

Effect of Dimethyldichlorosilane on the Oxygen Permeated Through a Siloxane-Based Polyurethane Ionomer

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ABSTRACT: The oxygen permeated through the film made by a polyurethane (PU) ionomer is demonstrated to be a siloxane-based polyurethane ionomer by infrared spectra. For siloxane-based polyurethane ionomer molecules in an aqueous solution, the surface tension was found to decrease slightly with an increase in the concentration of dimethyldichlorosilane (DMDCS) but to increase slightly with an increase in the ratio of NCO to OH. Owing to the increased phase volume of siloxane-based polyurethane ionomer molecules resulting from the hydrogen bonding effect and/or intermolecular interaction in the aqueous solution, the number-average particle sizes of these ionomer molecules increase considerably with an increase in the DMDCS concentration and the NCO/OH ratio, respectively. More importantly, the volume of the oxygen permeated through the film was found to be larger for the film made by the PU ionomer molecule with 0.02% (by weight) DMDCS than for the film made by the PU ionomer molecule without DMDCS. Our experimental results also suggest that the use of DMDCS in preparing siloxane-based polyurethane ionomers does substantially raise the amount of oxygen diffusing into the film made by these ionomer molecules. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 981–988, 1997

Key words: dimethyldichlorosilane; polyurethane ionomer

INTRODUCTION

In recent years, polyurethanes, due to their unique properties, can be used as dialysis membrane, ultrafiltration membrane, artificial kidney, artificial lung, desalination, etc., and have been utilized intensively with membranes. There is just a small amount of literature concerning the permeability of air to polyurethane (PU) film made by the siloxane-based polyurethane ionomer. In 1917, Ziegel¹ did study the diffusivity of the permeability of oxygen, nitrogen, and argon, respectively, into four different kinds of PU membranes. McBride et al.² further investigated the diffusivity

of hydrogen, oxygen, and carbon dioxide, respectively, into three kinds of PU membranes and found that the diffusivity of gas decreases with an increase in the amount of hard segment of the PU membrane and with an increase in the molecular weight of gas as well. However, the diffusivity of gas, on the other hand, increases as the amount of the soft segment of PU membrane increases. Economically, membrane used to separate gases must possess a high separation coefficient and permeability; but these two factors, in fact, conflict each other.³ To overcome this problem, the use of modified membranes with special functional groups is suggested. Since the gas permeation of the PU membrane relates to the composition of the PU substance was reported in the literature,^{4–7} we attempted to study the factors affecting the composition of siloxane-based PU ionomers^{8–11} and to further investigate the permeability of oxygen in the films made by these ionomers.

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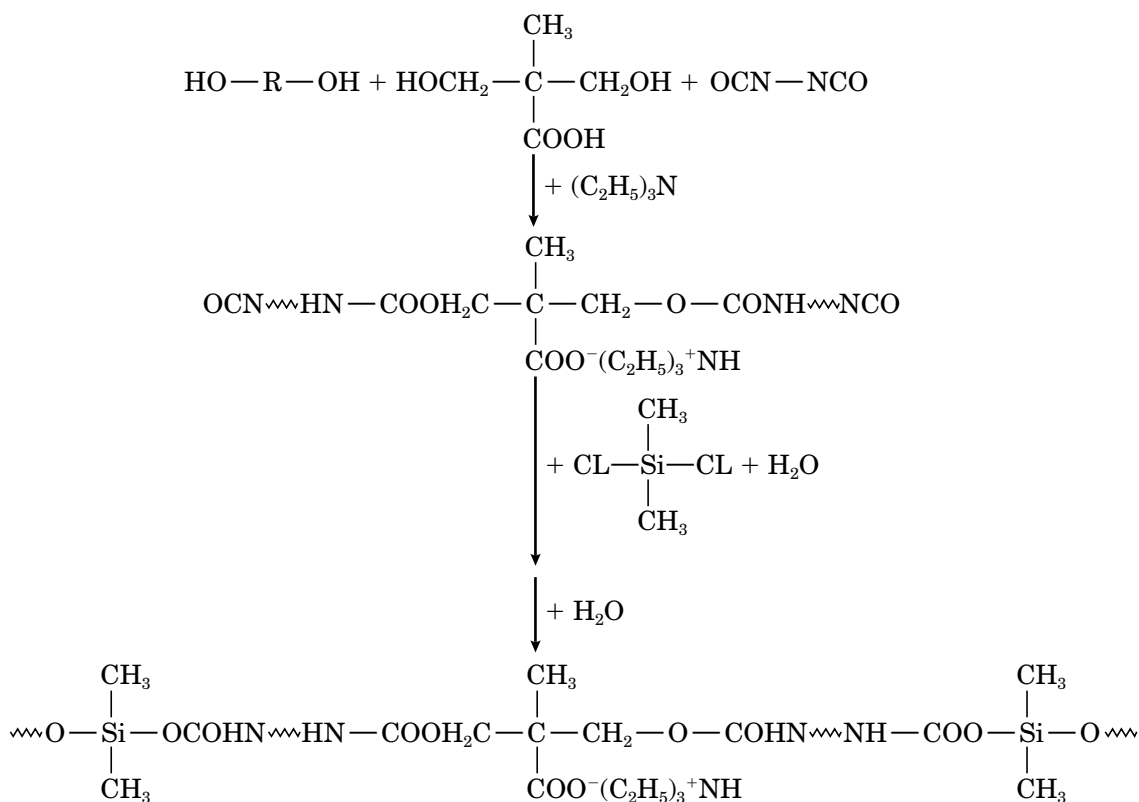
EXPERIMENTAL

Materials

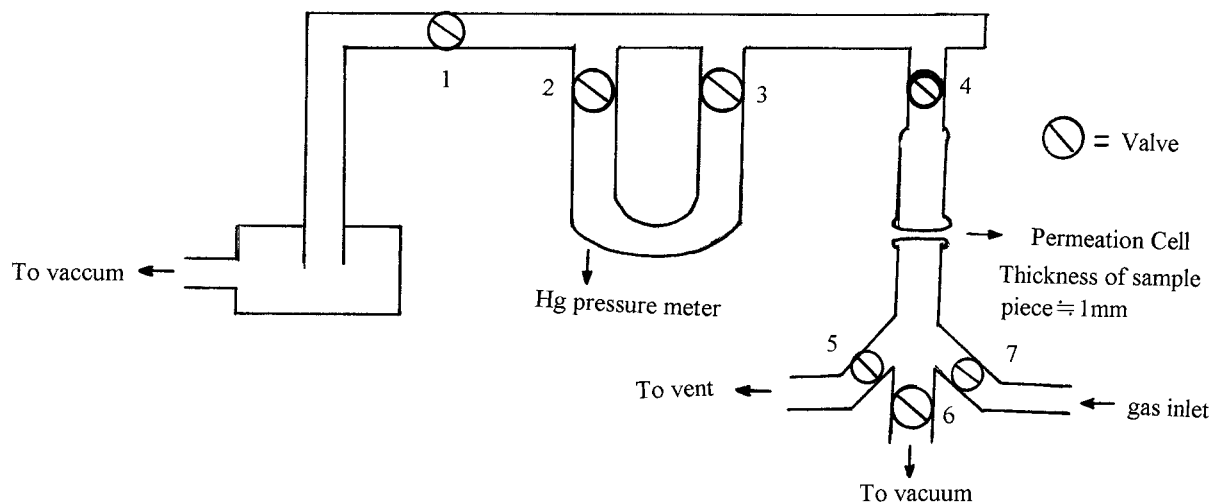
Dimethyl dichlorosilane (DMDCS) and isophorone diisocyanate (IPDI) were obtained from Aldrich Chemical Co., Inc. (U.S.A.). Dimethylol propionic acid (DMPA) and *N,N*-dimethylacetamide were purchased from Alcolac Industrial Chemicals (U.S.A.) and J. T. Baker Chemicals (U.S.A.), respectively. Triethylamine, diethylenetriamine, and acetone were supplied by Merck Co. (U.S.A.). Polyester (made by the reaction of adipic acid with 1,6-hexanediol and diethylene glycol) with a molecular weight of 2800 (OH number = 40.1) and polyethylene glycol (molecular weight = 6000) were supplied by Tai Chin Chemical Industry Co., Ltd. (Taiwan) and Sino-Japan Chemical Co. (Taiwan), respectively. Epoxy resin (BE-501, EW = 508) was received from Chang Chun Petrochemical Co., Ltd. (Taiwan). All of these chemicals were used without further purification.

Method

A 1000 mL four-necked reaction kettle equipped with a stirrer, thermometer, and condenser was charged with 0.018 equivalent of polyester (molecular weight \approx 2800; OH number = 40.1), 0.003 equivalent of polyethylene glycol (molecular weight \approx 6000), 0.009 equivalent of epoxy resin (BE-501; EW \approx 508) and 0.06 equivalent of dimethylol propionic acid in the presence of 20 g *N,N*-dimethylacetamide. Subsequently, a 0.12–0.182 equivalent of isophorone diisocyanate was added slowly and then reacted in the presence of 0.2% (by weight) dibutyltin dilaurate at around 100°C for about 3 h to form a NCO-terminated PU prepolymer. A 0.03 equivalent of triethylamine was then reacted with this NCO-terminated prepolymer dissolved in 72 g of acetone to form a quaternized NCO-terminated PU prepolymer. This quaternized NCO-terminated PU prepolymer immediately reacted further with hydrolytes of dimethyl dichlorosilane, and 340 g water was then added to form the siloxane-based PU ionomers shown below.



Siloxane-based PU ionomer



Scheme 1

After removing the acetone by blowing it out *in vacuo*, the viscosities and surface tensions of siloxane-based PU ionomer aqueous solutions with approximately 15% solids were fully investigated using a Brookfield viscometer and a FACE surface tensiometer, CBVP-A3 type (Kyowa Interface Science Co., Japan), respectively. A dynamic light scattering spectrophotometer DLS-700 (Otsuka Electronic Co., Japan) was used to explore the number-average particle sizes of siloxane-based PU ionomers present in the aqueous solution. The siloxane-based PU ionomer aqueous solution with 15% solids was poured into a polypropylene dish to 1 mm thickness, dried in oven at 60°C; it was used for tensile and elongation testing by an Instron 1130 (U.S.A.), and the oxygen permeation testing of this film was done by using the apparatus similar to the Yanaco Gas Permeability Analyzer Model GTR-10. Scheme 1 illustrates this procedure.

To examine the oxygen permeated through the siloxane-based PU ionomer film, an oxygen gas having a high partial pressure is allowed to diffuse into the one side of PU ionomer film, while the other side of this film is placed under low partial pressure or vacuum. During the measurements, the valves labeled 1, 2, and 6 are closed; but valves 5 and 7 are open. In this condition, the volume of oxygen permeated through the siloxane-based PU ionomer film is able to be measured through the variation of the low pressure side using a Hg pressure meter.

RESULTS AND DISCUSSIONS

The infrared (IR) spectra for IPDI, hydrolyte of DMDCS, NCO-terminated PU prepolymer, and

siloxane-based NCO-terminated PU prepolymer are given in Figures 1–4. The NCO functional group of IPDI will react rapidly with polyester, epoxy resin, polyethylene glycol, and dimethylol propionic acid to form the NCO-terminated PU prepolymer, illustrated by the formation of the absorbance peaks at around 1540 cm^{-1} (NHCO), 3500 cm^{-1} (NH), and 1720 cm^{-1} (C=O), and by almost the total disappearance of the absorbance peak at around 2275–2500 cm^{-1} (NCO), shown in Figure 3 in comparison to that of Figure 1. In addition, the formation of the siloxane-based PU prepolymer is demonstrated by the strong absorbance peaks appearing at around 2600 cm^{-1} [$(\text{C}_2\text{H}_5)_3^+\text{NH}$], 1100 cm^{-1} (Si—O—CH₂—) and 1275 cm^{-1} (Si—CH₃), given in Figure 4.

The surface tension for the siloxane-based PU ionomer aqueous solution as a function of the concentration of DMDCS and of the ratio of NCO to OH, respectively, at room temperature, is given in Figures 5 and 6. Figure 5 shows that the surface tension decreases slightly with an increase in the concentration of DMDCS used to prepare the siloxane-based PU ionomer as a result of more hydrophobic chains of DMDCS adsorbed at the air–water interface. Interestingly, as the ratio of NCO to OH increases, the surface tension of siloxane-based PU ionomer aqueous solution appears to increase slightly. In general, the increased NCO functional group of the ionomer molecule may easily react with the water molecule to form more hydrogen bonding or may have strong intermolecular interaction. This interaction and/or the hydrogen bonding effect may make the rearrangement of the hydrophobic chains of the ionomer

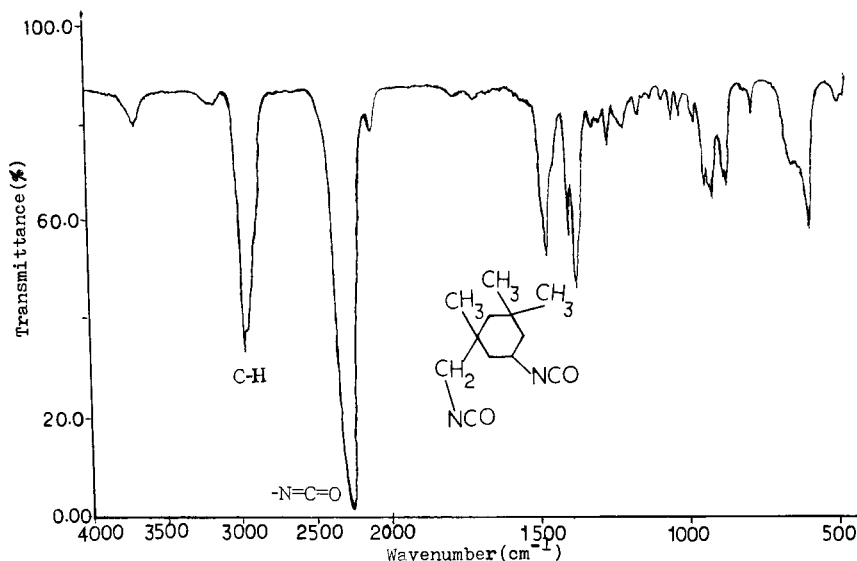


Figure 1 Spectra of isophorone diisocyanate at $25 \pm 0.05^\circ\text{C}$.

molecules adsorbed at the air–water interface to become even more ordered. Therefore, the surface tension of this ionomer aqueous solution increases. In order to further explore the stability and dispersion for these ionomer molecules present in aqueous solution, the number-average particle sizes of these ionomers as a function of respective DMDCS and NCO/OH were fully investigated, and the results are given in Figures 7 and 8. In Figure 7, it clearly indicates that, for the siloxane-based PU ionomer, the number-average particle sizes appear to increase with an increase

in the concentration of DMDCS. This is because increased hydrophobic chains of DMDCS attached to the backbone of PU ionomer molecules are likely to prevent intramolecular interaction of the PU ionomer molecule itself but, on the other hand, may enhance the intermolecular interaction between the PU ionomer molecules themselves. The intermolecular interaction may substantially increase the phase volume of the PU ionomer molecule, thus causing the average particle sizes of this ionomer molecule to become large. Similarly, the number-average particle sizes of PU ionomer

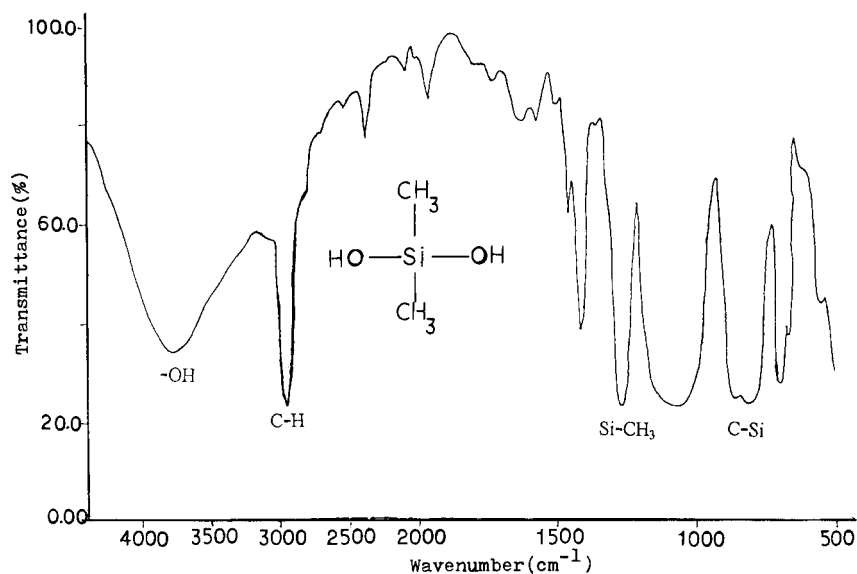


Figure 2 Spectra of the hydrolyte of DMDCS at $25 \pm 0.05^\circ\text{C}$.

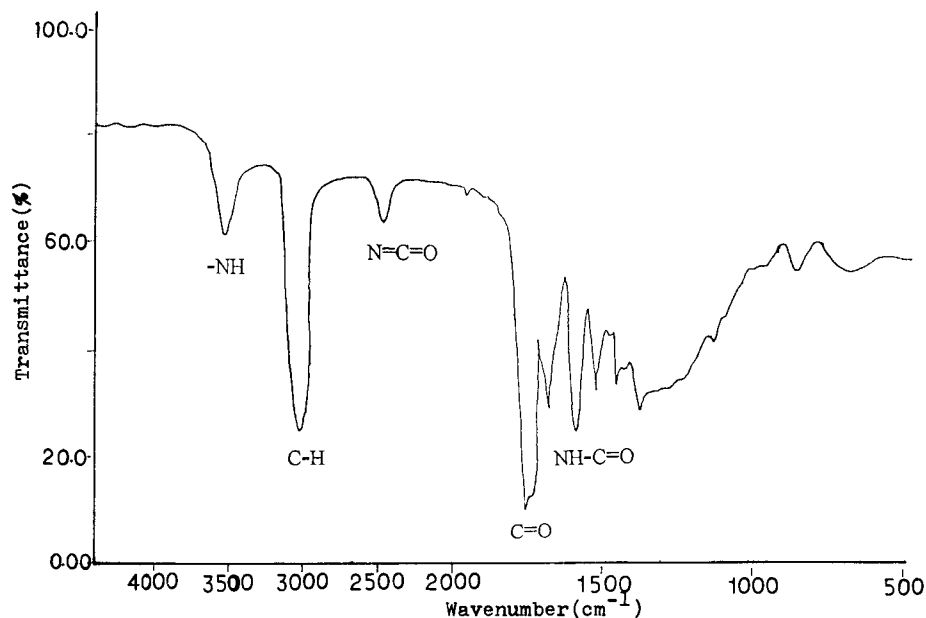


Figure 3 Spectra of the NCO-terminated polyurethane prepolymer formed after 3 h reaction, at $25 \pm 0.05^\circ\text{C}$.

molecules are seen to increase with an increase in the ratio of NCO to OH, shown in Figure 8. Increased phase volume of these ionomer molecules due to intermolecular interaction and/or the hydrogen bonding effect resulting from increased NCO functional groups of PU ionomer molecules may be the reason to explain why the number-

average particle sizes of these ionomer molecules increase appreciably.

The volume of oxygen permeated through the PU ionomer film with and without the hydrolytes of dimethyldichlorosilane ($-\text{O}-\text{Si}-\text{O}-$) as a function of time is shown in Figure 9. It was found that the volume of oxygen permeated through the

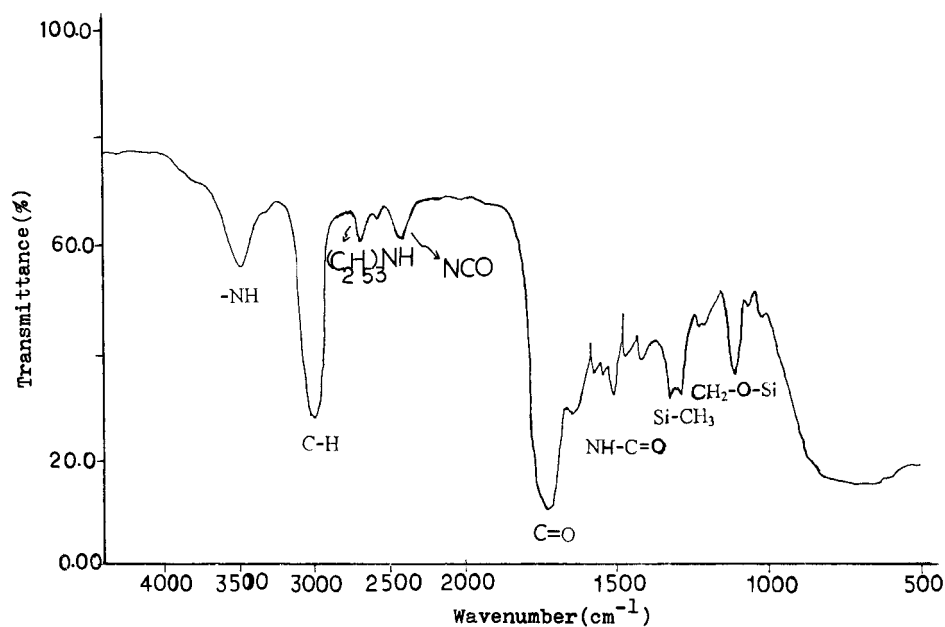


Figure 4 Spectra of the siloxane-based NCO-terminated polyurethane prepolymer at $25 \pm 0.05^\circ\text{C}$.

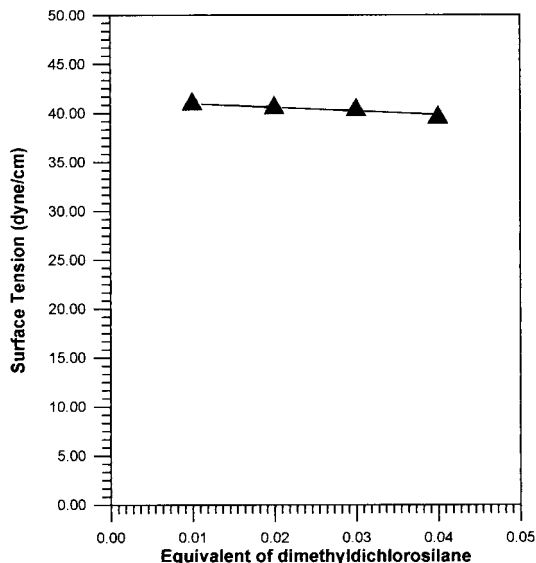


Figure 5 Plot of the surface tension vs. the equivalent of dimethyldichlorosilane used to prepare siloxane-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

film is seen to be larger for the film cast from the PU ionomer with the hydrolytes of dimethyldichlorosilane than for the film cast from the PU ionomer without the hydrolytes of dimethyldichlorosilane in aqueous solution. The film made by the PU ionomer with 0.02% (by weight) hydrolytes of DMDCS is believed to have more porosities. This may be the reason to explain why the volume of

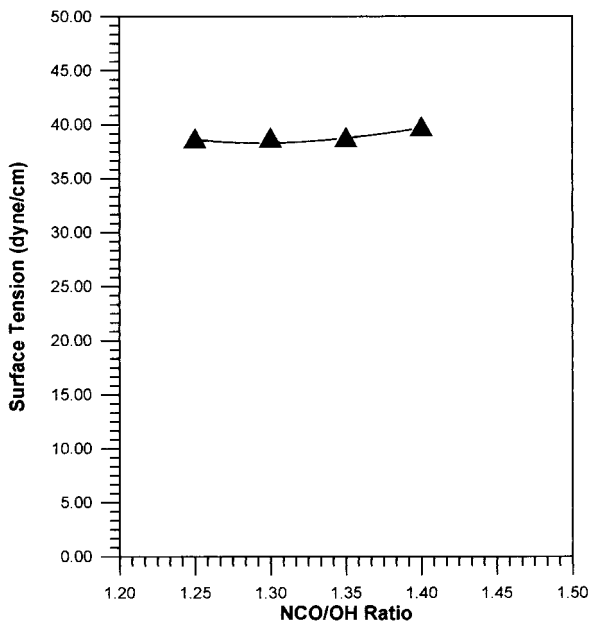


Figure 6 Surface tension for siloxane-based PU ionomer as a function of NCO/OH ratio at $25 \pm 0.05^\circ\text{C}$.

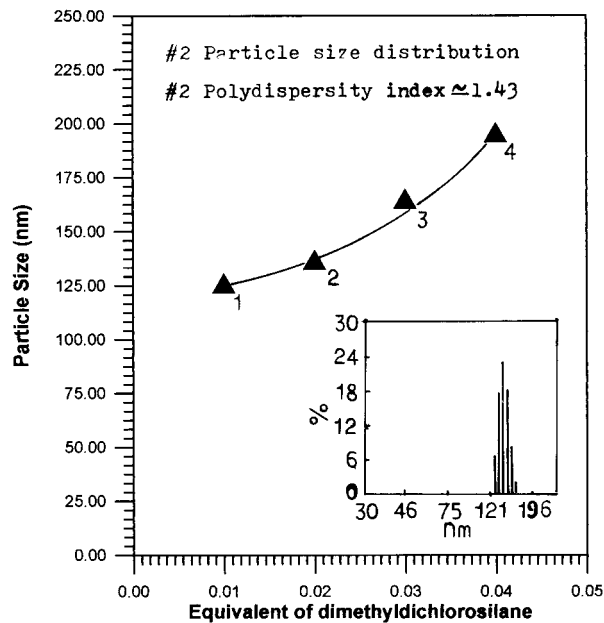


Figure 7 Plot of the number average particle size vs. the equivalent of dimethyldichlorosilane used to prepare siloxane-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

oxygen diffusing into the film made by the siloxane-based PU ionomer is large. To evaluate the oxygen permeability of film made by the siloxane-based PU ionomer, we further investigated the amount of oxygen permeated through a unit area

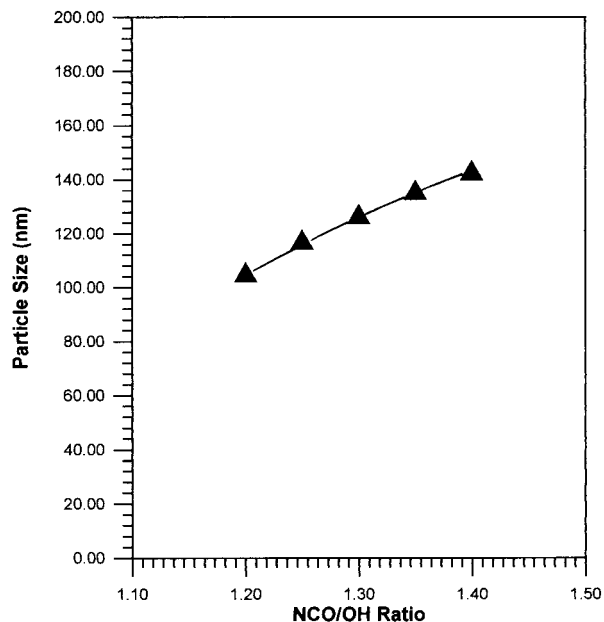


Figure 8 Number average particle size for siloxane-based PU ionomer as a function of NCO/OH ratio at $25 \pm 0.05^\circ\text{C}$.

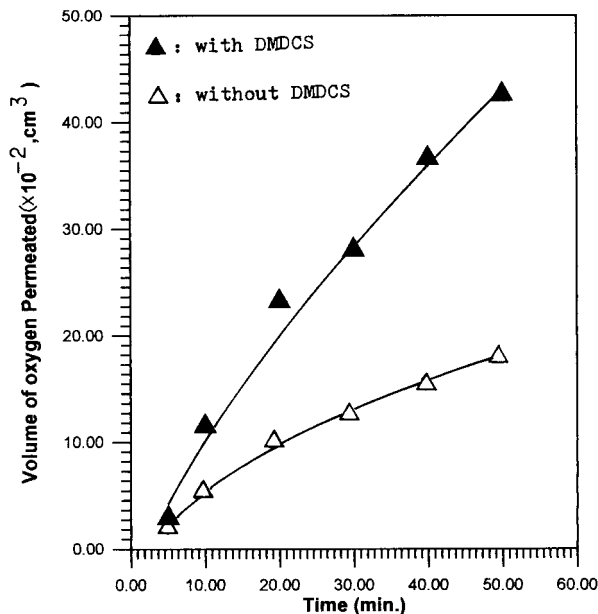


Figure 9 Volume of oxygen permeated through the film made by siloxane-based PU ionomer as a function of time at $25 \pm 0.05^\circ\text{C}$.

of this film as a function of the concentration of DMDCS linked to the backbone of the PU ionomer molecule, given in Figure 10. Figure 10 clearly indicates that the amount of oxygen permeated

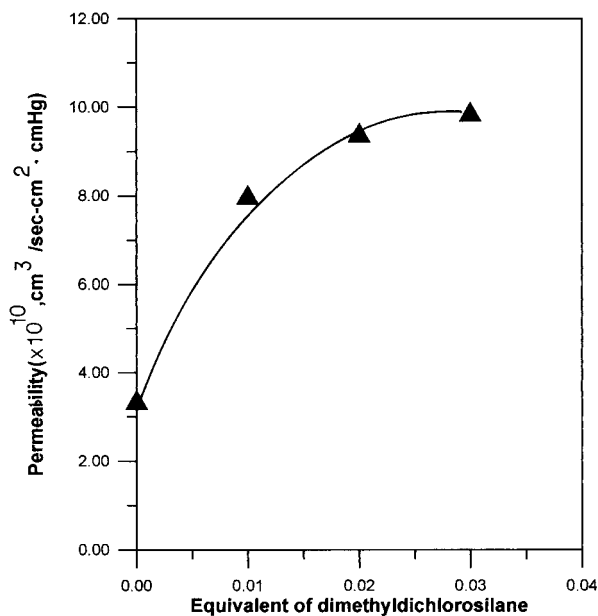


Figure 10 Plot of the oxygen permeability of the film as a function of the equivalent of dimethyldichlorosilane, at $25 \pm 0.05^\circ\text{C}$.

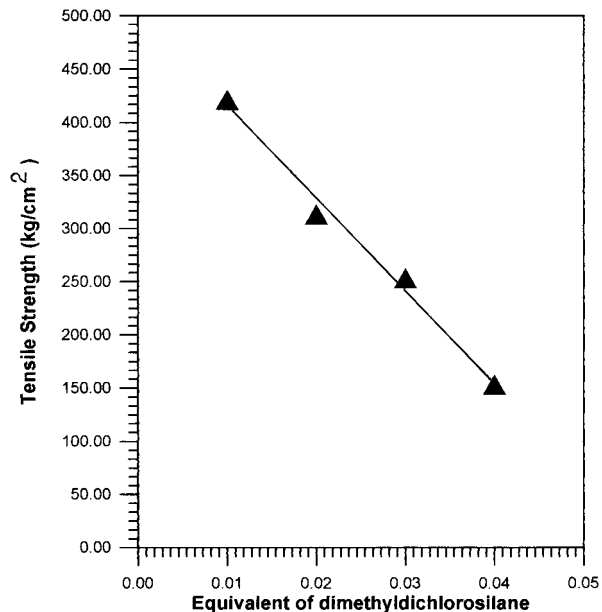


Figure 11 Plot of the tensile strength vs. the equivalent of dimethyldichlorosilane used to prepare siloxane-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

through the film increasing with an increase in the concentration of DMDCS can be attributed to more porosities formed. This also demonstrates that increasing the amount of DMDCS linked to the backbone of the PU ionomer molecule does indeed help to increase the volume of oxygen permeated through the film made by this ionomer.

The tensile strength of self-cured films of the siloxane-based PU ionomer is given in Figures 11 and 12. Figure 11 shows that the tensile strength of dry film at breaking point appears to decrease dramatically with an increase in the concentration of DMDCS. Increased hydrophobic chains of DMDCS attached to the backbone of PU ionomer molecules possibly prevent the formation of the hydrogen bonding and greatly weaken the capability of crosslinking of PU ionomer molecule. Thus, the tensile strength of the film made by the siloxane-based PU ionomer becomes weaker as the concentration of DMDCS increases. It is interesting to note that as the ratio of NCO to OH increases, the tensile strength of the film cast from the siloxane-based PU ionomer becomes stronger, shown in Figure 12. This is possibly due to the increased hydrogen bonding effect and to the increased NCO functional groups built on the backbone of the PU ionomer molecules, thus resulting in strengthening the capability of these ionomer molecules.

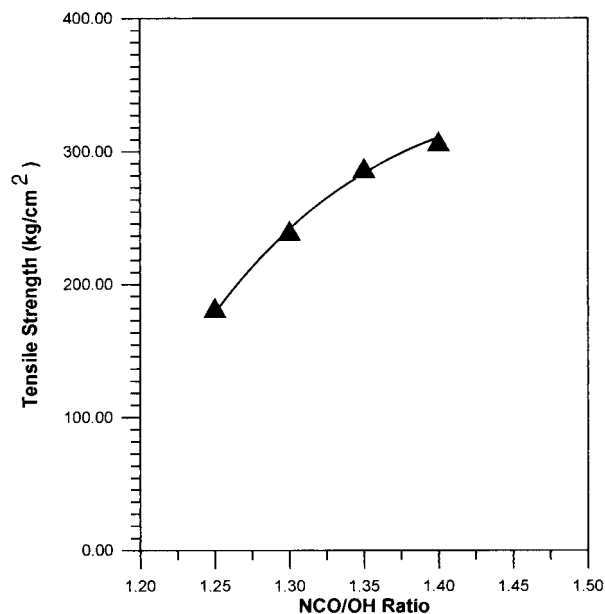


Figure 12 Tensile strength for siloxane-based PU ionomer as a function of NCO/OH ratio at $25 \pm 0.05^\circ\text{C}$.

CONCLUSION

The oxygen permeability of the film made by the PU ionomer, successfully synthesized at our lab, is demonstrated to be a siloxane-based PU ionomer by IR spectra. For siloxane-based PU ionomer molecules in an aqueous solution, the surface tension was found to decrease slightly with an increase in the concentration of DMDCS as a result of more hydrophobics of DMDCS linked to the backbone of the PU ionomer molecules adsorbed at the air–water interface. However, the increase of the surface tension, on the other hand, with an increase in the ratio of NCO to OH may be attributed to the result of the rearrangement of the hydrophobics of siloxane-based PU ionomer molecules at the air–water interface to become even more ordered. Owing to the increased phase volume of ionomer molecules resulting from the hydrogen bonding effect and/or intermolecular interaction in the aqueous solution, the number-av-

erage particle sizes of these ionomer molecules as a function of respective DMDCS and NCO/OH ratios appear to increase considerably. More importantly, the volume of the oxygen permeated through the film was found to be larger for the film made by the PU ionomer molecule with 0.02% (by weight) DMDCS than for the film made by the PU ionomer molecule without DMDCS. Our experimental results also indicate that the increased amount of oxygen permeated through the film depends upon the concentration of DMDCS used to prepare siloxane-based PU ionomers, and that use of DMDCS in PU ionomer molecules does substantially raise the amount of oxygen diffusing into the film made by these ionomer molecules. To deal with the tensile strength of self-cured films of the siloxane-based PU ionomer, it is interesting to find out that the tensile strength of these films will be strengthened by raising the NCO/OH ratio instead of increasing the concentration of DMDCS.

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