On the gas permeability of hydroxyl terminated polybutadiene based polyurethane membranes

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Abstract

A series of hydroxyl terminated polybutadiene (HTPB) based polyurethanes (PU) were synthesized by solution polymerization with different kinds of polyols and diisocyanates, hard segment contents, NCO/OH value, polymerization methods and annealing time. The segregation between hard and soft segments was manifested by incompatibility between hard and soft segment, steric hindrance of urethane groups and the extent of interchain hydrogen bonding. Hydrogen bonding index (HBI) measured by FTIR was employed to show the extent of interchain hydrogen bonding, which affects the segregation and hence gas permeability of the prepared membranes. Membranes with high HBI were seen to have low segregation and hence low gas permeability. Membranes with mixed diisocyanates of polar 4,4'-diphenylmethane diisocyanate (MDI) and nonpolar isophorone diisocyanate (IPDI), lower hard segment content and NCO/OH value, and one-stage polymerization methods exhibit higher gas permeability.

Keywords: Polyurethane membrane; Hydroxyl terminated polybutadiene; Gas permeability; Hydrogen bonding index

1. Introduction

PU are multi-block copolymers usually consisting of hard segments and polyether or polyester soft segments. These polymers possess very attractive bulk mechanical properties due to the presence of phase-separated structures. It's applications are varied, such as medical implants, membranes, adhesives, and coatings. HTPB is a viscous liquid, which is easy to cast. It's superior hydrolytic stabilities and high mechanical property performances show surprising utility in many fields [1–3]. HTPB based polyurethanes can be used for gas separation because of their low temperature flexibility and high segregation between hard and soft segments.

The purpose of this study is to synthesize the HTPB based PU membranes and investigate the segregation and gas permeability properties of the prepared membranes. Factors that affect the segregation and gas permeability of the prepared PU membranes studied include: different kinds of polyols and diisocyanates, hard segment contents, polymerization methods, annealing time and NCO/OH value. The degree of segregation between hard and soft segments was studied in terms of incompatibility (solubility parameter difference), steric hindrance and extent of hydrogen bonding. HBI measured by FTIR was utilized to manifest the segregation and gas permeability of the prepared membranes.

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2. Experimental

The chemicals used for this study were MDI, IPDI, 2,4-toluene diisocyanate (TDI), hydroxyl terminated polybutadiene (HTPB, equivalent weight 1370 g, average functionality 2.3), poly(butylene adipate) glycol (PBA) of M.W. 2000, poly(caprolactone) glycol (PCL) of M.W. 2000, poly(oxypropylene) glycol (PPG) of M.W. 2000, poly(oxyethylene) glycol (PEG) of M.W. 2000, 1,4-butane diol (1,4-BD) used as chain extender and dibutyltin dilaurate (DBTDL) as catalyst. Tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were used as solvents.

2.1. Preparation of polyurethane membranes

The preparation of polyurethane solutions employed different kinds of polyols, diisocyanates, hard segment contents, polymerization methods and NCO/OH values as shown in Table 1. The one-stage PU polymers were prepared by adding proper weights of polyol, chain extender and solvents with suitable ratio of THF and DMF to the reaction vessel under a nitrogen atmosphere. After adding a suitable amount of diisocyanate and mixing evenly, the mixture was heated to 60°C slowly. The reaction proceeded in the presence of the catalyst DBTDL and was stopped as the –NCO groups were completely consumed, as confirmed by the disappearance of the infrared (IR) absorption at 2280 cm^{-1}. Then the reaction solutions were diluted to 15 wt% solid content.

The two-stage polyurethanes were polymerized first by a –NCO terminated prepolymer and then chain extended with 1,4-BD. The compositions were the same as the above one-stage polymerized polyurethanes.

Membranes for testing were prepared by pouring the solution mixture onto a glass plate to a thickness of 400 μm. The solvent in the casting solution was evaporated by degassing at 50°C for 24 h. 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% for at least three days before they were used for property tests.

2.2. Gas permeation measurement

Oxygen and nitrogen permeabilities of membranes were determined by using the Yanaco GTR-10 gas permeability analyzer. Detailed procedure for measuring the gas permeation had been reported in a previous publication [4]. The gas permeability was determined by the following equation:

$$P = \frac{q \cdot l}{(p_1 - p_2) \cdot A \cdot t}$$

where P is the gas permeability (cm^3 (STP).cm.cm^{-2}.s^{-1}.cmHg^{-1}), q/t is the volumetric flow rate of gas permeation (cm^3 (STP)/s), l is the membrane thickness (cm), p_1 and p_2 are the pressures (cmHg) and A is the effective membrane area (cm^2).

2.3. Properties measurement

The solubility parameter (δ) was estimated by the calculation of Fedors' molar attraction constant data and also checked by the intrinsic viscosity method [5,6]. A SEIKO SSXC 5000 DSC was used to measure the thermal properties. The temperature was controlled within the range between -150°C and 300°C and the heating rate was 10°C/min. WAXD scans were generated by a Shimadzu XD-5 diffractometer equipped with monochromatized copper radiation. Data were obtained from 5 to 40° at a scan rate of 2°/min. FTIR spectra were obtained from a BIO-RAD FTS-7.

3. Results and discussion

3.1. Hydrogen bonding index

The obvious polar difference between nonpolar HTPB soft segment and polar hard segment makes these membranes possessing microphase separation. In this study DSC and WAXD data did not provide a satisfactory illustration of the crystallinity and free volume, which are the major factors that affect the segregation and gas permeability. Therefore, the change of interchain hydrogen bonding was utilized to study the microphase separation. Infrared technique is possibly the most suitable for measuring the extent of hydrogen bonding [7–16].
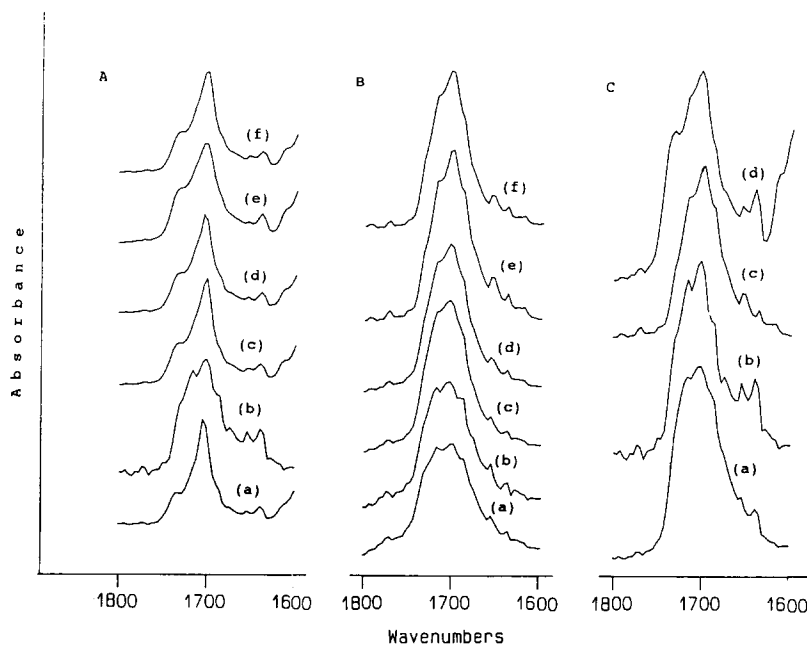
Fig. 1. FTIR spectra in the range of 1600–1800 cm^{-1}. (A) HTPB/MDI/1,4-BD (NCO/OH=1.0/1.0): (a) 1/9/8, (b) 1/6/5, (c) 1/5/4, (d) 1/4/3, (e) 1/3/2, (f) 1/2/1. (B) HTPB/IPDI/1,4-BD (NCO/OH=1.0/1.0): (a) 1/2/1, (b) 1/3/2, (c) 1/5/4, (d) 1/9/8, (e) 1/12/11, (f) 1/15/14. (C) HTPB/IPDI/1,4-BD (NCO/OH value): (a) 1/4.25/4 (0.85/1.0), (b) 1/4.5/4 (0.9/1.0), (c) 1/5.5/4 (1.1/1.0), (d) 1/6/4 (1.2/1.0).
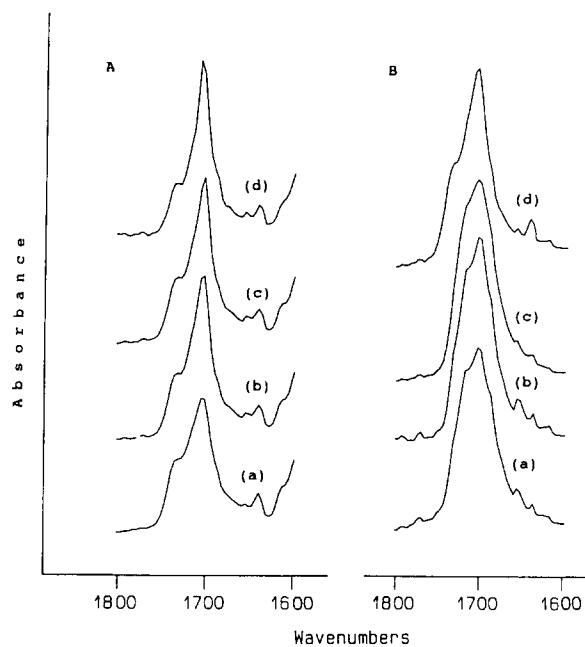

Fig. 2. FTIR spectra of different annealing treatment time (h) in the range of 1600–1800 cm^{-1}. (A) HTPB/MDI/1,4-BD (1/3/2): (a) 0, (b) 24, (c) 48, (d) 80. (B) HTPB/IPDI/1,4-BD (1/9/8): (a) 0, (b) 80; HTPB/TDI/1,4-BD (1/4/3), (c) 0, (d) 80.

Figs. 1 and 2 show that the carbonyl absorption region between 1800 and 1600 cm^{-1}, the carbonyl absorption band splits into two peaks. 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} (IPDI and TDI series) and 1734 cm^{-1} (MDI series). 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 in the soft domains or at the interface [11,12]. These soft to soft segment and soft to hard segment interactions can lead to different polymer morphologies and properties. In these butadiene-containing polyurethanes, hydrogen bonding occurs only between urethane segments since the carbonyl in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors.

The extent of the carbonyl absorption group participating in hydrogen bonding is expressed by hydrogen bonding index (HBI), which is defined as the relative absorbances of the two carbonyl peaks [7].

$$HBI = \frac{A_{C=O,bonded}}{A_{C=O,free}}$$

Where $A_{C=O,bonded}$ and $A_{C=O,free}$ are, respectively, the absorbance of bonded and free carbonyl groups.

HBI may also be expressed as

$$HBI = \frac{C_{bonded}\varepsilon_{bonded}}{C_{free}\varepsilon_{free}}$$

Where C is the concentration and ε is the absorption coefficient of bonded and free carbonyl groups. Pimentel and McClellan [8] indicated that $\varepsilon_{bonded}/\varepsilon_{free}$ is between 1.0 and 1.2, while 1.71 was used in Ref. [11]. Owing to the same diisocyanate series (i.e. same chemical structure) of PU solution and testing temperature, the ratio can be assumed as a constant value. The purpose of this study only needs the change of HBI value (as shown in Table 1) to indicate the trend of the degree of segregation of the same diisocyanate series. The greater HBI values indicate increased participation of the carbonyl group in hydrogen bonding and the lower the degree of segregation between hard and soft segments.

3.2. One- and two-stage polymerization effects

Fig. 3 shows that the gas permeabilities of the two-stage process are all lower than that of the corresponding one-stage process. One-stage polymerized PU have significantly less hard segments, which consist of a single diisocyanate unit, than that of the two-stage polymerized PU. One-stage polyurethanes result in a broader distribution of hard segment than the two-stage of the same stoichiometry. The single diisocyanate unit hard segments are easier to disperse in the soft segments than longer hard segments do.

Abouzahr et al. [17] reported that the effect of the polymerization method was almost offset by the high incompatibility between hard and soft segments of conventional polyether PU. However, the different trend was observed in this study that one-stage polymerized PU exhibit a higher segregation as more polar single diisocyanate units mixed with nonpolar HTPB. This can be corroborated by the lower hydrogen bonding index of one-stage polymerization than that of two-stage polymerization as shown in Table 1.

3.3. Effect of polyols

Table 2 shows that polyether urethanes (PPG, PEG) membranes possess higher gas permeabilities than polyester urethanes (PBA, PCL) membranes. The PU membranes with PEG are found to be less permeable
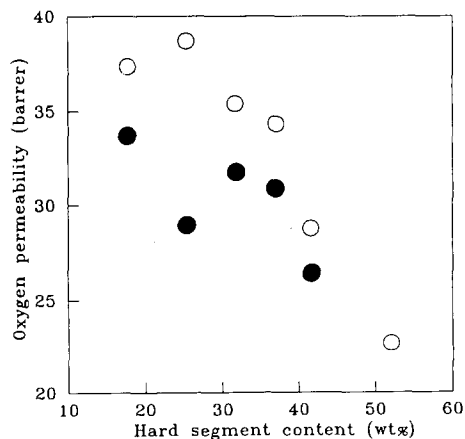

Fig. 3. Effect of polymerization method on the oxygen permeability of MDI based PU membranes (○) one-stage method (●) two-stage method.

Table 1
Composition and some properties of PU membranes

Composition	NCO/OH	HBI	$T_{gs}(C°)$	Composition	NCO/OH	HBI	$T_{gs}(°C)$
HTPB/MDI/1,4BD				HTPB/IPDI/1,4BD			
1/9/8	1.0	2.2566	−70.6	1/15/14	1.0	1.2672	−70.3
1/6/5	1.0	2.1345	−71.1	1/12/11	1.0	1.1981	−71.4
1/5/4	1.0	2.0298	−71.7	1/9/8	1.0	1.0987	−72.0
1/4/3	1.0	1.8739	−72.5	1/6/5	1.0	1.1094	−72.1
1/3/2	1.0	1.3911	−74.3	1/5/4	1.0	1.0625	−72.9
1/2/1	1.0	1.7387	−73.7	1/4/3	1.0	1.0397	−73.9
1/6/5[a]	1.0	2.2353	−69.3	1/3/2	1.0	1.0526	−73.9
1/5/4[a]	1.0	2.1176	−69.9	1/2/1	1.0	1.0433	−74.7
1/4/3[a]	1.0	1.9526	−71.6	1/6/5[a]	1.0	1.2206	−71.6
1/3/2[a]	1.0	2.0133	−71.7	1/5/4[a]	1.0	1.1029	−71.9
1/2/1[a]	1.0	1.8754	−72.3	1/4/3[a]	1.0	1.0508	−72.2
HTPB/TDI/1,4BD				1/3/2[a]	1.0	1.0675	−72.8
1/4/3	1.0	1.0619	−73.9	1/2/1[a]	1.0	1.0601	−73.5
1/3/2	1.0	1.1159	−74.6	1.4.25/4	0.85	1.0346	−73.6
1/2/1	1.0	1.0424	−74.8	1/4.5/4	0.9	1.0481	−73.5
HTBP/MDI/IPDI/1,4BD				1/5.5/4	1.1	1.0942	−72.4
1/1/2/2	1.0	1.1172	−74.2	1/6/4	1.2	1.1317	−72.0
1/2/1/2	1.0	1.2873	−73.1				
1/3/1/3	1.0	1.4092	−72.5				

[a]Were polymerized by two-stage method and the others by one-stage method.

Table 2
Gas permeabilities[a] of different polyols based PU membranes by two-stage polymerization method

Membranes composition (equivalent ratio)	Gas permeability $(cm^2/s\ cmHg) \times 10^{1.0}$		Separation factor (P_{O_2}/P_{N_2})
	P_{O_2}	P_{N_2}	
HTPB/MDI/1,4BD(1/3/2)	28.96	11.79	2.46
PCL/MDI/1,4BD (1/3/2)	13.68	7.39	1.85
	(17.37)	(14.09)	(1.23)
PBA/MDI/1,4BD (1/3/2)	11.53	5.85	1.97
	(15.79)	(12.03)	(1.31)
PPG/MDI/1,4BD (1/3/2)	16.72	9.50	1.76
PEG/MDI/1,4BD (1/3/2)	14.93	7.86	1.90

[a]The data in the parenthesis are taken from [19].

Table 3
Solubility parameter[a] of raw materials

Materials	HTPB	PCL	PBA	PPG	PEG	IPDI	TDI	MDI	1,4-BD
Solubility parameter $(\delta, cal^{1/2}/cm^{3/2}$	8.67	9.14	9.36	9.68	9.87	8.66	10.74	13.95	11.00

[a]Obtained by estimation method [5,6].

than that with PPG segments. These results are in the same trend as that of Hsieh et al. [18–20].

HTPB based PU membranes perform higher gas permeabilities than the conventional polyether or polyester PU membranes, as shown in Table 2. This is due to the fact that the HTPB soft segment has no potential for hydrogen bonding and is less polar than the conventional polyether or polyester soft segment. This can be explained, as shown in Table 3, that the largest solubility parameter difference was observed between HTPB and MDI comparing with the other polyols. Thus, the HTPB based polyurethanes tend to have more segregation than conventional polyurethanes.

Takada and coworkers [21] reported that the double bonds along the main chain may have an affinity for oxygen, which will contribute to the P_{O_2} of polyacetylene films. HTPB based PU membranes have a higher separation factor too. The unsaturation bonds, which distribute in the main chain of HTPB, allow the better affinity to oxygen.

3.4. Effect of diisocyanates

Figs. 4 and 5 show that the gas permeabilities of MDI based PU membranes of both two polymerization process are higher than those of other diisocyanate based membranes. The gas permeabilities of the IPDI and 2,4-TDI based PU membranes are almost the same at the same stoichiometry.

There are two symmetric, ordered aromatic rings in the main chain of MDI. The level of structure order falls in the following sequence: MDI > TDI > IPDI. Intermolecular interactions decrease in the reverse order presumably due to the steric effects. The above explanation fails to account for the higher gas permeability of MDI based PU membranes. Table 3 shows that the solubility parameter difference decreases in the following sequence: δ_{MDI}–δ_{HTPB} > δ_{TDI}–δ_{HTPB} > δ_{IPDI}–δ_{HTPB}. Larger solubility difference (i.e. more incompatibility) causes higher segregation. The competition of the above two effects shows that incompatibility has the superior influence on the segregation and gas permeability.

The gas permeability of PU membranes with mixed MDI and IPDI were observed to be higher than that of membranes with single MDI or IPDI. The gas permeability of the mixed diisocyanate system goes up as the hard segment content goes up. This phenomenon can
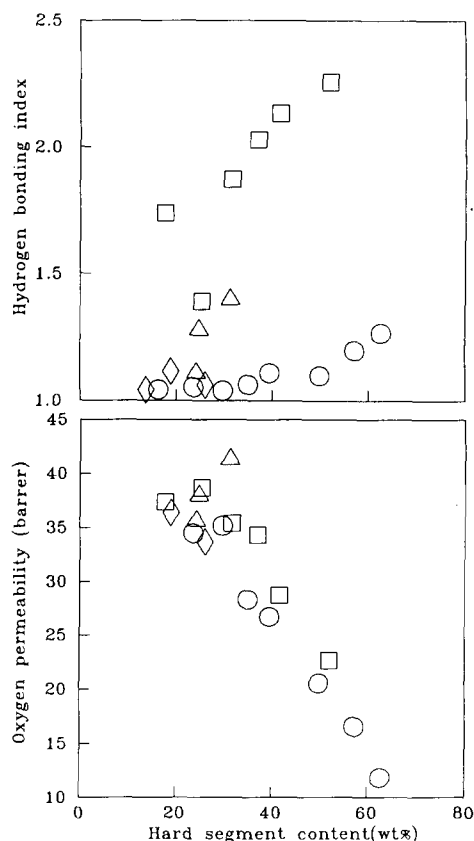

Fig. 4. Effect of hard segment content of one-stage polymerized PU on the hydrogen bonding index and oxygen permeability (O) HTPB/IPDI/1,4-BD, (□) HTPB/MDI/1,4-BD, (△) HTPB/IPDI/MDI/1,4-BD, (◇) HTPB/TDI/1,4-BD.

be explained as that the synergistic effect of high polarity of MDI and the asymmetric structure of IPDI contribute to the increase of segregation and hence gas permeability.

3.5. NCO/OH ratio effect

The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH groups. Various cross-linking densities can be the contribution of different NCO/OH value, with multiple functionality of HTPB. As the NCO/OH ratio is larger than one, the three dimensional structures of allophanates or polar urea structure will be formed and the number of urethane groups are increased. The existence of three dimensional allo-
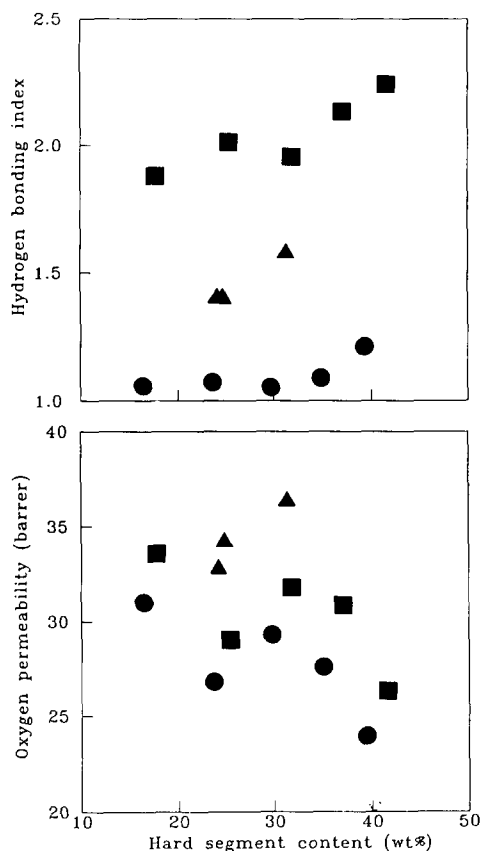
Fig. 5. Effect of hard segment content of two-stage polymerized PU on the hydrogen bonding index and oxygen permeability (●) HTPB/ IPDI/1,4-BD, (■) HTPB/MDI/1,4-BD, (▲) HTPB/IPDI/MDI/ 1,4-BD.

phanate structure restricts the mobility of molecular chain and enlarge the activation energy for the diffusion of gas. The increase of these polar groups (urea and urethane) enhance the intermolecular attraction of hard to hard segments, which can be verified by the increase of HBI as the increase of NCO/OH value. The increase of activation energy and intermolecular attraction of hard to hard segments tend to decrease the gas permeability as shown in Fig. 6. This result is similar to that of Cao et al. [22], but different from Pegoraro et al. [23].

3.6. Hard segment content

Figs. 4 and 5 show that regardless of any type of single diisocyanate the higher the hard segment content

is, the lower is the gas permeability. Except that there is a slight disruption on the gas permeability trend at low hard segment content. These results of HTPB based PU membranes are contrary to that of conventional polyol based PU membranes of Hsieh [19]. The degree of crystallinity fails to explain the trend of gas permeability as the hard segment content increased. However, McBride et al. [24] reported that an increase in the hard segment content produces an increase in the activation energy, which may be the suitable explanation for the result of this study. There is a contradiction to the above gas permeability decreasing trend at low hard segment content. The reason may be that the effect of incompatibility is stronger than that of the increase of activation energy at low hard segment content.

Figs. 4 and 5 show that the increase of HBI of single diisocyanate based PU membranes as the increase of hard segment content. The increase of HBI shows that the fraction of bonded C=O groups is dominant and the intermolecular attraction is increased also. This phenomenon will increase the phase mixing and decrease the gas permeability of nonpolar HTPB based PU membranes.

3.7. Solubility parameter

The polarity difference between nonpolar HTPB polyol and polar urethane group (MDI, 1,4-BD) will cause a segregation of the prepared HTPB based PU
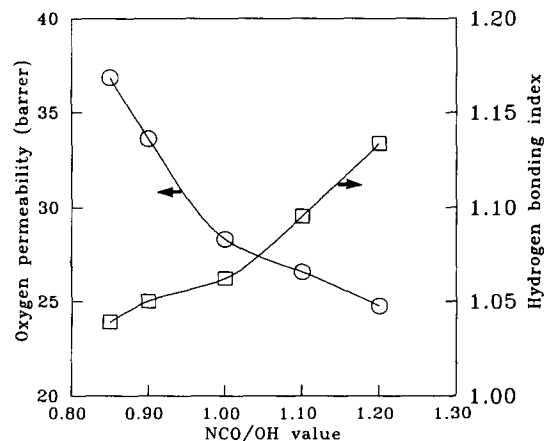

Fig. 6. Effect of NCO/OH value on the oxygen permeability (○) and hydrogen bonding index (□) of one-stage IPDI based PU membranes.

membranes. The determination of solubility parameter of raw materials is briefly considered here. The chemical structure of HTPB can be simplified as $HO(-CH_2-CH=CH-CH_2-)OH$.

Table 3 shows that HTPB has the least solubility parameter, however, MDI has the largest value among these materials.

3.8. Differential scanning calorimetry

Different diisocyanates of segmented polyurethanes were studied by DSC, which shows the glass transition temperature of soft segment (T_{gs}).

Table 1 shows that the T_{gs} are almost the same at low hard segment content and no melting temperature of hard segments are observed. At high hard segment content these T_{gs} are slightly affected by the hard segment content. The absence of a high melting transition temperature and the invariant T_{gs} are due to an amorphous material of the HTPB based PU. This phenomenon indicates that these polymers have the same degree of segregation at low hard segments. And a slight increase of phase mixing occurs at high hard segment content, the reason being due to the incompatibility of the nonpolar hydrocarbon soft segment and the polar hard segment [25,26].

Meanwhile, the two-stage polymerized PU membranes show a slightly higher T_{gs} than their one-stage analogies as shown in Table 1, due to the lower degree of segregation present in the two-stage polymerized PU.

3.9. Wide angle X-ray diffraction

Each WAXD pattern in this study renders a single, diffused scattering peak with a maximum intensity at about $2\theta = 20°$, indicating that no substantial evidence of either hard or soft segment crystallinity is found in the WAXD patterns for the HTPB based PU membranes [27].

3.10. Annealing treatment

Because of the lower stability in oxidative environment of HTPB, the annealing treatment will produce hydroxyl and carbonyl group. Also, the annealing of HTPB might introduce both the chain scission and cross-linking to the sample. Chiu et al. [28] reported
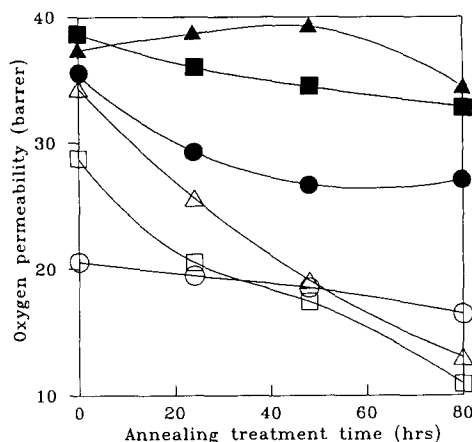

Fig. 7. Effect of annealing treatment time on the oxygen permeability of one-stage HTPB based PU membranes (HTPB/MDI/1,4-BD) (▲) 1/2/1, (■) 1/3/2, (●) 1/4/3, (△) 1/5/4, (□) 1/6/5, (○) 1/9/8.

that the chain scission reaction and cross-linking appeared to be dominating the annealing behavior of HTPB based PU at 80°C. Owing to the increase of these polar groups, the HBI is increased as the annealing time increased although annealing increase the hard–soft segment compatibility. Fig. 2 shows that the bonded C=O absorbance was increased and the free C=O absorbance decreased as the annealing time increased. The gas permeabilities of HTPB based PU membranes decrease as the annealing time increases as shown in Fig. 7.

4. Conclusions

The hard segment of the prepared membranes of this study are amorphous. These amorphous materials do not have larger extent of hydrogen bonding between hard and soft segments. Hence the driving force for segregation must arise from the high degree of incompatibility between the polar hard segment and nonpolar HTPB soft segment.

The measurement of HBI exhibits the appropriate method for illustrating the degree of segregation of nonpolar HTPB based PU membranes. Higher value of HBI was observed for higher NCO/OH values, annealing time and hard segment content with two-stage polymerized method. Degree of segregation and gas permeability are increased as the HBI decreased.

Membranes with mixed diisocyanates of MDI and IPDI exhibit higher gas permeabilities than that with single diisocyanate. Membranes with MDI possess higher gas permeability than those with other diisocyanates. PU membranes from one-stage polymerization have higher gas permeabilities than those from two-stage polymerization.

The gas permeability decreases with the increase of NCO/OH values, annealing treatment time and hard segment content. The gas permeabilities and selectivities of these HTPB based PU membranes are higher than those of conventional polyether and polyester PU membranes of previous researchers.

Acknowledgements

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