



DIFFUSION OF ETHANOL AND WATER THROUGH PU MEMBRANES

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Abstract—A series of hydroxyl-terminated polybutadiene (HTPB) and 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI)-based polyurethanes (PUs) were synthesized by solution polymerization. PU membranes were prepared by a dry/wet phase inversion method. The effects of membrane formation method and preparation condition on gas permeability and permeability ratio (ethanol permeability/water permeability) were investigated. We found that the variation in morphology of these membranes was contributed to by the difference in surface energy between the nonpolar HTPB soft segment and the polar hard segment. The permeation of the ethanol/water mixture and permeability ratio were tested by pervaporation and the side-by-side method. The permeability of water or ethanol using the side-by-side test through dry/wet membranes, which are prepared using different phase inversion conditions, can be controlled from 50 to 1100 g/m².hr. A strange phenomenon was discovered, in that the permeation increased with the increase of hard segment content of PU membranes, while the permeability ratio decreased. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Polymer membranes have been used for the separation of water/ethanol mixtures by pervaporation using, for example, cellulose acetate [1], polyvinyl alcohol [2, 3], chitosan [4], asymmetric Nylon 4 [5] and the IPN of PU membranes [6, 7]. Alcohol permselective membranes from aqueous alcohol solutions have been prepared by crosslinked polybutadiene [8, 9] prepared by a dry method. But the permeability of the crosslinked polybutadiene membrane is small (1.2 g/m².hr). On the other hand, in commercial transdermal drug delivery systems (TDDSs), the best ethanol permeabilities through membranes are reported to be controlled between 50 and 70 g/m².hr [10, 11].

The purpose of this study is to prepare membranes possessing the nonswelling characteristics in ethanol/water mixtures and with a different controlled released permeability for ethanol. HTPB-based PU membranes prepared by the dry method easily swell in an ethanol/water mixture and hence are unsuitable for the controlled delivery of an ethanol/water mixture. In this study, a mixed process of dry/wet phase inversion is used for the preparation of smooth, elastic and nonswelling, asymmetric PU membranes. These HTPB-based PU membranes cannot be formed by the wet method only because the viscosity of these PU solutions are too low for the membrane preparation. The effects of different membrane formation conditions, such as PU composition, concentration of casting solution and coagulation medium, and the membrane formation process on the

resulting membrane formation and asymmetric structure were studied.

EXPERIMENTAL

Materials

The chemicals used in this study were 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI, Desmodur W of Mobay Co.), hydroxyl-terminated polybutadiene (HTPB, R-45M of Arco Co.), 1,4-butanediol (1,4-BD) as a chain extender, and dibutyltin dilaurate (DBTDL) as catalyst. Dimethyl formamide (DMF) and toluene are used as solvents for the preparation of the PU solution. Different compositions of water/ethanol mixture are used as a coagulation medium or feed for the preparation or diffusion test of dry/wet PU membranes.

Preparation of PU membrane

The two-stage PUs were polymerized first by an -NCO terminated prepolymer and then chain extended with 1,4-BD to give a 25 wt% solid content after the theoretical -NCO content had been achieved. This was diluted to 15–20 wt% solid content after the chain extending reaction had proceeded for 30 min. The reaction was terminated as the -NCO groups were completely consumed, as confirmed by the disappearance of the infrared (IR) absorption at 2280 cm⁻¹.

Dry membranes were prepared by pouring the solution mixture on to a glass plate to a thickness of 600 μm. The solvent in the casting solution was evaporated by degassing at 50°C for 24 hr. The dried PU membranes were peeled from the plate after it had been immersed in deionized water for several hours. The PU membranes were dried in a desiccator and stored at a relative humidity of 50% and at 25°C for 5 days before testing.

Dry/wet membranes were prepared by pouring the PU solution on to a glass plate to a thickness of 600 μm using a Gardner knife [12–15]. The solvent in the casting solution

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was evaporated by degassing at room temperature for 5 min and then immersed in the coagulation medium at different temperatures (15, 20 and 25°C) and compositions (90, 70, 50 and 30 wt% ethanol content of aqueous solution) for 10 min. Finally, the prepared membranes were dipped in distilled water for 20 min and dried in vacuum at room temperature for 48 hr for the removal of residual solvent in the membrane. The different compositions of PUs in this study are HTPB/H₁₂MDI/1,4-BD = 1/4/3, 1/8/7 and 1/12/11, which possess 33.08, 50.56 and 60.79 wt% hard segment content, respectively. Dry/wet membranes are all prepared using a 20°C coagulation medium, except for studying the effect of temperature of the coagulation medium.

Infrared spectroscopy

Infrared spectra of dry films were obtained using a Jasco FTIR-300E spectrometer. The films were pressed against a 45° germanium crystal. Spectra were collected at a resolution of 2 cm⁻¹. The peak due to bonded C=O stretching is centered at 1700 cm⁻¹ and that due to free C=O stretching is centered at about 1717 cm⁻¹. The peak of bonded N-H stretching is at 3320 cm⁻¹ and that of free N-H stretching is at 3442 cm⁻¹. The infrared absorbance of the total carbonyl groups detected by FTIR-ATR (attenuated total reflectance) was calculated by the addition of the respective hydrogen bonded C=O absorbance and free hydrogen bonded C=O absorbance. The infrared absorption bands of the butadiene soft segment are the *trans*-1,4 form at 972 cm⁻¹, *trans*-1,2 form at 912 cm⁻¹ and *cis*-1,4 form at 685 cm⁻¹. The C=O/C=C ratio on the surface is the ratio of total C=O absorbance with *trans*-1,4 form C=C absorbance. A larger value of this ratio indicates a larger hard segment content on the surface of the membrane.

Hydrogen bonded carbonyl bands will correspond to those groups that are in the interior of hard segments, while the free bands may correspond to those groups in the hard segment domains or at the interface [16]. In the butadiene-containing polyurethanes, hydrogen bonding occurs only between urethane segments of the N-H and C=O group, since the carbonyls in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors. The extent of the N-H group participating in hydrogen bonding is expressed by the hydrogen bonding index (HBI), which is defined as the relative absorbencies of the two N-H group peaks [17], i.e. $HBI = A_{N-H, bonded} / A_{N-H, free}$, where $A_{N-H, bonded}$ and $A_{N-H, free}$ are the absorbance of bonded and free N-H groups, respectively.

SEM

The structures of the prepared membranes were examined by a Hitachi Model S570 scanning electron microscope (SEM).

Pervaporation experiment

A traditional pervaporation apparatus was used in this study [18]. The permeation rate was determined by the weight of the permeate. The permeability is defined as the weight of water/ethanol mixture permeated through 1.0 m² area of membrane per hour. Most of the experiments were conducted at 25°C. The feed temperature was studied in the range 25–65°C. The compositions of the feed solutions and permeate were measured by gas chromatography (China Chromatography, GC 8700T).

Side-by-side test

Membranes were put within the cell of the side-by-side apparatus, as shown in Fig. 1. Equal amounts of ethanol and water were added to the donor and receiver, respectively. The donor and receiver were stirred with a magnetic stirrer at 37°C. A 1 μl sample, which was analyzed by GC, was taken from the donor and receiver every 2 hr. The permeability is defined as the weight of water or ethanol diffused through 1.0 m² area of membrane per hour. The

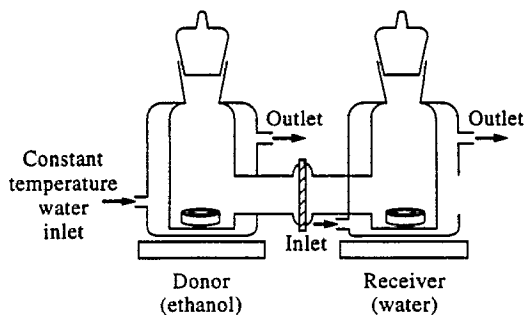


Fig. 1. Apparatus for side-by-side test.

permeability ratio is defined as the ratio of ethanol permeability to water permeability.

RESULTS AND DISCUSSION

Pervaporation test

Effect of preparation method. For this test, dry/wet membranes are prepared by dipping in a 90 wt% ethanol content coagulation medium. Pervaporation tests are operated with a 90 wt% ethanol content of feed, which gave the largest permeation rate of both dry/wet and dry membranes. Figure 2 shows that the permeabilities of the ethanol/water mixture for dry/wet membranes are all 6- to 10-fold larger than that of corresponding dry membranes. This phenomenon may be due to the fact that dry membranes possess a dense and homogeneous polymer structure, while dry/wet membranes are porous in substrate and possess a thin skin layer.

Effect of hard segment content. Figure 3 shows that the permeability of an ethanol/water mixture of 90 wt% ethanol content diffusing through dry/wet membranes changed with either a different hard segment content or preparation conditions of the ethanol/water coagulation medium of 50, 70 and 90 wt% ethanol content, respectively. The permeability increases with increase of hard segment content. However, the swelling behavior of the HTPB soft segment decreases and the intermolecular attraction

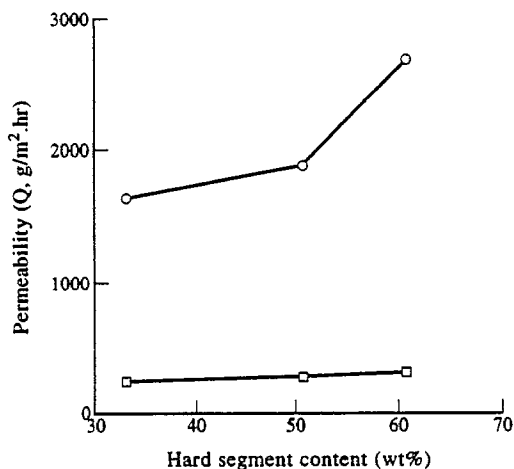


Fig. 2. Effect of membrane preparation method on permeability: (○) dry/wet; (□) dry.

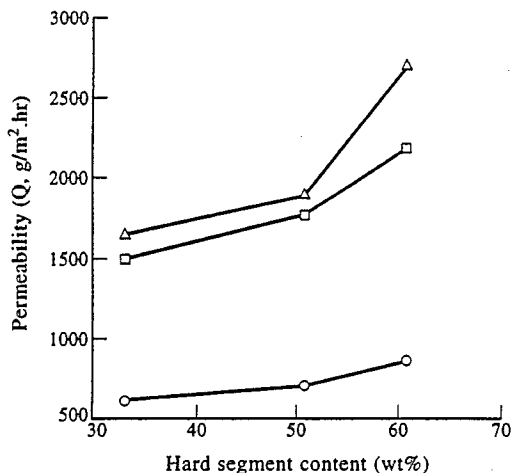


Fig. 3. Effect of hard segment content and concentration of coagulation medium on permeability. (○) 50, (□) 70, (Δ) 90 wt% ethanol content of coagulation medium.

increases as the hard segment increases. The increase of intermolecular attraction can be expressed by the extent of hydrogen bonding between hard segments, i.e. HBI values. The HBI value increases with increase of hard segment content for all three coagulation medium prepared membranes, as expressed in the next two sections. As discussed in a previous report [19], this indicates that the sorption ability has a preferential effect on the PU elastomer as the hard segment content increases. The increase of hard segment content of the PU elastomer induces an increase in sorption effect predominantly on the permeability of the ethanol/water mixture [20, 21], and hence increases the permeability.

Effect of concentration of coagulation medium. The pervaporation results of the 90 wt% aqueous ethanol solution feed through membranes prepared using different coagulation media are shown in Fig. 3. It shows that the permeability of membranes fall in the following sequence of ethanol content of coagulation medium: 90 wt% > 70 wt% > 50 wt%. This phenomenon might be explained by the change of surface composition and SEM graph, as discussed in the following section.

Surface composition and SEM graph. The surface composition of these HTPB-based PU membranes was measured by FTIR-ATR and represented as the C=O/C=C ratio, which is a ratio of hard to soft segment content on the surface. The variation of surface composition with respect to membrane formation method and concentration of coagulation medium is shown in Fig. 4. The C=O/C=C ratios of the surface of dry/wet membranes are all larger than that of dry membranes and decreases with increase of ethanol content of the coagulation medium. This could be explained by the polar coagulation medium of water and ethanol, which induces more polar hard segment migration to the surface of the dry/wet membranes. Membranes prepared by dipping in 50 wt% ethanol content coagulation medium have the largest hard segment content on the surface.

The amount of hard segment dispersed in the surface will affect the membrane morphology. More

N-H groups are hydrogen bonded in PU membranes with a higher hard segment content and the separation between nonpolar HTPB soft segment and hard segment is decreased. The increase of hard segment content increases the intermolecular attraction of these nonpolar HTPB-based PUs [19, 22]. This could be proved by the change of hydrogen bonding index (HBI) of the PU membranes prepared with different coagulation media. The HBI values with 33.08 wt% of hard segment content change from 1.683, to 1.455, to 1.257 as the ethanol concentration of the coagulation medium varies from 50, to 70, to 90 wt%. While the HBI values of membranes with 50.56 or 60.79 wt% of hard segment content change from 1.800, to 1.627, to 1.500 or from 1.871, to 1.729, to 1.648, respectively. Membranes prepared by dipping in 50 wt% ethanol content coagulation medium have the largest HBI values and hence are more dense than the other two types of membranes. This could also be proved by the SEM graph, as shown in Fig. 5. Membranes prepared by dipping in 50 wt% ethanol content coagulation medium possess the smallest void concentration and are more dense than the other two types of membranes.

Effect of coagulation temperature. In this and the following section, dry/wet membranes were prepared by dipping in 70 wt% ethanol content coagulation medium, due to the medium permeability of these membranes as discussed in the above section. Figure 6 shows that the permeability increases with increase of coagulation temperature. In general, the increase of coagulation temperature has two effects on membrane formation. One is that more hard segment, with the larger surface energy of the hard segment, migrates to the top surface of the membranes, giving the more homogeneous composition of the surface, which induces the more dense membrane structure. The other is the increase of mixing rate between polymer solution and coagulation medium [23]. Easier phase separation, which induces more porous membrane structure, occurs with membranes prepared at higher coagulation

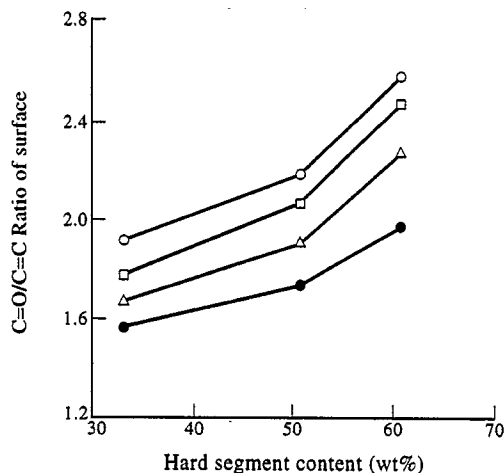
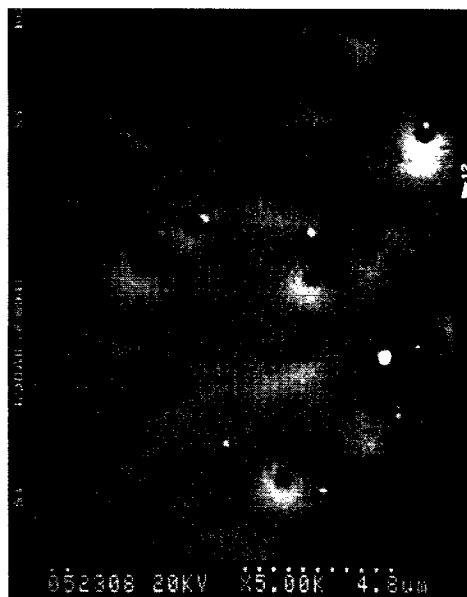


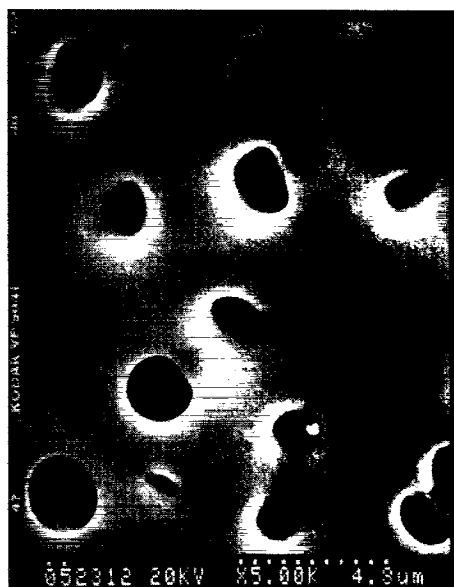
Fig. 4. Effect of preparation method and different concentration of coagulation medium on C=O/C=C ratio of surface. (○) 50, (□) 70, (Δ) 90 wt% ethanol content of coagulation medium; (●) dry membranes.



(a) 50 wt%



(b) 70 wt%



(c) 90 wt%

Fig. 5. Effect of ethanol concentration of coagulation medium on PU morphology (SEM graph). (a) 50 wt%, (b) 70 wt%, (c) 90 wt% ethanol content of coagulation medium.

temperatures. The competition of the above two effects shows that the increase of demixing rate has a larger influence on the phase separation and hence the increase of permeability, as the coagulation temperature is increased.

Effect of polymer content. Figure 7 shows that the permeability decreases on increasing the polymer content of the casting solution from 15, to 18, to 20 wt%. These results might be due to the fact that an increase in the initial polymer concentration in the casting solution leads to a much higher polymer concentration on the surface. Thus, an increase in polymer concentration decreases the rate of casting

solution undergoing liquid-liquid demixing, resulting in a denser structure [24] and increasing the top layer thickness.

Side-by-side test

Effect of hard segment content. Membranes were put in the side-by-side cell. The operation times of the permeation tests are 6, 8 and 12 hr for membranes with hard segment contents of 60.79, 50.56 and 33.08 wt%, respectively. The lower the hard segment content of the membrane is, the longer the operation time. Figure 8 shows that the permeability of water and ethanol are both increased as the hard segment

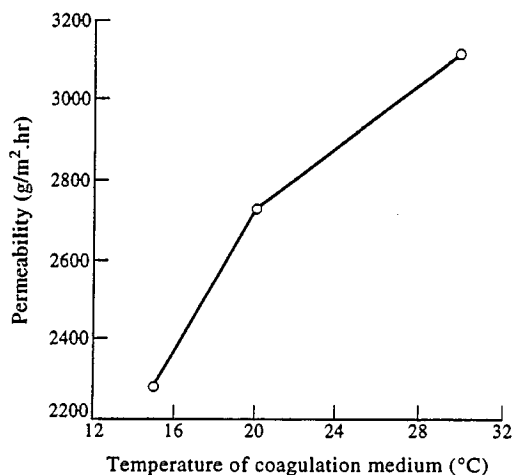


Fig. 6. Effect of temperature of coagulation medium (°C) on permeability.

increases. The increase of hard segment content of the PU elastomer induces the increase of sorption effect on the permeability of the ethanol/water mixture [20, 21]. As explained in the above pervaporation section, the sorption ability has a preferential effect on the diffusion phenomenon of these PU elastomers.

Figure 8 shows that the permeability ratio of ethanol with water decreases with increase of hard segment content. The HTPB segment is hydrophobic and interacts with ethanol and swells easily. The HTPB soft segment interacts with the hydrophobic moiety of the ethanol of the feed and the OH groups of ethanol remain exposed on the polymer surface, which then has the preferential sorption ability with water. On the other hand, the increase of the polar hard segment content increases the affinity of the membrane with water over that with ethanol. This may be the reason for the decrease of permeability ratio as the hard segment content increases.

Effect of concentration of coagulation medium. The membrane compositions used in this section are all with an equivalent ratio of HTPB/H₁₂MDI/1,4-BD = 1/8/7 due to the more even and lower defect

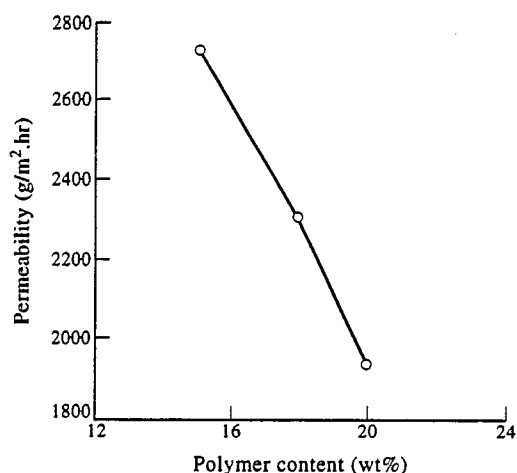


Fig. 7. Effect of polymer content (wt%) on permeability.

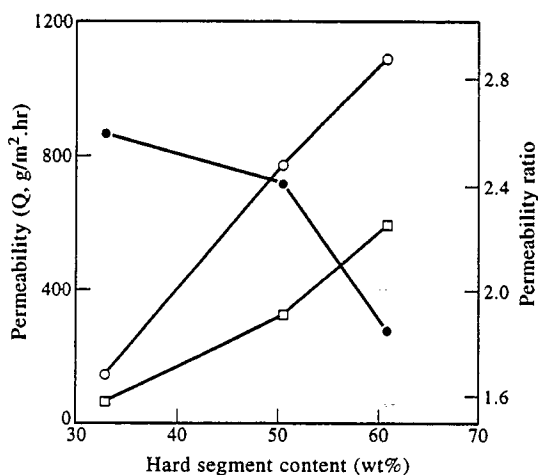


Fig. 8. Effect of hard segment content on permeability of ethanol (○) and water (□) and permeability ratio (●) using side-by-side test.

membrane formed, compared with other PU compositions.

Figure 9 shows that both the permeability of the two solvents and the permeability ratio of ethanol with water both increase with the increase of ethanol content in the coagulation medium. The reason may be that the compatibility between the PU polymer and water is lower than that with ethanol. Meanwhile, there is a toluene solvent in the casting solution, which is insoluble with water and induces the decreasing demixing rate between casting solution and coagulation medium. Then dense membranes are easily formed along with the decrease of demixing rate when dipped in the lower ethanol content coagulation medium. A lower permeability and permeability ratio are gained when the membranes are prepared in the low ethanol content coagulation medium due to the dense structure formed.

Effect of temperature of coagulation medium. Dry/wet membranes used in this and the following

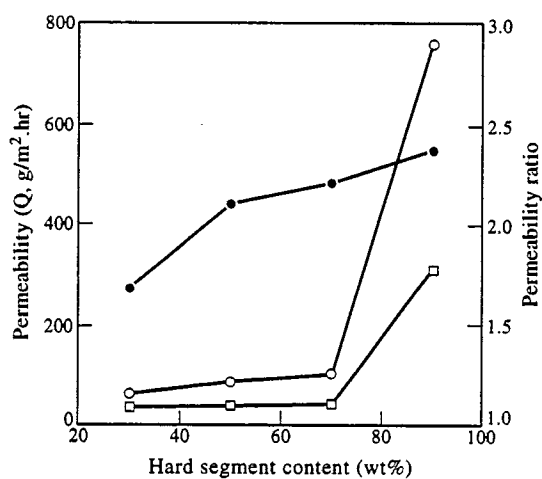


Fig. 9. Effect of ethanol content of coagulation medium on permeability of ethanol (○) and water (□) and permeability ratio (●) using side-by-side test.

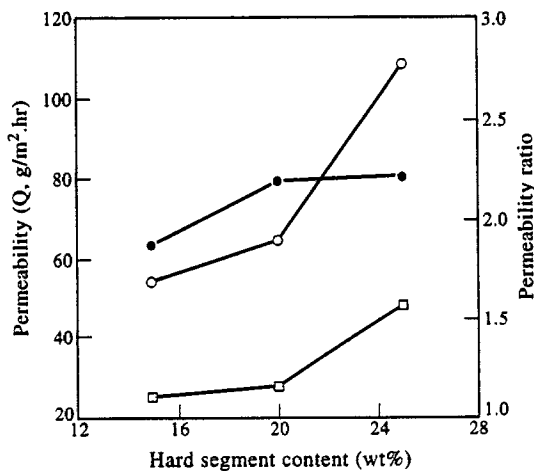


Fig. 10. Effect of temperature of coagulation medium on permeability of ethanol (○) and water (□) and permeability ratio (●) using side-by-side test.

section were prepared by dipping in 70 wt% aqueous ethanol solution and using PUs with an equivalent ratio of HTPB/H₁₂MDI/1,4-BD = 1/8/7 due to the more uniform surface skin of the membranes formed.

Both higher ethanol and water permeabilities are obtained when the membranes are immersed in the ethanol/water mixture at higher coagulation temperatures, as shown in Fig. 10. The permeability ratios remain nearly constant for these three coagulation temperatures. The demixing rate between the casting solution and coagulation solvent is raised when the temperature of the coagulation medium is increased and hence induces a more porous surface skin of the membrane.

Effect of polymer content. The permeability of water and ethanol and the permeability ratio all decreased with increase of polymer concentration in the casting solution, as shown in Fig. 11. The increase of polymer concentration increases the solid content and viscosity of the casting solution. After being dipped in coagulation medium, the formation

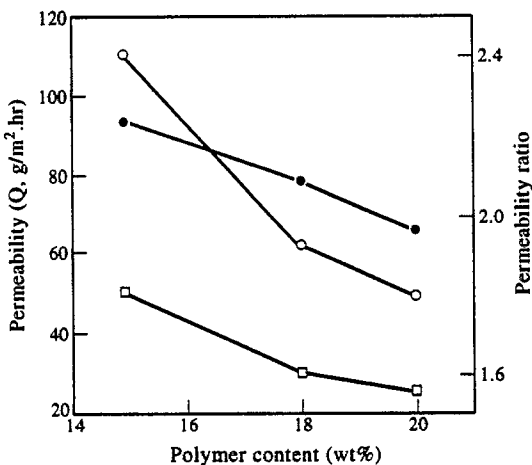


Fig. 11. Effect of polymer content on permeability of ethanol (○) and water (□) and permeability ratio (●) using side-by-side test.

resistance of polymer-poor phase is increased and hence a more dense membrane structure is formed as the polymer content of the casting solution is increased.

CONCLUSIONS

The permeabilities of membranes prepared by a dry/wet phase inversion method are all 6- to 10-fold higher than those of membranes prepared by the dry method. Permeability increases as the hard segment content increases and for membranes prepared by dipping in concentrated ethanol aqueous solution coagulation medium. Membranes dipped in 50 wt% ethanol content coagulation medium have the largest hard segment content on the surface. Membranes prepared by the dry/wet phase inversion method possess nonswelling characteristics in the ethanol/water mixture and controlled release abilities for ethanol.

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