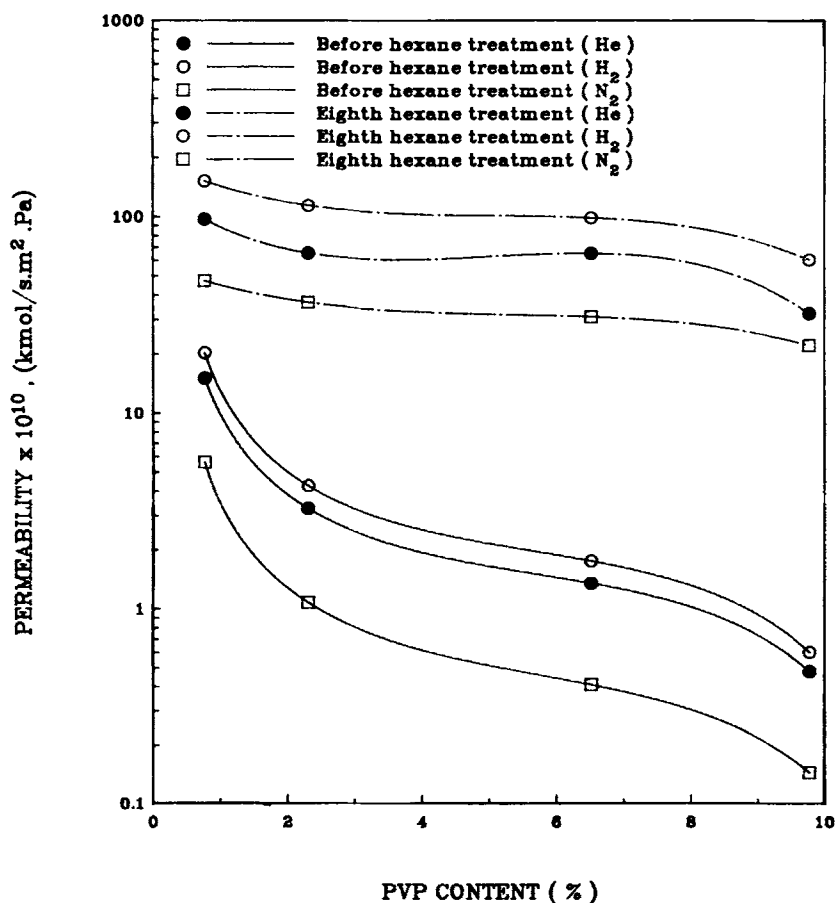


Fig. 2. Gas permeability data before and after hexane treatment. Membranes, 1h-4h; operating conditions same as Figure 1.

hexane solvent alone was used instead of the solution including silicone and curing agents. This procedure is called hexane treatment hereafter and such hexane treatments were repeated eight times. As the data in Figure 2 show, an enormous increase in the permeability was observed after the hexane treatment. When the increase in the permeability after the eighth hexane treatment is plotted versus PVP content in the casting solution, a unique relationship is found (Fig. 3), indicating that the PVP content in the casting solution has a strong effect for the enlargement of the pore.

It is known from our separate investigation⁹ that a part of PVP added into the casting solution remains in the membrane even after the gelation procedure is completed. These PVP molecules are supposed to remain even after the membranes are dried. The presence of PVP molecules seems to be necessary to form first pores (small pores) around PVP molecules when membranes are gelled.⁹ A strong increase in the permeability at a high PVP content shown in Figure 3 can therefore be understood by assuming that PVP left in dry membranes respond to hexane treatment and the first pores are enlarged. The mechanism of the pore enlargement is not known, however, at this stage. On the other hand, the second pores (large pores) the formation of which does not require the presence of PVP molecules respond only little to hexane treatment.

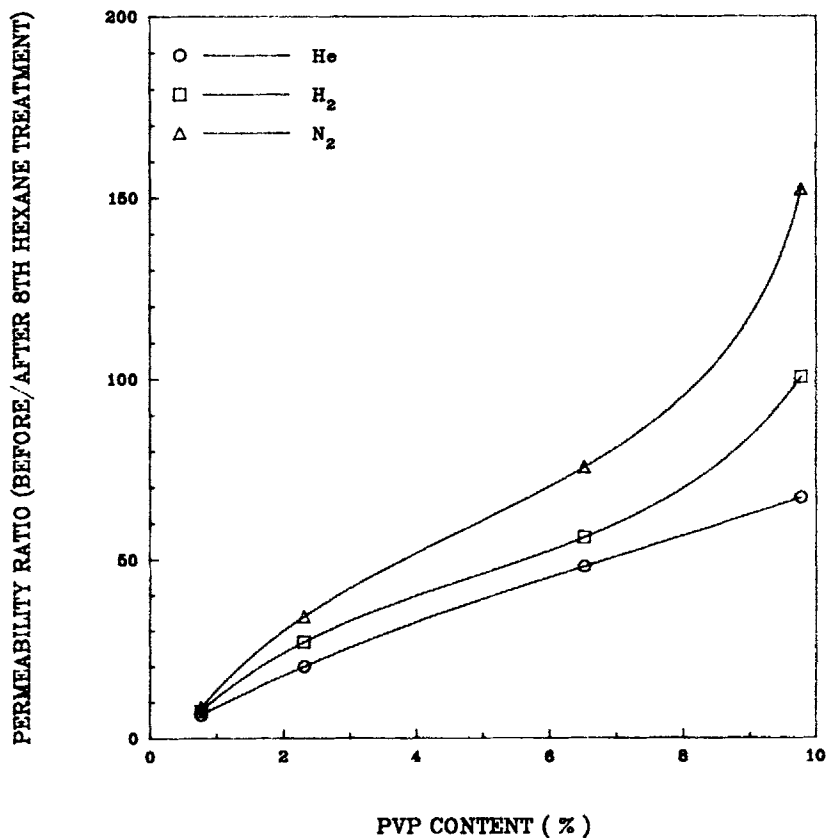


Fig. 3. Gas permeability after eighth hexane treatment versus PVP content.

The membranes 1h, 2h, 3h, and 4h which were hexane treated eight times were further subjected to six silicone coatings. The results of the permeation experiments with these coated membranes are shown in Figure 4. Surprisingly, the same pattern as that observed for membranes without hexane treatment arose. Namely, the order in the permeability of membrane 1h is

before hexane treatment > after the 6th coating

> after the 2nd coating > after the 1st coating

while the order in the permeability for membrane 4h is completely reversed

after the 1st coating > after the 2nd coating

> after the 6th coating > before hexane treatment

The above results indicate that the membrane had a memory of the polymeric structure which prevailed prior to the hexane treatment, and responded to the silicone coating procedure faithfully as if they had not been hexane-treated.

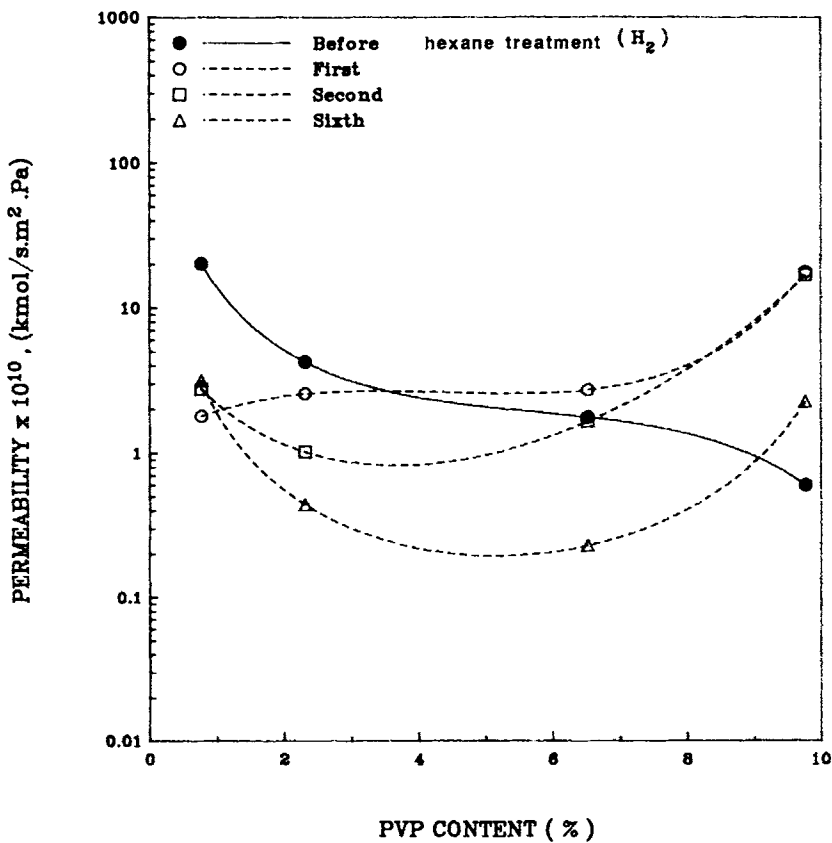


Fig. 4. Gas permeability data after hexane treatment and silicone coating. Membranes, 1h-4h; operating conditions same as Figure 1.

CONCLUSION

When poly(vinyl pyrrolidone) is used as an additive to the casting solution the average pore size of the membrane decreases with an increase in the amount of polyvinyl pyrrolidone additive. When the membrane is dried and surface coated an increase in the membrane pore size by hexane solvent and a decrease in the membrane pore size by the coating occur simultaneously. The membrane performance reflects the result of the superimposition of these two opposing effects. The degree of the pore size increase by hexane solvent is greater when the amount of PVP additive is greater.

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