

Water-Vapor-Permeable Polyurethane Resin

C. P. Chwang,¹ S. N. Lee,¹ J. T. Yeh,² C. Y. Chen,³ D. Y. Chao³

¹ Department of Chemistry, Fujen University, Taipei, Taiwan, Republic of China

² Graduate School of Fiber and Polymer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Republic of China

³ Institute of Applied Chemistry, Chinese Culture University, Hwa Kang, Yang Ming Shan, Taipei, Taiwan, Republic of China

Received 26 July 2001; accepted 19 February 2002

ABSTRACT: The reaction of methylene diphenylene diisocyanate with ethylene glycol, dimethyl dimethoxysilane, dimethyl diethoxysilane, and other additives in the presence of *N,N*-dimethylformamide and toluene to form the structure of water-vapor-permeable polyurethane (PU) resin was proven with Fourier transform infrared spectra. Experimental results clearly showed that the amount of oxygen that permeated the film made with the PU resin increased with an increase in the concentration of ethylene glycol, diethylene glycol, or triethylene glycol. This was due to an increased number of hydrophilic groups attached to the backbone of the PU resin molecules. These hydrophilic groups, because of the intermolecular interactions between PU resin molecules, made PU resin molecules form an expanded conformation with large porosities. Interestingly, the water vapor permeability of the PU resin appeared to increase with an increasing concentration of ethylene glycol, dimethyl dimethoxysilane, or dimethyl diethoxysilane but

not to increase with an increasing concentration of diethylene glycol, triethylene glycol, or poly(ethylene glycol) with dimethyl dimethoxysilane. The former was due to intermolecular interactions resulting in an expanded conformation with large porosities, but the latter was due to intramolecular interactions resulting in a compact conformation or a micellelike structure with small porosities. Therefore, the water vapor permeability of the former increased, but the latter remained unchanged or decreased. Our experimental results suggest that the use of poly(ethylene glycol) 400, ethylene glycol, dimethyl dimethoxysilane, and other strong hydrophilic compound in the preparation of modified PU resins substantially raises the amount of water vapor diffusing into films made with these resins. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2002-2010, 2002

Key words: water vapor; polyurethane

INTRODUCTION

In the 1970s, makers of leather bags, shoes, and garments, because of the rapid development of downstream processing industries, enabled the supply of polyurethane (PU) leather to increase significantly. Although the PU synthetic leather industry in Taiwan has enjoyed rapid growth, the investment environment, because of the appreciation of the new Taiwan dollar, the shortage of laborers, and the increase in wages in the past 2 decades, has been deteriorating. In fact, 80% of the downstream manufactures moved off the island to continue their production in mainland China and Southeastern Asia countries known for large labor forces and low labor costs. For this reason, the domestic capacity of PU synthetic leather is gradually shrinking. However, according to government data, global production of PU synthetic leather was 308 million yards in 1994, of which 200 million yards

was produced in Taiwan. This was far ahead of the other nations in the world and accounted for over 50% of global production.

Sales of PU synthetic leather began to decline in the latter part of 1984. Until now, there has not been any sign of recovery. The PU leather industry has gone from bad to worse. To overcome this poor situation, the PU synthetic leather industries should upgrade their production technology and/or develop new products to meet various demands. Therefore, we have attempted to help our PU synthetic leather industry to improve water vapor permeability and oxygen or air permeability^{1,2} for PU leather made with modified PU resins.

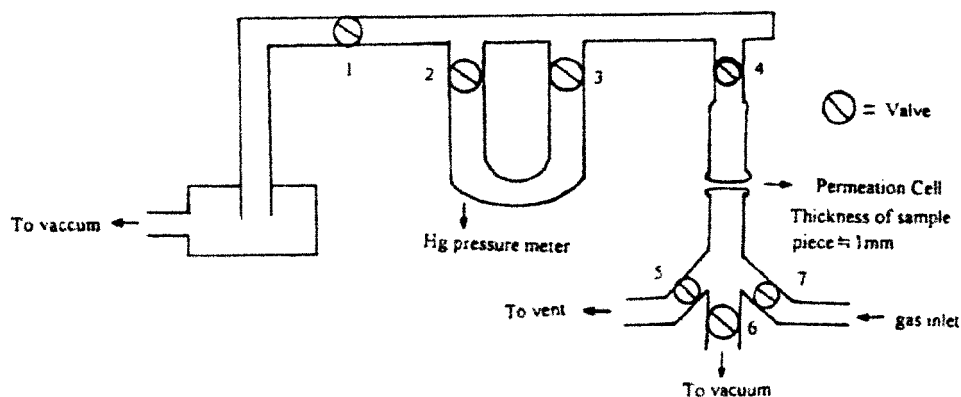
EXPERIMENTAL

Materials

Methylene diphenylene diisocyanate (MDI) was obtained from Aldrich Chemical Co., Inc. (United States). Dimethyl dimethoxysilane (KBM 22) and dimethyl diethoxysilane (KBE 22) were supplied by Shin-Etus Chemical Co., Ltd. (Chiyoda-Ku, Tokyo, Japan). *N,N*-Dimethylformamide (DMF) and toluene were pur-

Correspondence to: D. Y. Chao.

Contract grant sponsor: National Science Council of Taiwan.

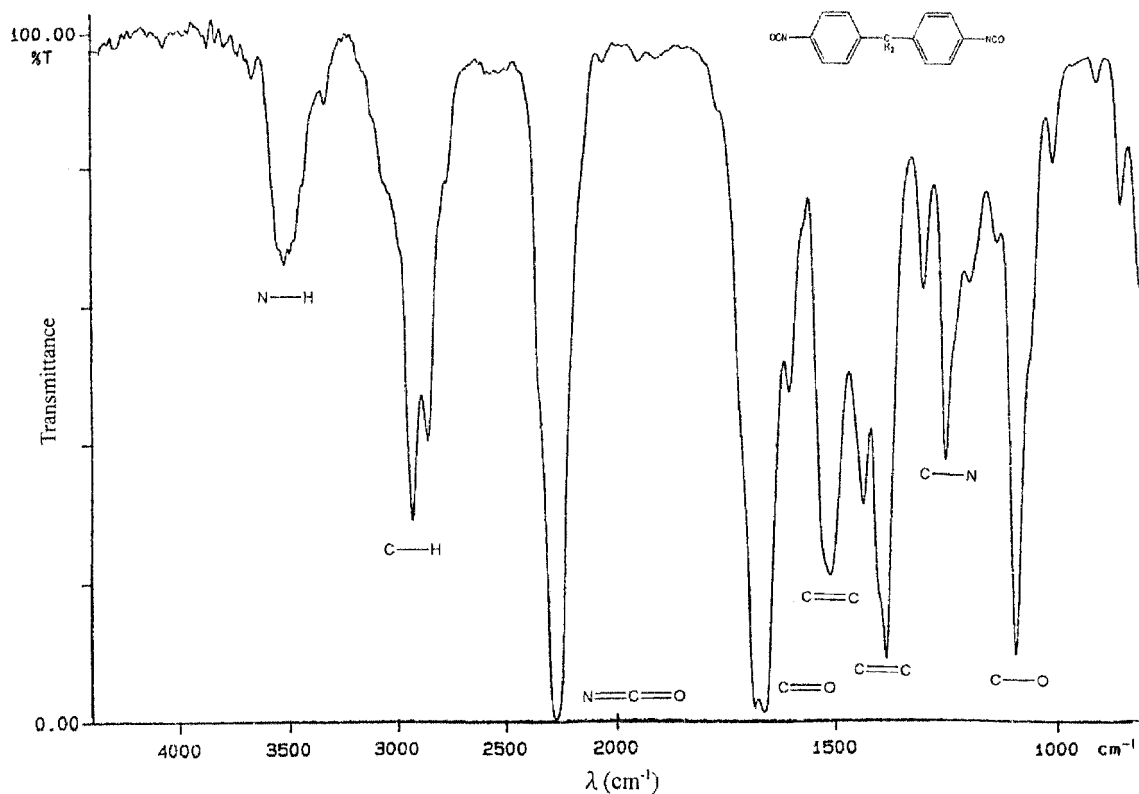


Scheme 1

chased from Junsei Chemical Co., Ltd. (Japan). 1,4-Butane glycol, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), 2,2-dimethyl-1,3-propanediol (NPG), propylene glycol (molecular weight ≈ 1000), and polyester (made by the reaction of adipic acid with 1,6-hexanediol and DEG) with a molecular weight of 2800 were received from Tai Chin Chemical Industry Co., Ltd. (Kaoshiung, Taiwan). Poly(ethylene glycol) (PEG; molecular weight ≈ 400) and C.I. Acid Green 20 were supplied by Sino-Japan Chemical Co. (Taipei, Taiwan) and Kon Fu Chemical Industry, Ltd. (Taipei, Taiwan), respectively. All of these chemicals were used without further purification.

Method

A 1000-mL, four-necked reaction kettle equipped with a thermometer, condenser, and stirrer was charged with 80 g of polyester (molecular weight ≈ 2800 , OH number ≈ 40.1), 10 g of poly(propylene glycol) (molecular weight ≈ 1000), 2.93 g of C.I. Acid Green 20, 2.08 g of NPG, 0.815 g of dimethyl diethoxysilane, and 12.6 g of 1,4-butane glycol (or EG or DEG or TEG) in the presence of DMF and toluene. Subsequently, 55 g of MDI (NCO/OH ≈ 1.0) was added slowly and then reacted around 80–85°C for about 4.0 h to form the water vapor permeability of a PU resin that was 30%

Figure 1 Spectrum of MDI at $25 \pm 0.05^\circ\text{C}$.

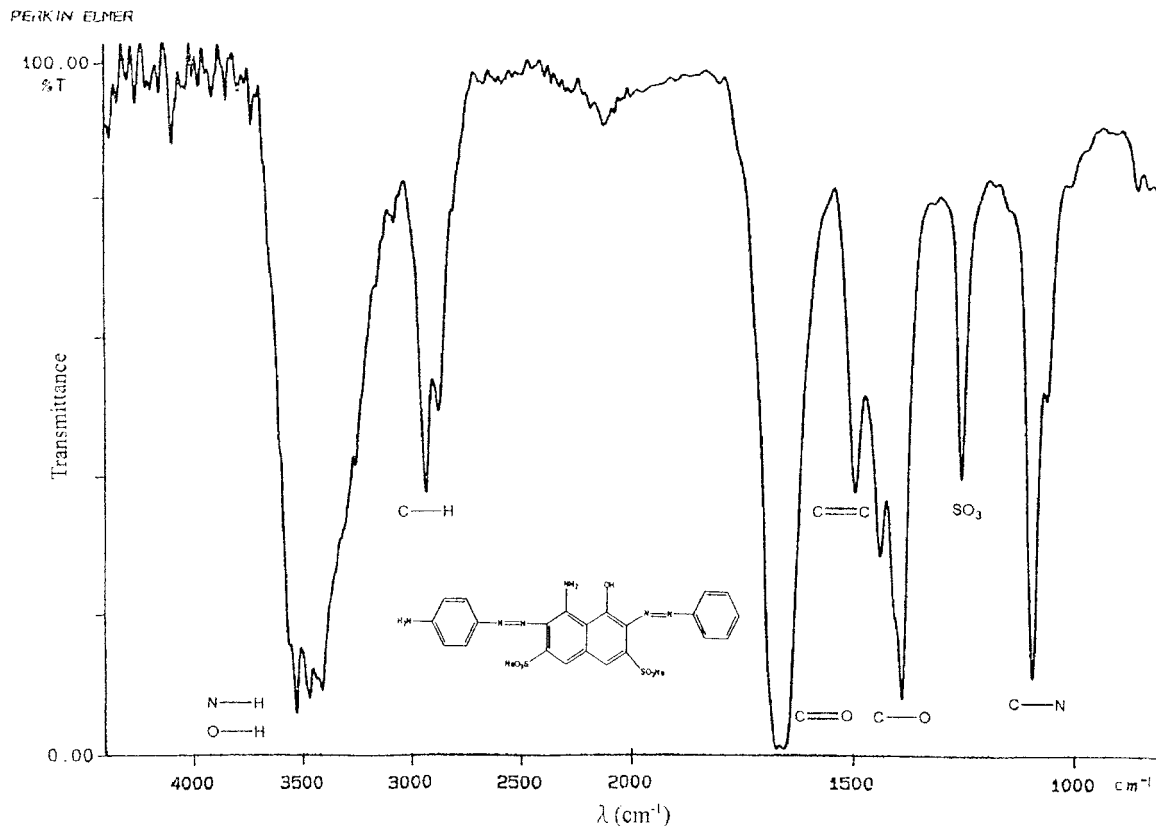


Figure 2 Spectrum of C.I. Acid Green 20 at $25 \pm 0.05^\circ\text{C}$.

solids. This PU resin solution was poured into a rectangular glass dish to a 1-mm dish thickness and dried in an oven at 60°C . This 1-mm thin film, with almost no volatile solvents, was cast to be a dumbbell shape with a narrow width of 10 ± 0.5 mm and a narrow length of 60 ± 0.5 mm and was used for tensile and elongation testing with an Instron GT-7010-A2 (Go-tech Testing Machine, Inc., Kaoshiung, Taiwan). The oxygen permeation testing of this film, with an area of 4π and a thickness of 1 mm, was carried out with an apparatus similar to the Yanaco GTR-10 gas permeability analyzer (Japan) and shown in Scheme 1. Oxygen gas with a high partial pressure was allowed to diffuse into the one side of the film made with the PU resin at a constant time of 24 h, whereas the other side of the film was placed under low partial pressure or vacuum. During the measurements, the valves labeled 1, 2, and 6 were closed, but valves 5 and 7 were open. The gas permeability coefficient³⁻⁵ was obtained from the following equation:

$$P = V_r L / A \Delta p$$

where P is the gas permeability coefficient, V_r is the volume flux of gas permeability under standard conditions, L is the thickness of the film, A is the cross area of gas permeability, and Δp is the difference in pressure between two sides of the film. The amount of

water vapor absorption for the 1-mm film placed on top of a round beaker for 24 h was obtained by the subtraction of the dry film from the wet film at $25 \pm 0.05^\circ\text{C}$. The experimental errors for these measurements were estimated to be within $\pm 0.5\%$.

RESULTS AND DISCUSSIONS

The infrared spectra for MDI, C.I. Acid Green 20, and EG are given in Figures 1-3. The reaction of MDI with EG, C.I. Acid Green 20, and other additives in the presence of DMF and toluene to form PU resins containing EG is shown in Figure 4. In a comparison of Figures 1-3 and Figure 4, we can clearly see that the NCO absorbance peak around 2275 cm^{-1} disappears completely, and the formation of strong absorbance peaks appears around 3300 (NH), 3300-3500 (OH), 1720 (C=O), 1540 (NHCO), and 1250 cm^{-1} (SO_3). These results demonstrate that the reaction of MDI with polyester, poly(propylene glycol), C.I. Acid Green 20, EG, and other additives in the presence of DMF and toluene does indeed form water-vapor-permeable PU resins. The oxygen permeability of the film made with a PU resin as a function of the diol concentration, given in Figure 5, appears to increase with an increasing concentration of the diol. This may due to increased hydrophilic groups attached to the back-

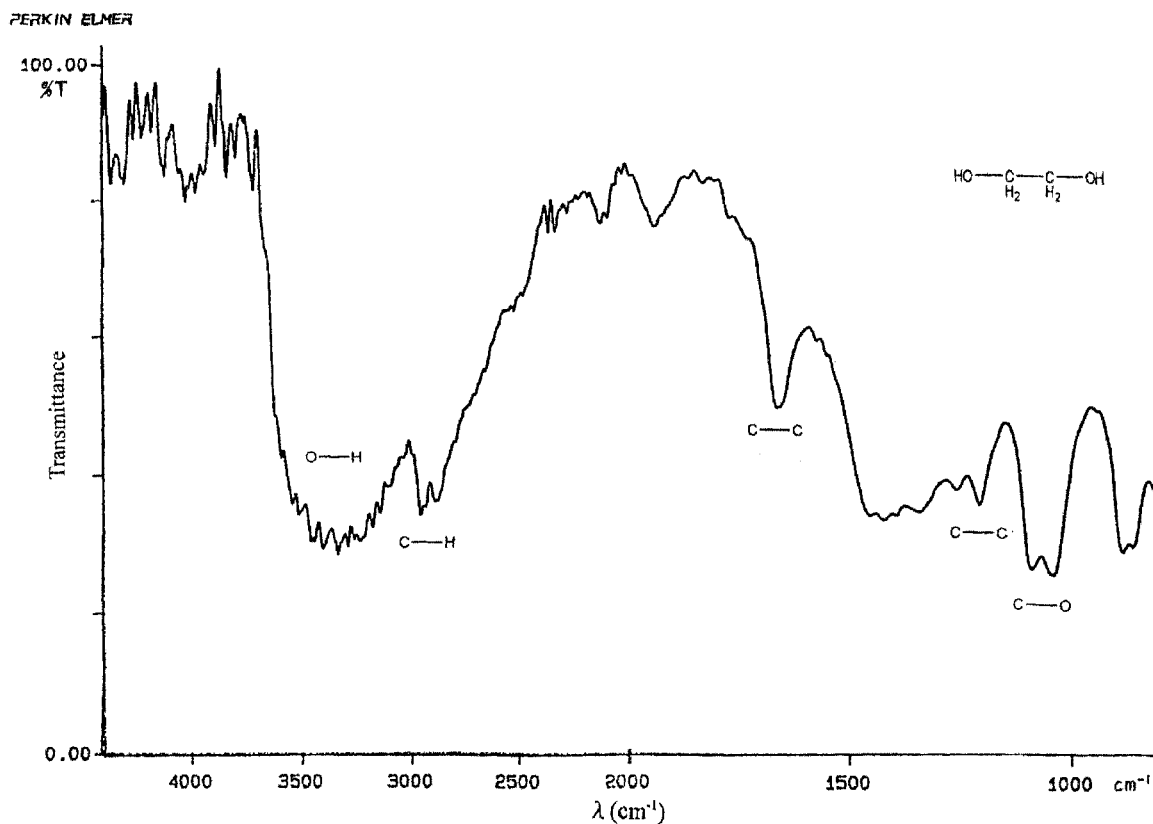


Figure 3 Spectrum of EG at $25 \pm 0.05^\circ\text{C}$.

bone of the PU resin molecule. These hydrophilic groups due to intermolecular interactions of PU resin molecules may make PU resin molecules form an expanded conformation with large porosity. Therefore, the oxygen permeability of the PU film increases. Experimental results also show that the amount of oxygen permeated through the film made with the EG-based PU resin is greater than that of DEG-based or TEG-based PU resins. This is because the hydrophilic property is stronger for EG than for DEG or TEG. Obviously, the increased hydrophilic property of the PU film will definitely increase the oxygen diffusing into this film. To further evaluate the water vapor permeability of the film made with the PU resin, we fully investigated the amount of water vapor absorption of the film made with the diol, KBM 22, KBE 22, PEG 400, and PEG 400 with KBM 22, as shown in Figures 6–8. Figure 6 clearly indicates that for the PU film, the water vapor absorption gradually increases with an increasing concentration of the EG used to prepare the PU resin as a result of the increased hydrophilic property of the PU resin.

However, for the PU film, the water vapor absorption does not increase with an increase in the concentration of DEG and TEG used in the preparation of the PU resin. Because the hydrophobic property is greater for TEG or DEG than for EG, the increased hydrophobic property is likely to prevent the water vapor from

diffusing into the PU film. This may be the reason the water vapor absorption for the PU film slightly decreases or remains unchanged. Under the same experimental conditions, the water vapor absorption for the siloxane-based PU resin appears to dramatically increase with an increasing concentration of dimethyl dimethoxysilane and dimethyl diethoxysilane, respectively, as shown in Figure 7. The result of water vapor absorption is greater for the dimethyl dimethoxysilane-based PU resin than for the dimethyl diethoxysilane-based PU resin. In fact, this is related to the hydrophilic property. Because the dimethyl dimethoxysilane with a strong hydrophilic property due to intermolecular interactions between PU resin molecules may form an expanded conformation with large porosities, the dimethyl dimethoxysilane-based PU resin has high water vapor permeability. According to our previous study on oxygen-permeable PU ionomer,² dimethyl dimethoxysilane-based PU ionomers possess high oxygen permeability. Interestingly, the water vapor absorption for the PU film appears to be independent of the concentration of PEG 400 in the presence of a fixed concentration of dimethyl dimethoxysilane used to prepare the PU resin, but it drastically increases with an increasing concentration of PEG 400 in the absence of a fixed concentration of dimethyl dimethoxysilane, as shown in Figure 8. Furthermore, PEG 400 may be considered a hydrophilic

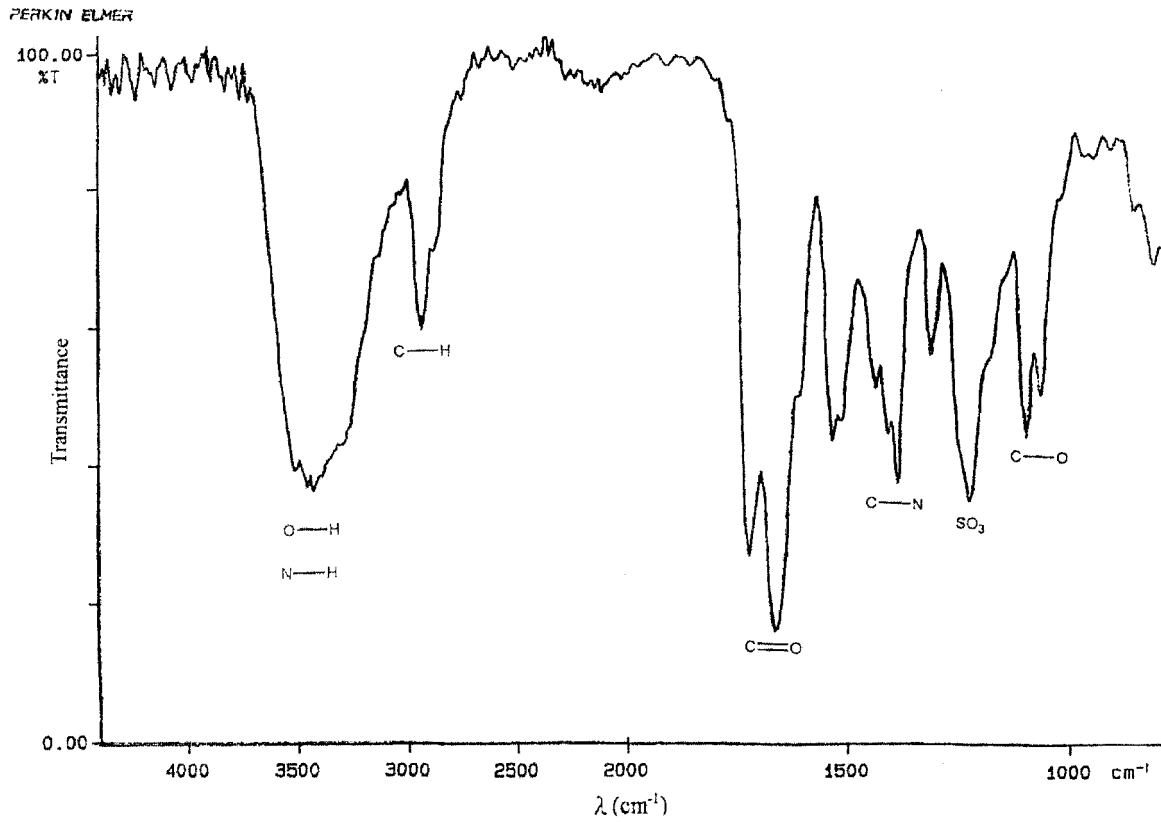


Figure 4 Spectrum of PU resin containing EG at $25 \pm 0.05^\circ\text{C}$.

molecule with no hydrophobic segment. For this reason, it is possible to form a more expanded structure with large porosity for the film made with PEG 400

than for the film made with EG, DEG, or TEG. This may be the reason the water vapor absorption appears to be larger for the film with PEG 400 than for the film

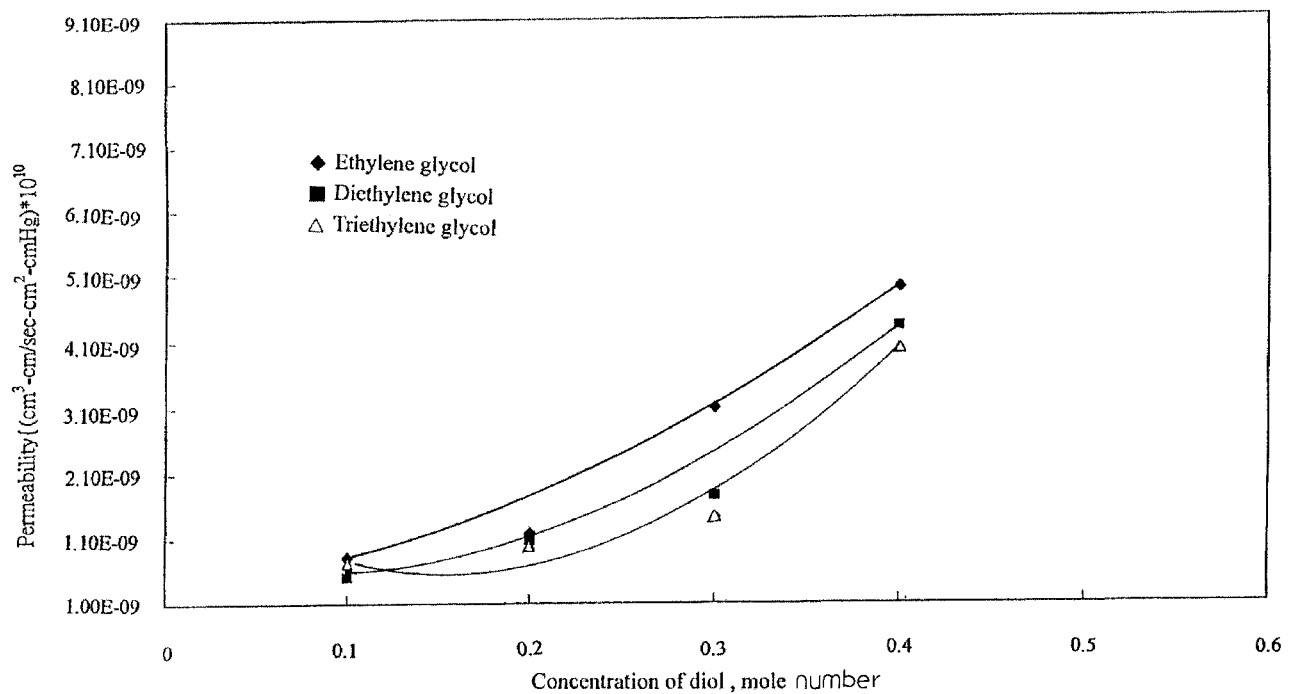


Figure 5 Plot of the oxygen permeability of a film made with PU resin as a function of the diol concentration at $25 \pm 0.05^\circ\text{C}$.

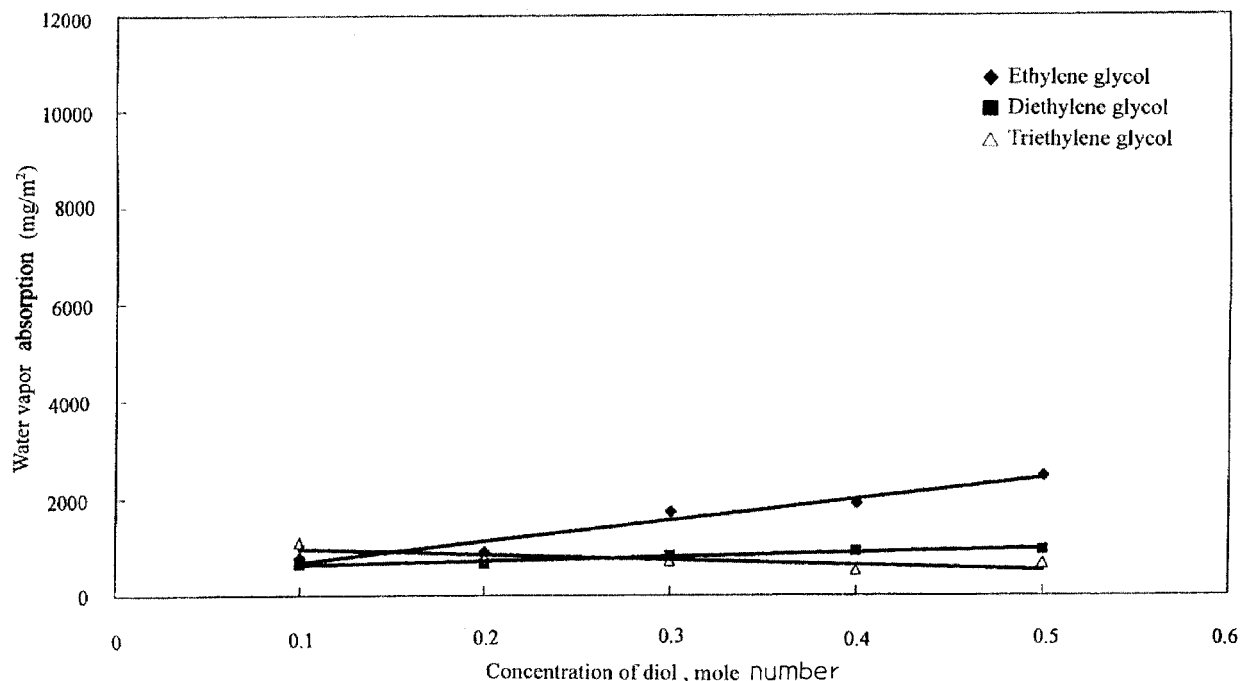


Figure 6 Plot of the water vapor absorption of a film made with PU resin as a function of the diol at $25 \pm 0.05^\circ\text{C}$.

with EG, DEG, or TEG. Anyway, according to our experimental results on water vapor absorption, we have no doubt that the greatly increased hydrophilic property of the PU resin is responsible for the increased water vapor permeability.

The tensile strength of a self-cured film of the PU resin, given in Figures 9–11, decreases with an increase in the concentration of the short-chain diol,

siloxane, and PEG for use in the preparation of the PU resin, respectively. A possible explanation for this behavior is the increased hydrophobic property of the PU resin molecules. This increased hydrophobic property may result in the prevention of intermolecular interactions between PU resin molecules, thereby greatly reducing the crosslinking capability of PU resin molecules. Additionally, the elongation of the

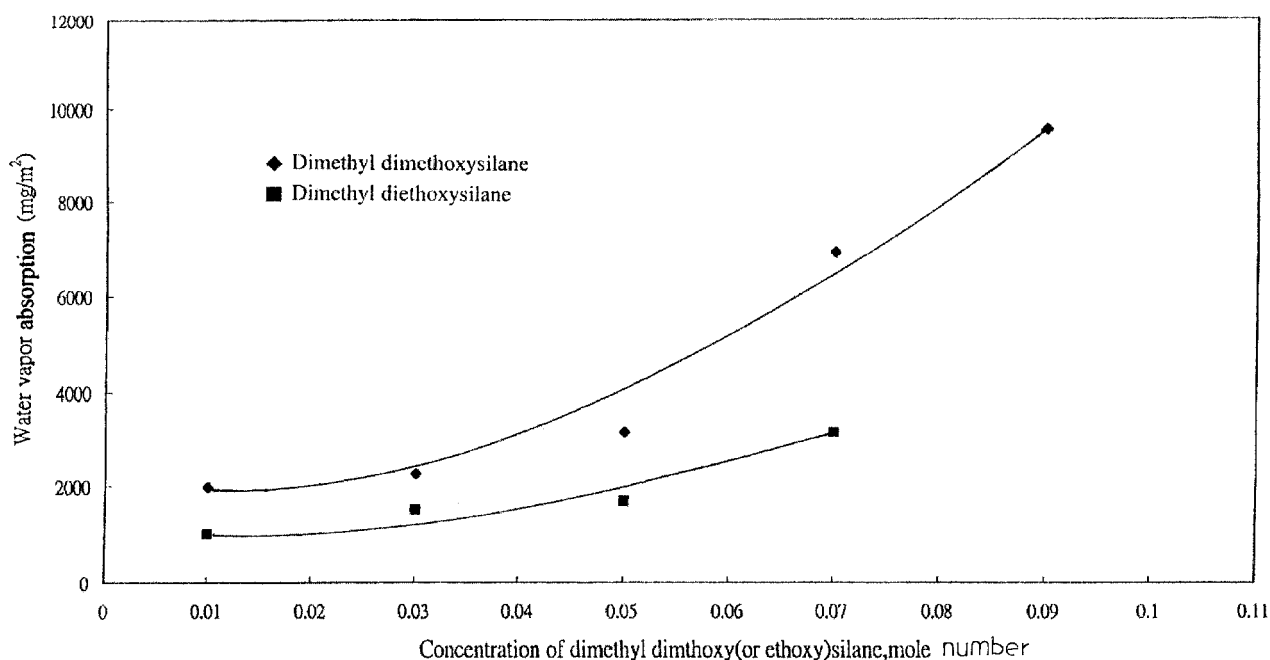


Figure 7 Plot of the water vapor absorption of a film made with PU resin as a function of dimethyl dimethoxysilane and dimethyl diethoxysilane at $25 \pm 0.05^\circ\text{C}$.

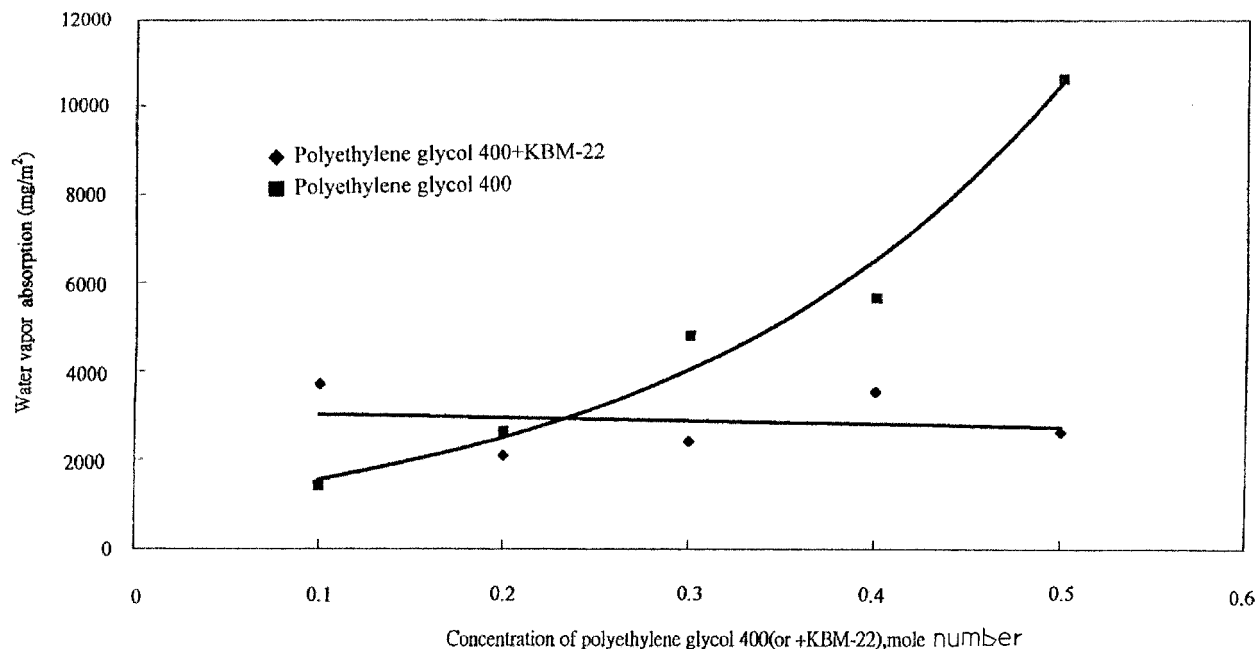


Figure 8 Plot of the water vapor absorption of a film made with PU resin as a function of PEG in the presence and absence of a fixed concentration of KBM-22 at $25 \pm 0.05^\circ\text{C}$.

dry film cast from the modified PU resin molecules at the breaking point decreases with an increasing concentration of EG, DEG, and TEG, as shown in Figure 12. The increased hydrophobic property of PU resin molecules due to their intramolecular interactions may make these PU resin molecules form a compact conformation or a micellelike structure, thereby caus-

ing the elongation of short-chain-diol-based PU resin molecules to be lower.

CONCLUSIONS

The reactions of MDI with C.I. Acid Green 20, EG, DEG, TEG, dimethylmethoxysilane, and other addi-

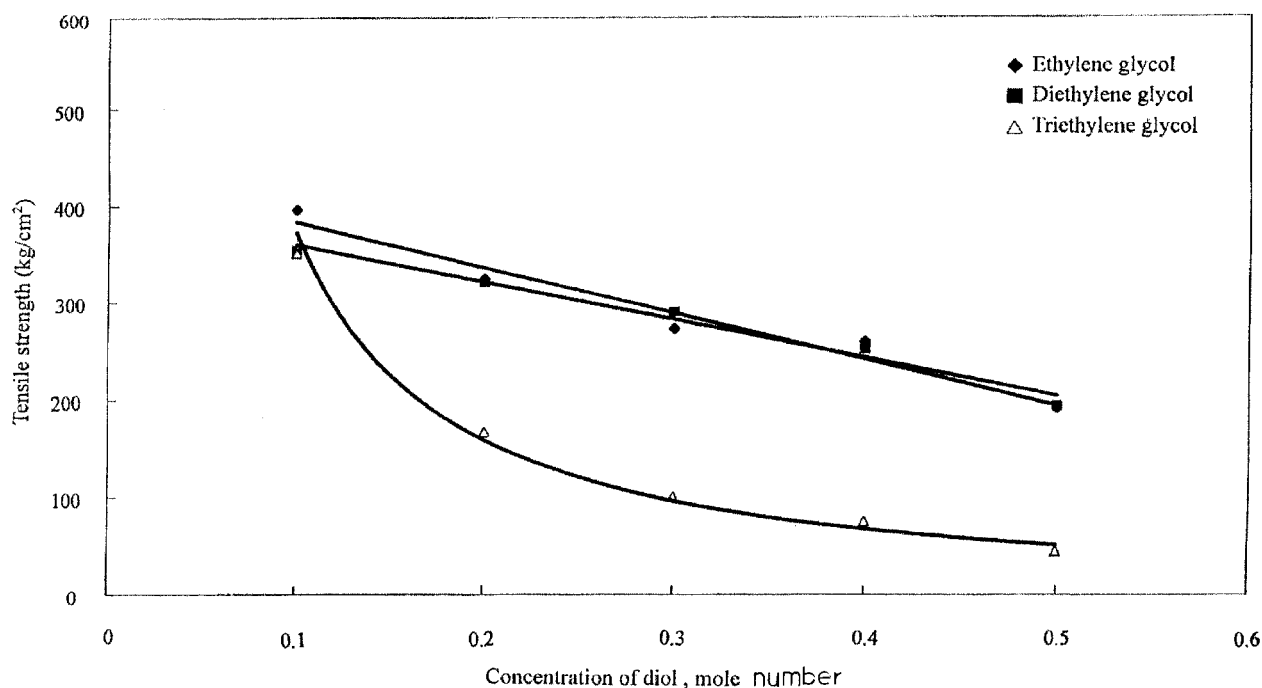


Figure 9 Plot of the tensile strength versus the diol concentration used to prepare PU resin at $25 \pm 0.05^\circ\text{C}$.

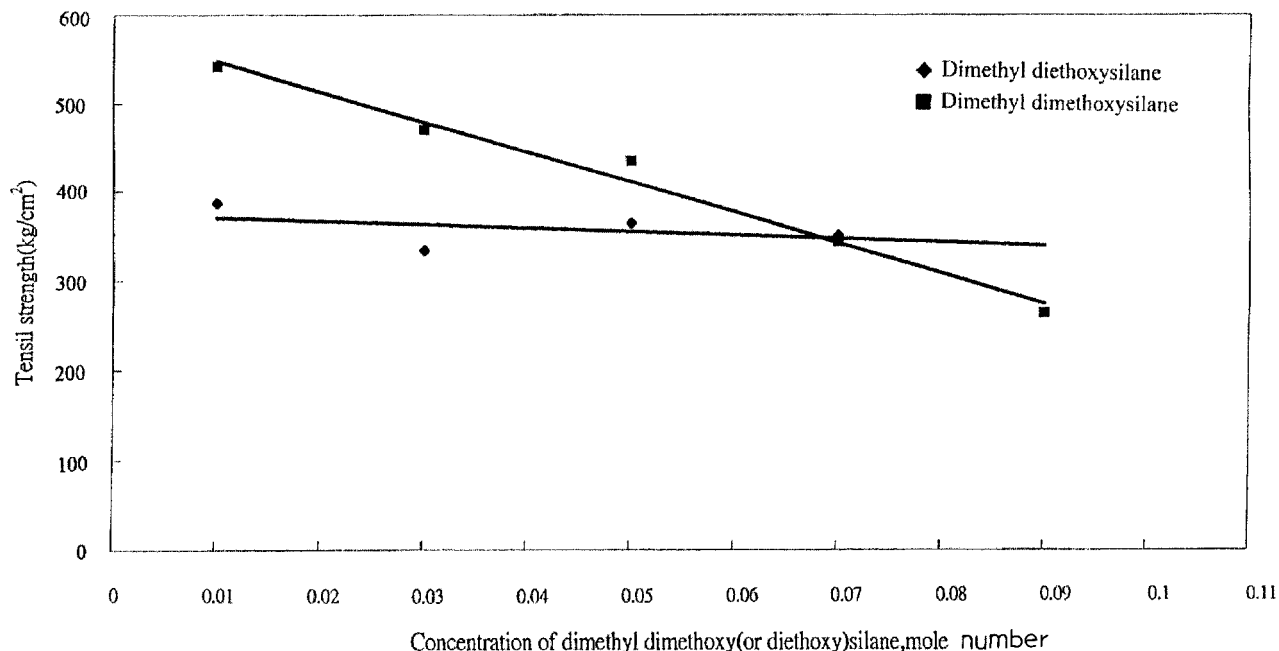


Figure 10 Plot of the tensile strength versus the concentrations of dimethyl dimethoxysilane and dimethyl diethoxysilane used to prepare PU resin at $25 \pm 0.05^\circ\text{C}$.

tives in the presence of DMF and toluene to form structures of water-vapor-permeable PU resin molecules have been proven by Fourier transform infrared spectra. Experimental results show that the amount of oxygen permeated through the film made with the PU resin increases with an increase in the concentration of EG, DEG, or TEG used to prepare the PU resin. The amount of oxygen that permeates through the film is

greater for the film made with the EG-based PU resin than for the film made with the DEG-based or TEG-based PU resins. This is the result of the greater number of hydrophilic groups of EG attached to the backbone of the PU resin molecule. Our experimental results also indicate that the water vapor absorption of the PU resin appears to increase with increasing concentrations of EG, dimethyl dimethoxysilane, di-

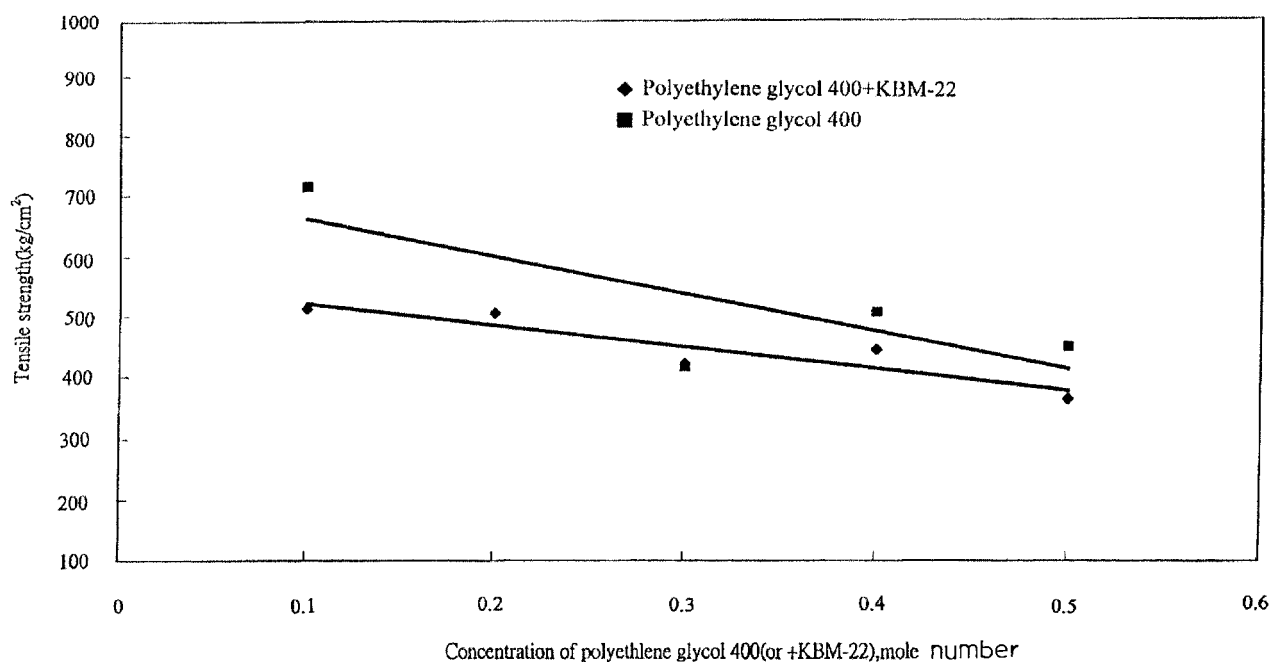


Figure 11 Plot of the tensile strength versus the concentration of PEG 400 in the presence and absence of a fixed concentration of KBM-22 used to prepare PU resin at $25 \pm 0.05^\circ\text{C}$.

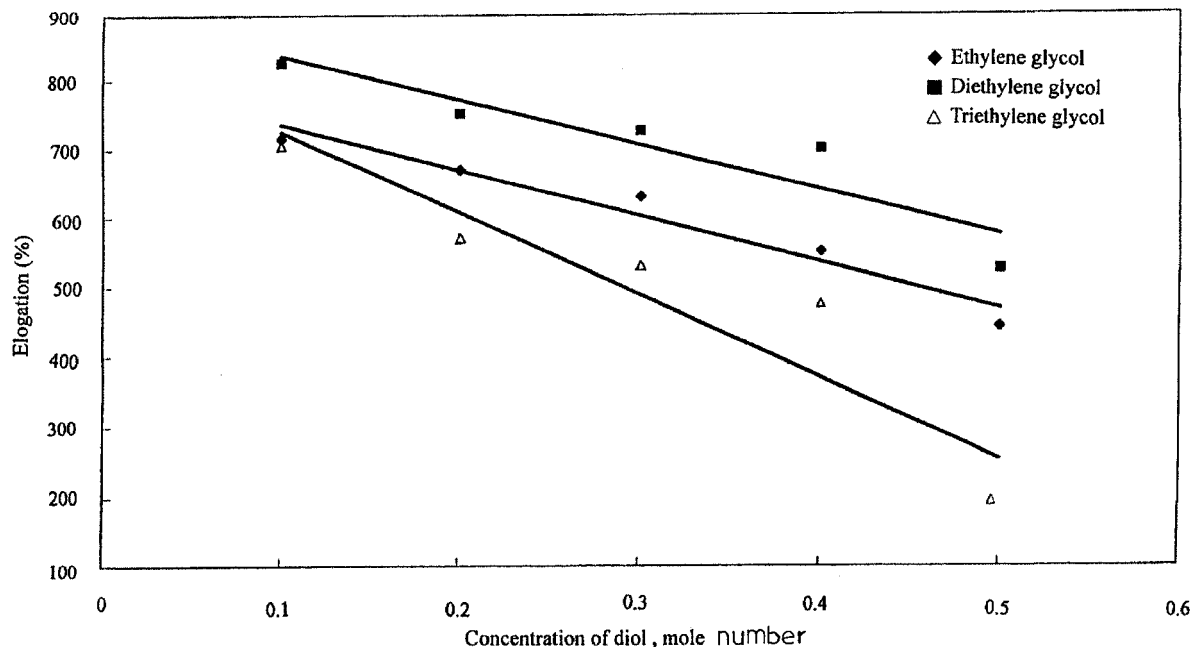


Figure 12 Plot of the elongation versus the diol concentration used to prepare PU resin at $25 \pm 0.05^\circ\text{C}$.

methyl diethoxysilane, and PEG but not to increase with increasing concentrations of DEG, TEG, and PEG 400 with KBM 22. The former is due to intermolecular interactions resulting in an expanded conformation with large porosities, and the latter is due to intramolecular interactions resulting in a compact conformation or a micellelike structure with small porosities. Therefore, the former water vapor permeability increases, but the latter remains unchanged or decreases. For the tensile strength of self-cured films of PU resin molecules, the tensile strength at the breaking point decreases with increasing concentrations of EG, DEG, TEG, dimethyl dimethoxysilane, dimethyl diethoxysilane, PEG 400, and PEG 400 with dimethyl dimethoxysilane. This may be the result of the compact conformation or micellelike structure formed because of the strong intramolecular interactions of PU resin molecules resulting from increased hydrophobic

groups. In addition, the elongation of short-chain-diol-based PU resin molecules at the breaking point, because of the intramolecular interactions of the PU resin molecules themselves, becomes lower as the concentration of the short-chain diol increases.

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