Water Vapor-Permeable Polyurethane Ionomer

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ABSTRACT: The reaction of toluene diisocyanate with 2,2,3,3-tetrafluoro-1-propanol (fluoro compound) or 3-glycidoxypropyl trimethoxysilane(siloxane compound) and other additives to form the structure of the fluoro-based or siloxane-based polyurethane (PU) ionomer has been proven by infrared spectra. Experimental results indicated that the amount of water vapor permeability of the film made by fluoro-based or siloxane-based PU ionomer appeared to gradually increase with increasing concentration of the siloxane compound or fluoro compound, as a result of the formation of more porosities. Our experimental results also showed that the water vapor absorption was seen to be larger for the film made by siloxane-based PU ionomer film than for the film made by fluoro-based PU ionomer film, as a result of increased hydrophilic groups attached to the backbone of the PU ionomer molecule. For the film prepared by siloxane-based PU ionomer, both tensile strength and elongation appeared to increase with an increase in the concentration of siloxane compound. This may be the result of the intermolecular interaction between siloxane-based PU ionomer molecules themselves, thus enhancing the crosslinking capability of the ionomer molecules. On the other hand, both tensile strength and elongation for the film prepared by fluoro-based PU ionomer decreased with increasing concentration of the fluoro compound, as a result of intramolecular interaction greatly reducing the crosslinking capability of the ionomer molecules. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3767–3773, 2006

Key words: water–vapor-permeable polyurethane ionomer; infrared spectra

INTRODUCTION

In the previous article, we dealt with the effect of respective ethylene glycol, dimethyl dimethoxysilane, and dimethyl diethoxysilane on the water vapor permeability of the film made by the ethylene glycol or dimethyl diethoxysilane-based polyurethane resin. Our experimental results indicated that the use of ethylene glycol or dimethyl dimethoxysilane or dimethyl diethoxysilane, due to an increased number of hydrophilic groups attached to the backbone of the polyurethane resin, did substantially increase the amount of water vapor diffusing into the film made by the polyurethane resin. Owing to the environmental protection becoming increasingly important, the organic solvent used as a diluent for the resin industry is gradually being replaced by a nonpollutant solvent. For this reason, we further attempted to study the effect of 2,2,3,3-tetra fluoro-1-propanol and 3-glycidoxypropyl trimethoxysilane, respectively, on the water-resistant and water vapor permeability of the film made by siloxane-based or fluoro-based polyurethane ionomer.

EXPERIMENTAL

Materials

Dimethylol propionic acid (DMPA) and *N,N*-dimethylacetamide (DMAC) were purchased from Alcolac Industrial Chemicals (USA) and J.T. Baker Chemicals (USA), respectively. Toluene diisocyanate (TDI), thriethylamine, diethylenetriamine, and acetone were obtained from Merck Co. (Darmstadt, Germany). Polyester (made by the reaction of adipic acid with 1,6-hexanediol and diethylene glycol) with a molecular weight of 2800 were received from Tai Chin Chemical Industry Co., Ltd. (Kaoshiung, Taiwan). 3-Glycidoxypropyltrimethoxysilane and 2,2,3,3-tetrafluoro-1-propanol were supplied by Shin-Etsu Chemical Co. Ltd. (Chiyoda-ku, Tokyo, Japan) and Acros Organics (Belgium), respectively. All these chemicals were used without further purification.

Method

A 0.024 equivalent of polyester (OH number ≅56) with an average molecular weight of 2000, 0.031 equivalent of 1,4-butane diol, and 0.063 equivalent of dimethylol propionic acid (DMPA) were charged into a 1000 mL four-necked Pyrex glass flask equipped with a stirrer, thermometer, and condenser containing 20 g of *N,N*-dimethylacetamide under agitation at 70°C.

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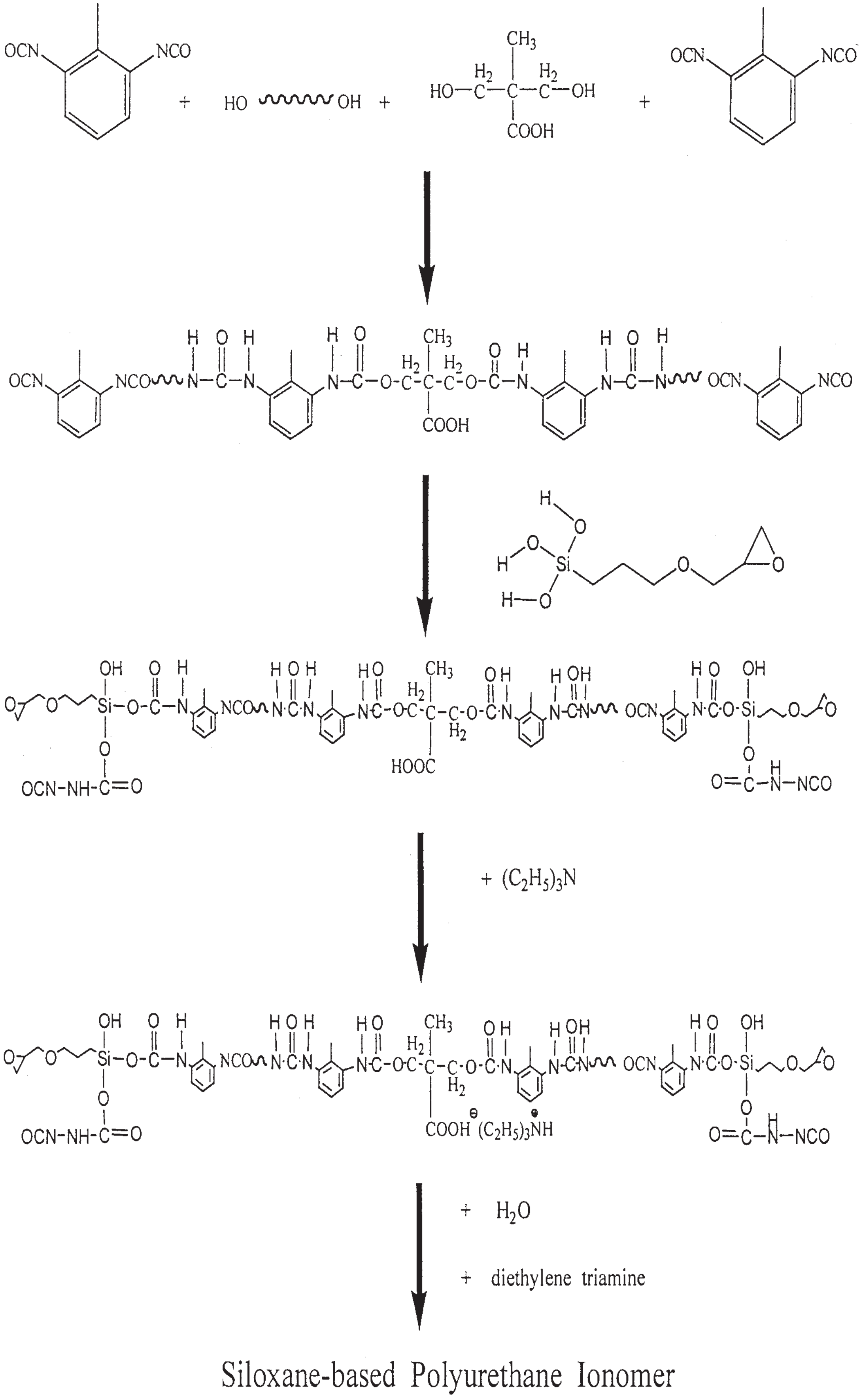

+ $(C_2H_5)_3N$
+ H_2O
+ diethylene triamine
Siloxane-based Polyurethane Ionomer

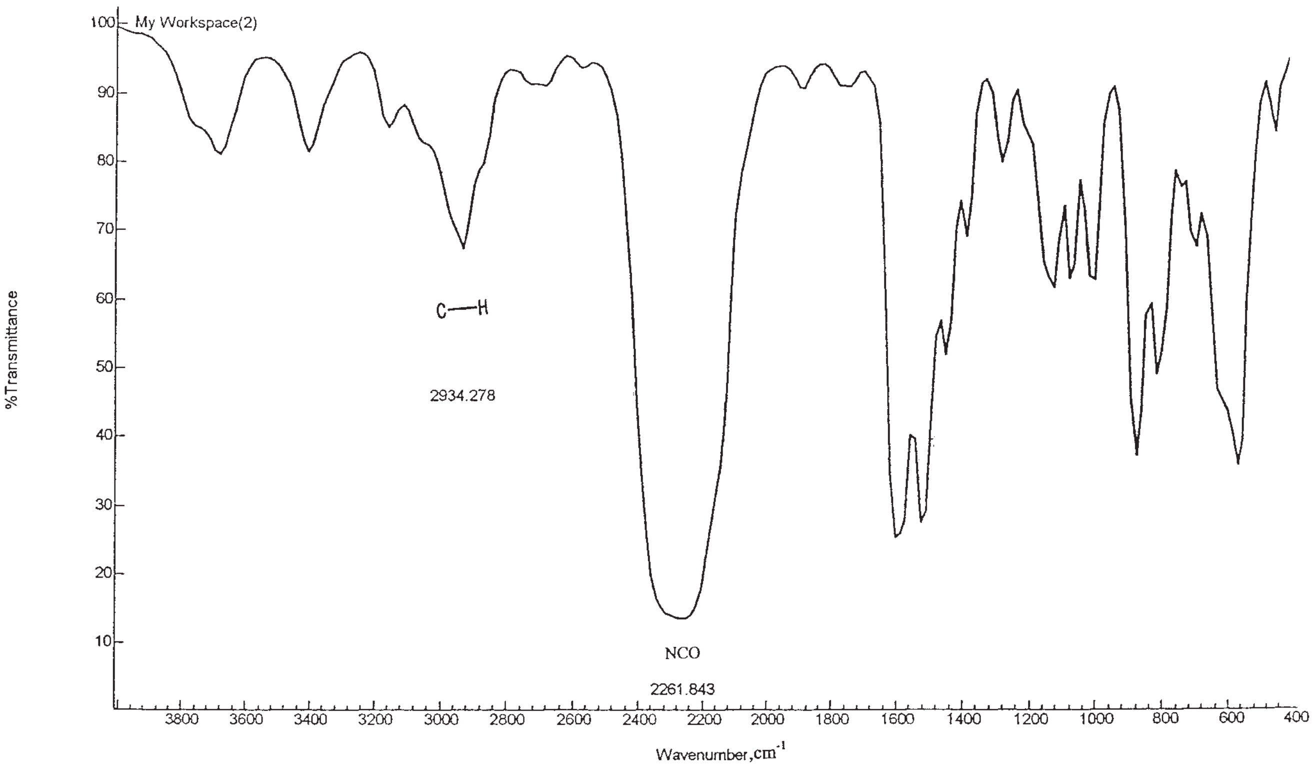

Figure 1 Spectrum of toluene diisocyanate at 25 ± 0.05°C.

In the above flask a 0.135 equivalent of toluene diisocyanate (TDI:NCO/OH ≅1.14–1.16) and 0.0005–0.007 equivalent of 2,2,3,3-tetrafluoro-1-propanol or 3-glycidoxypropyl trimethoxysilane was subsequently added and reacted in the presence of 60 g acetone at 80–83°C for about 2.5 h to form NCO-terminated polyurethane (PU) prepolymer. A 0.035 equivalent of triethylamine was then reacted with this NCO-terminated PU prepolymer to form a quaternized NCO-terminated PU prepolymer.[1–5] Water (100 g) was then added to form the fluoro-based or siloxane-based polyurethane ionomer. The acetone was completely removed from the fluoro-based or siloxane-based PU ionomer liquids by an evaporation technique. The final fluoro-based or siloxane-based PU ionomer aqueous solution, with approximately 28% solid content, was used for average partical size, tensile strength, and elongation testing by a dynamic light scattering spectrophotometer (DLS-700, Otsuka scattering photometer) and Instron 1130 (USA), respectively. A 7-cm diameter of the film with a round shape made by the siloxane or fluoro-based PU ionomer molecule was fixed on the top of the beaker containing water vapor absorbing agent, $CaCl_2$, 3 cm away from the film. This beaker was put into the container under controlled temperature and humidity at 40 ± 2°C and 90 ± 5%, respectively. After 1 h, the water vapor permeable beaker was taken out and its weight was measured to be a_1(mg), and another hour, its weight was a_2(mg). The water vapor permeability was calculated as follows:

$$P = \frac{A}{S}; A = \frac{(a_1 - a_3) + (a_2 - a_1) + (a_3 - a_2)}{3}$$

where P is the water vapor permeability (g/m^2h); S the film area (cm^2), and A the average increased weight per hour. The amount of the water vapor absorption for the 1-mm film placed on top of a round beaker for 24 h was obtained by the substration of the dry film from the wet film at 25 ± 0.05°C. The experimental errors for these measurements were estimated to be within ± 0.5%. The reaction of toluene diisocyanate with 3-glycidoxypropyl trimethoxysilane or 2,2,3,3-tetra fluoro-1-propanol and other additives to possibly form the structure of a siloxane- or fluoro-based polyurethane ionomer is given as follows: (see previous page)

RESULTS AND DISCUSSIONS

The infrared spectra for TDI and 3-glycidoxypropyl trimethoxysilane are given in Figures 1–2. The reaction of toluene diisocyanate with 3-glycidoxypropyl trimethoxysilane or 2,2,3,3-tetrafluoro-1-propanol and other additives to form NCO-terminated PU prepolymer is illustrated by the formation of the absorbance

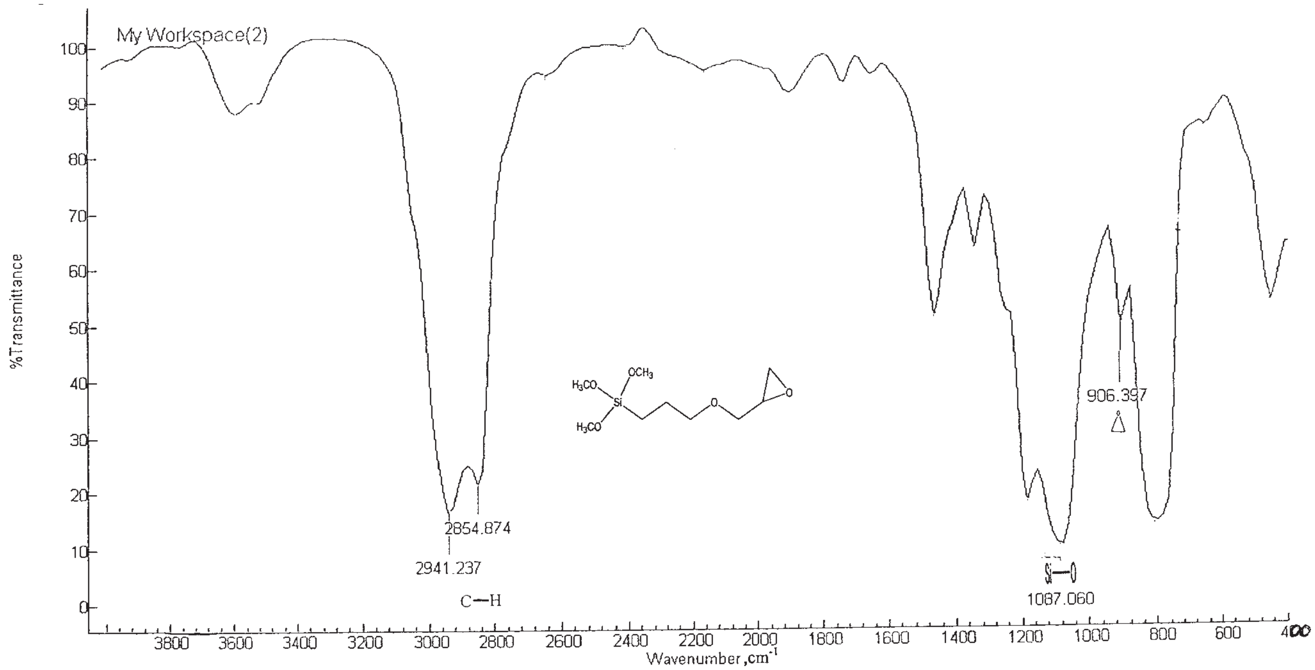

Figure 2 Spectrum of 3-glycidoxypropyl trimethoxysilane at 25 ± 0.05°C.

peaks at around 1230 cm^{-1} (NHCO) 3300 cm^{-1} (NH), 1720 cm^{-1} (C═O), and 1020 cm^{-1} (Si—O) and by almost the disappearance of the absorbance peak at around 2275 cm^{-1} (NCO) shown in Figure 3 in comparison to those of Figures 1–2. These results suggest that TDI reacted with 3-glycidoxypropyltrimethoxysilane or 2,2,3,3-tetra fluoro-1-propanol, polyester, and other additives does form a siloxane-based or fluoro-based PU ionomer. The water vapor permeability of the film made by the polyurethane ionomer as a function of 2,2,3,3-tetrafluoro-1-propanol or siloxane concentration, given in Figure 4, appears to slightly decrease with increasing concentration of the fluoro compound or siloxane. This may be due to strong

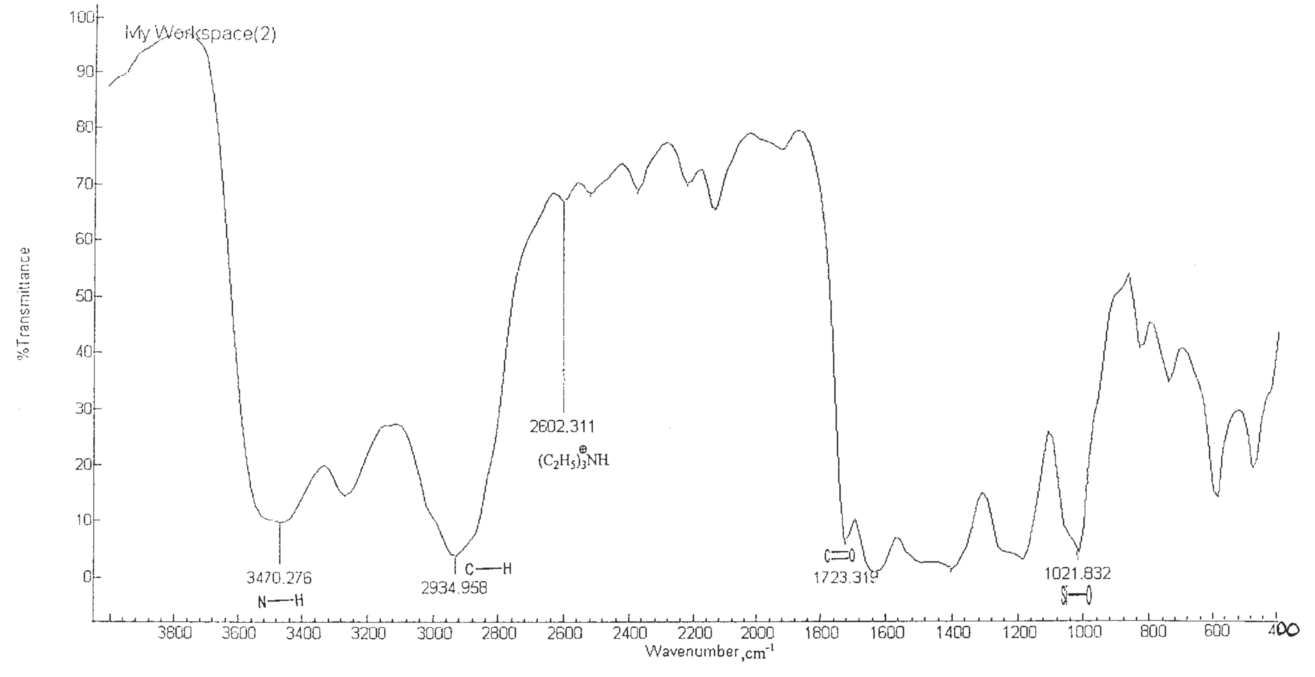

Figure 3 Spectrum of silane-based PU prepolymer formed after 1.5-h reaction, at 25 ± 0.05°C.

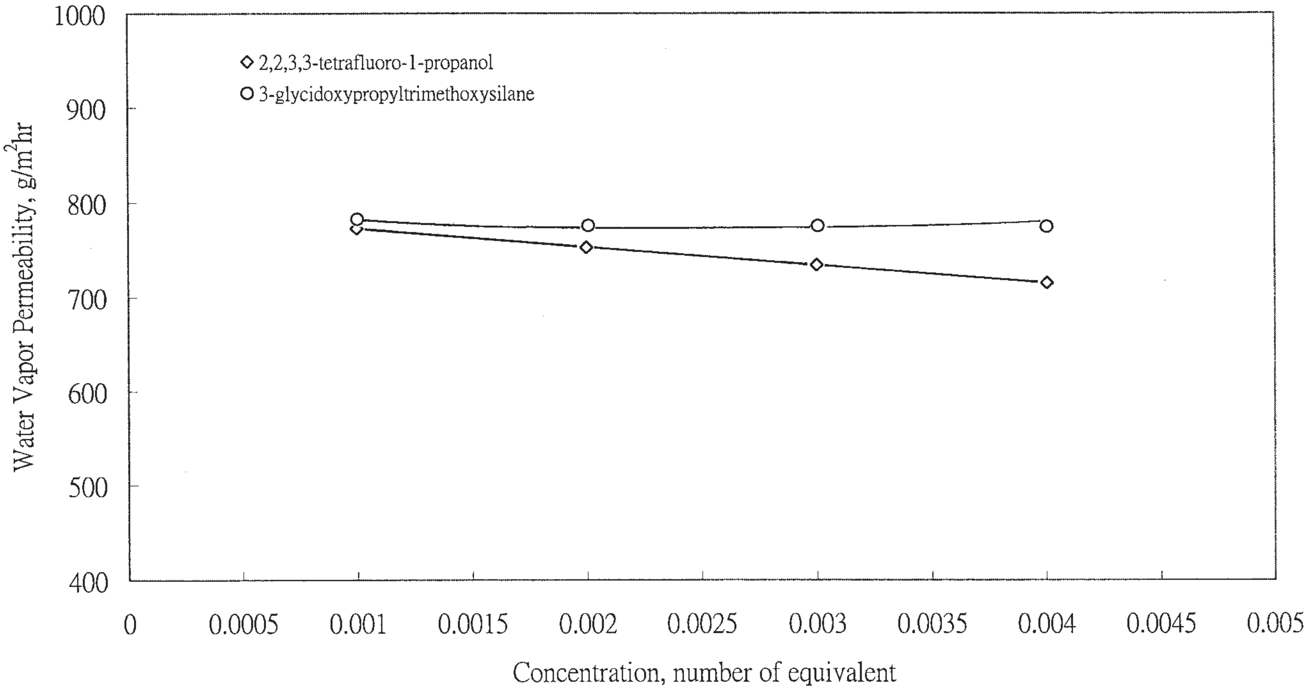

Figure 4 Plot of the water vapor permeability versus the concentration of siloxane or fluoro compound used to prepare the water vapor permeable PU ionomer, at 25 ± 0.05°C.

intramolecular interaction resulting from increasing hydrophilic groups attached to the backbone of the PU ionomer molecules. These intramolecular interactions may make PU ionomer molecules form compact conformation with small porosity. Therefore, the water vapor permeability of the PU film decreases. For the fluoro-based and siloxane-based PU film, however, the water vapor absorption gradually increases with increasing the concentration of 2,2,3,3-tetrafluoro-1-propanol and siloxane, respectively, used to prepare the fluoro-based and siloxane-based PU ionomer, given in Figure 5. Owing to the hydrophilic property appearing to be greater for siloxane compound than for fluoro compound, the increased hydrophilic property is likely to enhance the water vapor diffusing into the siloxane-based PU film. This may be the reason to explain why the water vapor absorption is greater for siloxane-based PU film than for fluoro-based PU film. The tensile strength of the self cured film made by fluoro-based or siloxane-based PU ionomer, given in Figure 6, appears to significantly decrease with increasing concentration of the fluoro compound but to increase with increasing concentration of the siloxane compound for use in the preparation of the fluoro-based or siloxane-based PU ionomer. The former, due to intramolecular interaction, may make the fluoro-based PU ionomer molecule form a compact conformation or micelle-like structure resulting in decreasing its tensile strength. The latter, due to intermolecular interaction, is possible to form an expanded conformation. This intermolecular interaction between PU ionomer molecules may greatly increase the crosslinking capability of PU ionomer molecules. Thus, the tensile strength of the siloxane-based PU ionomer film increases. In addition, the elongation of the dry film cast from the fluoro-based PU ionomer molecule at the breaking point decreases with increasing the concentration of the fluoro compound but slightly increases with increasing the concentration of the siloxane compound, shown in Figure 7. The increased hydrophobic property of the fluoro-based PU ionomer molecules due to their intramolecular interaction may enable the elongation of the fluoro-based PU ionomer film to decrease. On the other hand, however, increased hydrophilic property of the siloxane-based PU ionomer molecules due to their intermolecular interaction may increase their elongation.

CONCLUSION

The reaction of toluene diisocyanate with siloxane compound or fluoro compound and other additives to form the siloxane-based or fluoro-based polyurethane ionomers was successfully synthesized at our lab and their structures were demonstrated by FTIR spectra. The experimental results show that the amounts of water vapor permeated through the film made by the siloxane-based PU ionomer increase with increasing concentration of the siloxane compound, as a result of the formation of an expanded structure with large porosities resulting from intermolecular interaction

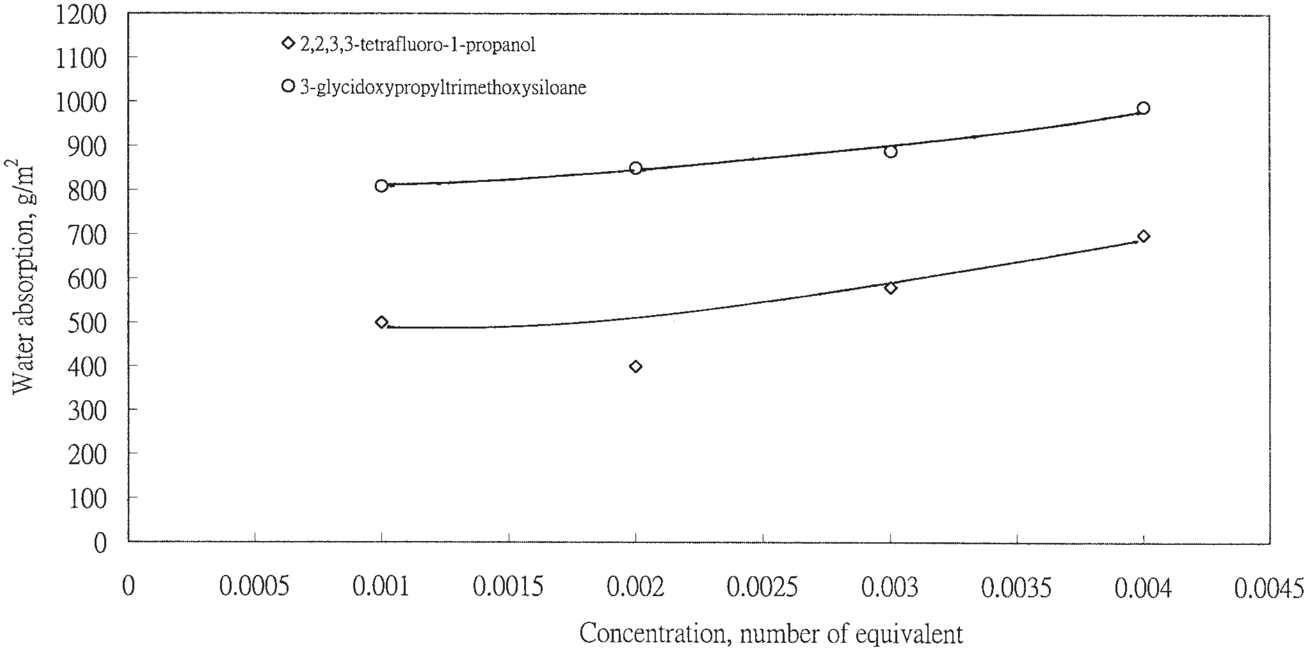

Figure 5 Plot of the water vapor absorption of the film made by siloxane-based or fluoro-based PU ionomer versus the concentration of fluoro compound and siloxane compound, at 25 ± 0.05°C.

between the PU ionomer molecules themselves. On the other hand, however, the amounts of water vapor permeated through the film made by the fluoro-based PU ionomer appear to decrease with increasing concentration of the fluoro compound. This may be the result of the formation of a compact structure or a micelle-like structure with small porosities due to intramolecular interaction of the PU ionomer molecule itself. Our experimental results also indicate that the water vapor absorptions for both siloxane-based and

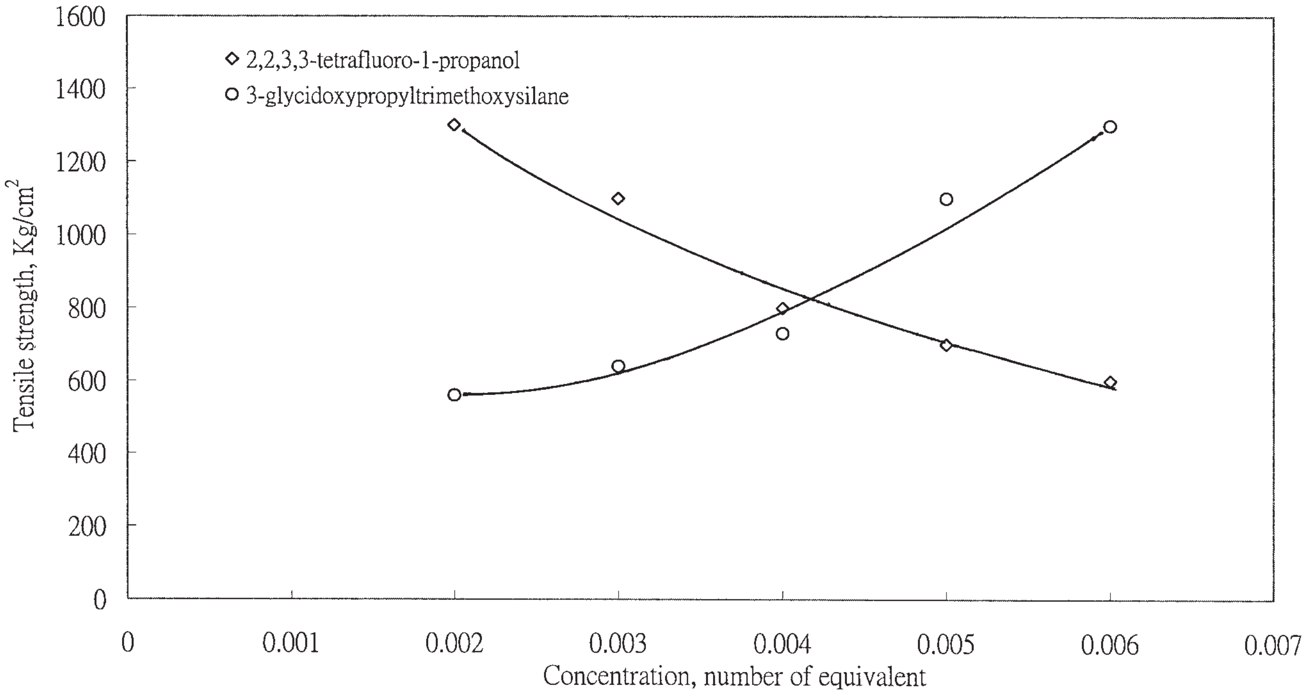

Figure 6 Plot of the tensile strength versus the concentration of siloxane or fluoro compound used to prepare the water vapor permeable PU ionomer, at 25 ± 0.05°C.

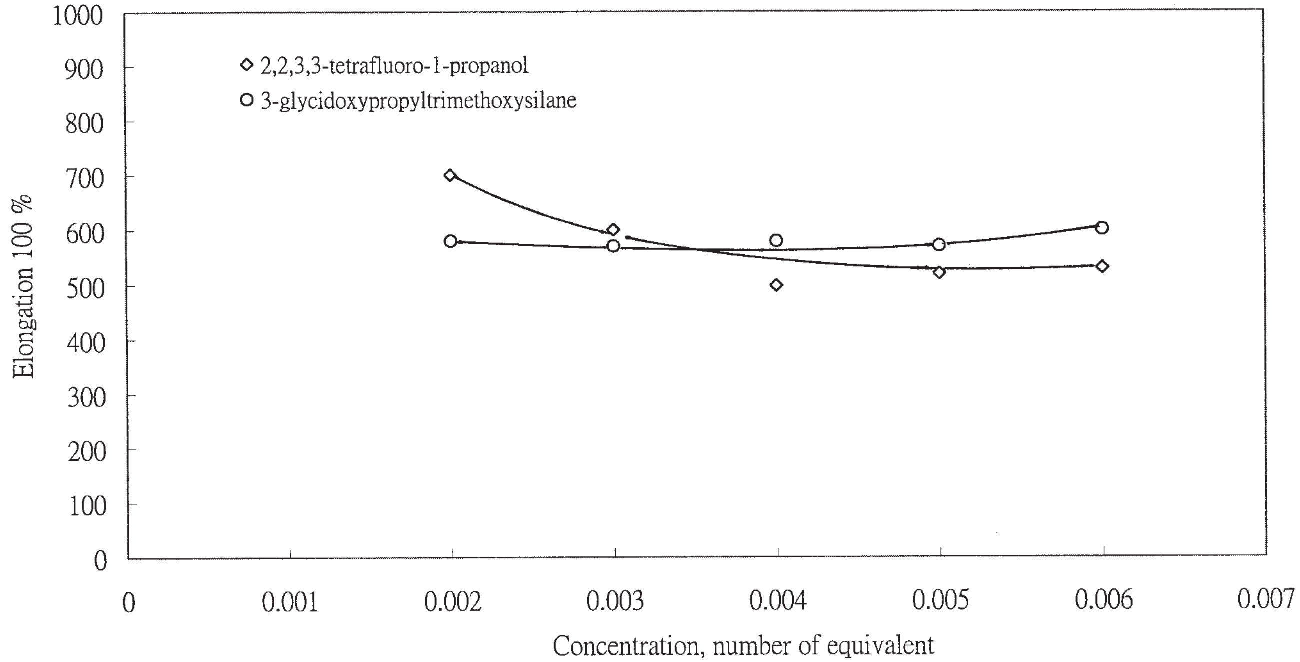

Figure 7 Plot of the elongation versus the concentration of siloxane or fluoro compound used to prepare the water vapor permeable PU ionomer, at 25 ± 0.05°C.

fluoro-based PU ionomer film appear to gradually increase with increasing concentration of siloxane and fluoro compound, respectively. For the tensile strength of self-cured film made by the respective siloxane-based and fluoro-based PU ionomer molecules at the breaking point, it increases with increasing concentration of the siloxane compound or fluoro compound, as a result of strong intermolecular interaction between the PU ionomer molecules themselves. Contrarily, for both siloxane-based and fluoro-based PU ionomer molecule systems, the elongation at the breaking point appears to decrease as the concentration of siloxane compound or fluoro compound increases. This is the result of the intramolecular interaction of PU ionomer molecule itself.

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