

Investigation and Gas Permeability of Polyurethane Complexes

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ABSTRACT: Ionic polyurethane (PU) membranes of hydroxyl-terminated polybutadiene (HTPB) and 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI) were polymerized by a two-stage method. The ionic group was introduced by adding *N*-methyldiethanolamine (MDEA) as the chain extender of which the tertiary amines were complexed with cobalt ions. It was found that the binding of hard segments and the flexibility of soft segments had subtle effects on the gas permeability. The effects of hard segment content and the amount of cobalt ion on the gas permeability and morphological properties were investigated. Fourier transform infrared (FTIR) spectroscopy was utilized to identify the segregation between hard and soft segments and structure change, which affect the transport properties. The hydrogen bonding index (HBI), frequency difference, and shift as a measure of the phase segregation and the average strength of the interpolymer hydrogen bonds were utilized to study the intermolecular interaction and transport property of the prepared PUs. The results of differential scanning calorimetry, thermogravimetric analysis (TGA), and FTIR measurements explain the complexation and, hence, the gas permeability.
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Key words: ionic polyurethane; cobalt chloride; gas permeability

INTRODUCTION

Polyurethanes (PU) are multiblock copolymers usually consisting of hard segments and polyether or polyester soft segments. These materials have been used to separate oxygen from air.^{1–5} The effect of chemical composition of PUs on the gas permeability may be due to the degree of phase segregation and to the nature of chain packing. Hydroxyl-terminated polybutadiene (HTPB)-based PUs can be used for gas separation because of their low temperature flexibility and high segregation between

hard and soft segments due to the nonpolarity of the HTPB soft segment.^{6–7}

Metal-containing polymer has become more and more popular for use in gas separation. Sakai et al.⁸ prepared Nafion–silver microcomposite membranes having a significantly improved O_2/N_2 selectivity ratio because of the affinity between oxygen and silver. Lai and coworkers^{9,10} reported that the gas permeability of polycarbonate (PC)–dimethyl formamide (DMF)– $CuCl_2$ or poly(methyl methacrylate) (PMMA)–DMF– $CuCl_2$ membranes were significantly improved as compared to pure PC or PMMA membranes. There are many studies about the use of cobalt compounds for oxygen enrichment from air.^{11–17}

The complexation of PU polymers was gener-

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ally obtained by incorporating a chain extender containing tertiary amines and then reacting with alkyl halides¹⁸ or glycolic acid.¹⁹ Others are formed by the use of sulfonate containing chain extender²⁰ or by the addition of LiClO₄ to the PU.^{21,22}

The purpose of this study is to understand the effect of cobalt chloride addition on the structure and gas permeability of HTPB-4,4'-dicyclohexylmethane (H₁₂MDI)-*N*-methyldiethanolamine (MDEA) based PUs. The effect of hard segment content, addition of cobalt chloride on characteristics, and gas permeability were studied. Hydrogen bonding index (HBI) values, IR wavenumber shift, glass transition temperature (T_g), and thermogravimetric analysis (TGA) were used for the identification of complexation, chain flexibility, and phase segregation.

EXPERIMENTAL

Materials

The chemicals used in this study were H₁₂MDI (Desmodur W of Mobay Co.), HTPB, (R-45M of ARCO Co.), 1,4-butanediol (1,4-BD), and MDEA as chain extender, and dibutyltin dilaurate (DBTDL) is used as catalyst. DMF and toluene are used as solvent for the preparation of PU solution. Cobalt chloride was used as complexation reagent.

Preparation of Polyurethane Membrane

The two-stage PUs were polymerized first by a —NCO-terminated prepolymer and then chain-extended with MDEA under 25 wt % solid content after theoretical —NCO content was reached. It was diluted to a 15 wt % solid content after the chain-extended reaction proceeded for 30 min. The reaction was terminated as the —NCO groups were completely consumed, as confirmed by the disappearance of the infrared absorption at 2280 cm⁻¹.

PU films were prepared by pouring the solution mixture onto a glass plate to a thickness of 600 μm. The solvent in the casting solution was evaporated by degassing at 65°C for 24 h. The dried PU films were peeled from the plate after it had been immersed in the deionized water for several hours. The PU films were dried in a desiccator

and stored at a relative humidity of 50% and 25°C for 5 days before testing.

Complexed films were prepared by adding cobalt chloride to the HTPB-H₁₂MDI-MDEA-based PU solutions. Membranes of different compositions in this study are denoted, for example, by 11211-1 : 3 Co or 187-1 : 4 Co. The numbers 11211 and 187 represent the equivalent ratio of HTPB/H₁₂MDI/MDEA = 1 : 12 : 11 and 1 : 8 : 7 or with hard segment content of 60.79 and 50.56 wt %, respectively. 1 : 3 Co or 1 : 4 Co means the addition of 1 : 3 or 1 : 4 mol ratio content of cobalt chloride with MDEA to the PU composition, respectively. The dried ionized films were peeled from the plate after it had been put in the refrigerator to the frozen state for several hours. All these films were then put in oven under vacuum at 70°C for 48 h to further degas the solvent residue. Finally, the samples were kept under vacuum at room temperature for at least 5 days prior to the property testing.

Infrared Spectroscopy

Infrared spectra of PU films were obtained on a JASCO FTIR-310E spectrometer. Spectra were collected at a resolution of 2 cm⁻¹. The peak due to hydrogen-bonded C=O stretching is centered at 1700 cm⁻¹ and that due to free C=O stretching is centered at ~ 1717 cm⁻¹, while the peak of bonded —NH stretching is at 3320 cm⁻¹ and that of free —NH stretching is at 3442 cm⁻¹. 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.²³ In these butadiene-containing PU, hydrogen bonding occurs only between urethane segments since the carbonyl in the urethane linkage and the urethane alkoxy oxygen are the only proton acceptors. The extent of the carbonyl absorption group participating in hydrogen bonding is expressed by the HBI, which is the relative absorbance of the hydrogen-bonded N—H peak ($A_{N-H,bonded}$), to that of free hydrogen-bonded N—H peak ($A_{N-H,free}$).²⁴ The frequency difference is defined as $\Delta\nu = \nu_f - \nu_b$, where ν_f and ν_b are the frequencies of maximum absorption for the free and hydrogen-bonded —NH group, respectively. The frequency difference, $\Delta\nu$, in the stretching frequency is considered as a measure

of the strength of the hydrogen bond between molecules.²⁵

Property Measurement

Testing of stress and strain at break were performed according to the ASTM D412 standard method at a crosshead speed of 50 cm/min, with a clamp distance of 3 in. A Du Pont 9000 instrument was used for DSC measurement, using liquid nitrogen for cooling and with a heating rate of 10°C/min in the temperature range between -120 and 150°C. ΔT_g is the temperature difference between glass transition temperature of the hard segment (T_{gh}) and glass transition temperature of the soft segment (T_{gs}). TGA thermograms were obtained by a Du Pont 951 thermogravimetric analyzer with a heating rate of 20°C/min in the temperature range from 50 to 600°C under a continuous nitrogen flow of 30 mL/min for the investigation of complex formation.

RESULTS AND DISCUSSION

Hydrogen Bonding Index

The polarity difference between nonpolar HTPB soft segment and polar hard segment and the interaction of cobalt ion with tertiary amine of MDEA makes these PU membranes possessing phase segregation. The change of interchain hydrogen bonding was utilized to study the phase segregation. Infrared technique is possibly the most suitable for measuring the extent of hydrogen bonding²⁶⁻³¹ of these PU membranes for the indication of the degree of phase segregation.

Figure 1 shows that the HBI values increase as the hard segment content increases, and decreases as the cobalt chloride content increases. There is a slight disruption on HBI value as the cobalt chloride content exceeds 0.25 mol ratio. The greater HBI values indicate increased participation of the N—H group in hydrogen bonding and the lower degree of segregation between hard and soft segments. This variation in hydrogen bonding is rather significant for the packing of segments, which will change the HBI values. Landro, Pegoraro, and Bordogna²⁸ reported that in the case of PU with a lower polyether chain a large number of N—H's are available to form hydrogen bonds of C=O and N—H groups between different chains,

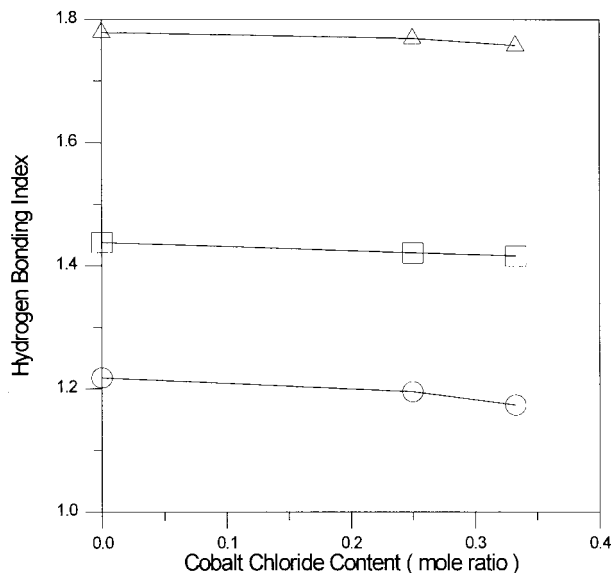


Figure 1 Effect of cobalt chloride content on the HBI value of membranes with different equivalent ratios. (O) 1 : 4 : 3, (□) 1 : 8 : 7, (Δ) 1 : 12 : 11.

which may result in a higher ratio of bonded N—H to free N—H.

With the addition of cobalt chloride, the cobalt ion interacts with the hard segment. The hydrogen bonding between the N—H and C=O group will be destroyed or decreased as the complexation reaction happens and hence, the decrease of HBI values as the cobalt chloride content increases. As the addition of cobalt chloride content exceeds 0.25 mol ratio, more hydrogen bondings are destroyed and hence more decrease of HBI values.

Frequency Difference and Shift

Frequency difference was utilized in this study to discuss the effect of cobalt chloride content on the intermolecular interactions and phase segregation. Coleman and coworkers²³ have used the frequency difference between hydroxyl groups and those of hydrogen bonded hydroxyl groups as a measure of the average strength of the intermolecular interactions. In this respect the average strength of the hydrogen bonds ($\Delta\nu$) of the intermolecule are decreased as the cobalt chloride content or hard segment content increased, as shown in Figure 2. Since the cobalt metal ion interacts with the tertiary amine of MDEA as well as the carbonyl and secondary amine in urethane linkage,³² the addition of cobalt chloride will change

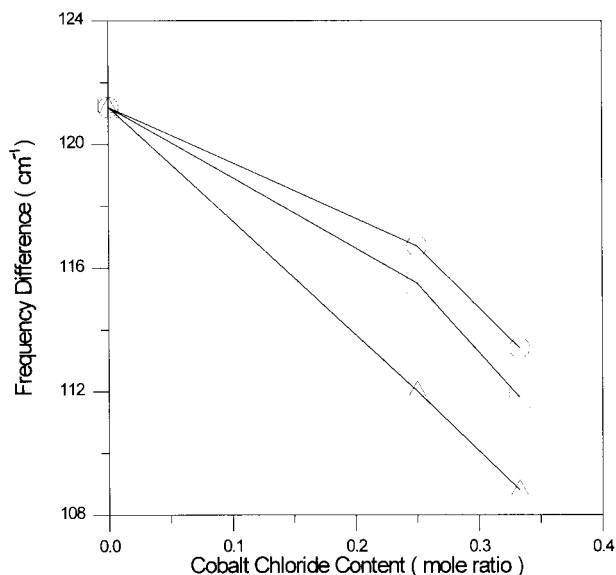


Figure 2 Effect of cobalt chloride content on the frequency difference ($\Delta\nu$) of membranes with different equivalent ratios. (○) 1 : 4 : 3, (□) 1 : 8 : 7, (△) 1 : 12 : 11.

the hydrogen bonding between hard segments. There is a sharp decrease of frequency difference as the cobalt chloride content exceeds 0.25 mol ratio. The reason is the same as that stated in the above section.

Table I shows that the extent of wavenumber shift of the bonded N—H group increases as the cobalt chloride content increases, since the cobalt ion interacts with the tertiary amine of MDEA as well as the carbonyl and secondary amine in urethane linkage. Upon complexation, the energy and force constant of the N—H group absorption

Table I Wavenumber of N—H Group Absorption

| Composition | Wavenumber (cm^{-1}) of Bonded N—H Group |
|---------------|---|
| 143 | 3320.8 |
| 143-1 : 4Co | 3325.3 |
| 143-1 : 3Co | 3328.6 |
| 187 | 3320.8 |
| 187-1 : 4Co | 3326.5 |
| 187-1 : 3Co | 3330.2 |
| 11211 | 3320.8 |
| 11211-1 : 4Co | 3330.0 |
| 11211-1 : 3Co | 3333.2 |

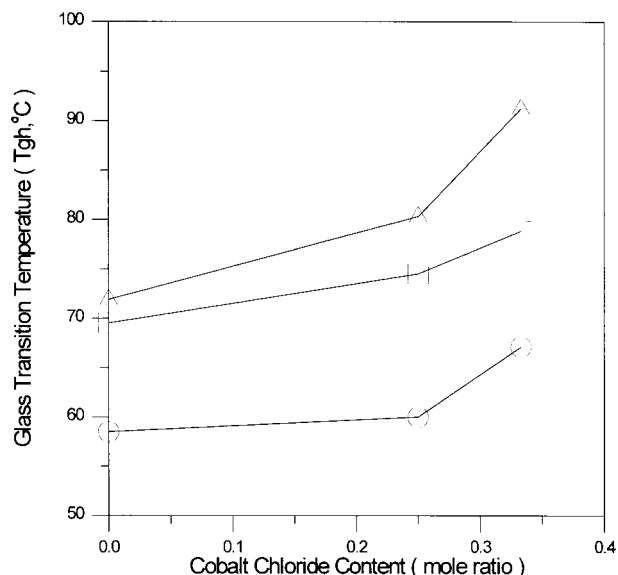


Figure 3 Effect of cobalt chloride content on the T_{gh} of membranes with different equivalent ratios. (○) 1 : 4 : 3, (□) 1 : 8 : 7, (△) 1 : 12 : 11.

increases and the absorption band is therefore shifted to a higher frequency than the addition of cobalt chloride.

Differential Scanning Calorimeter

Effect of hard segment and cobalt chloride content on segmented PUs were studied by DSC. Figures 3 and 4 show that the glass transition tempera-

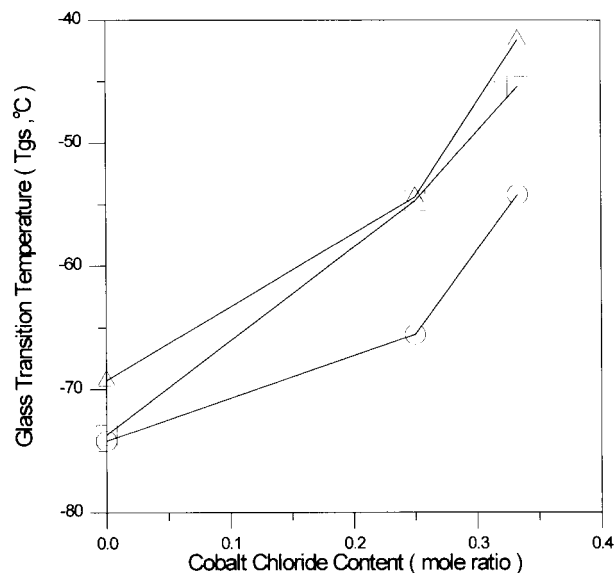


Figure 4 Effect of cobalt chloride content on the T_{gs} of membranes with different equivalent ratios. (○) 1 : 4 : 3, (□) 1 : 8 : 7, (△) 1 : 12 : 11.

ture of hard segments (T_{gh}) and soft segments (T_{gs}) increased as the hard segment or cobalt chloride content increased. There is a remarkable change of both glass transition temperatures and ΔT_g as the cobalt chloride content exceeds 0.25 mol ratio. The increase of T_{gh} indicated that the increase of hard segment content increased the intermolecular attraction and the area enlargement of hard segment domain. These phenomena will increase the phase mixing, which is due to the fact that the HTPB soft segment has no potential for hydrogen bonding. While the increase of T_{gs} indicated that the decrease of soft segment mobility, which is due to more free hydrogen-bonded hard segment, dispersed in the soft segment.

Since the cupric ion interacts with the tertiary amine of MDEA as well as the carbonyl and secondary amine in urethane linkage, a suitable amount of cobalt ion addition may enhance the binding between hard segments. The increase of T_{gh} as the addition of cobalt chloride supports the above argument. As the cobalt chloride content increased, the binding between hard segments increased, and hence the increase of T_{gh} . The number of C=O or N—H groups of hard segment dispersed in the soft segment increases as the hard segment content or the cobalt chloride content increases. Subsequently, the flexibility of the soft segment decreased, and hence the increase of T_{gs} .

The effect of cobalt chloride content on the morphology change may be evidenced by the difference of glass transition temperature between T_{gh} and T_{gs} (ΔT_g). Figure 5 shows that ΔT_g decreases as the cobalt chloride content increases. The reduction in ΔT_g indicates the increase of microphase homogeneity, that is, the amount of hard segment dispersed in soft segment region increased. Suitable amounts of cobalt chloride addition may be at ~ 0.25 mol ratio, and hence sharp changes of T_{gh} , T_{gs} , and ΔT_g occur at this cobalt chloride content. As the addition of cobalt chloride content exceeds 0.25 mol ratio, more cobalt chloride dispersed in the soft segment and then decreased the flexibility of soft segment. This may contribute to the sharp change of T_{gh} , T_{gs} , and ΔT_g of membranes containing 1 : 3 molar ratio of cobalt chloride.

Thermogravimetric Analysis

A three-step degradation was observed in all these three types of membranes. It is stable up to

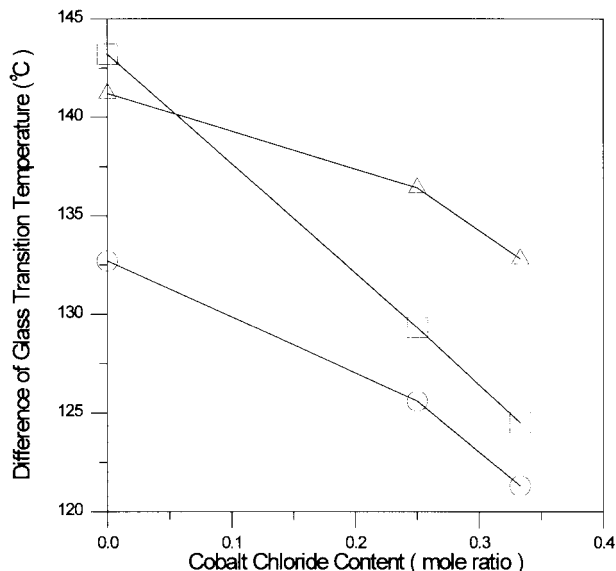


Figure 5 Effect of cobalt chloride content on the ΔT_g of membranes with different equivalent ratios. (O) 1 : 4 : 3, (□) 1 : 8 : 7, (Δ) 1 : 12 : 11.

300°C and the polymer remains almost intact in the first step. The quantity of gaseous components, mainly water, released in this step is relatively small.

A rapid weight loss starts at $\sim 300^\circ\text{C}$ up to 500°C. The main quantity of gaseous components, for example, water, carbon monoxide, and methane, are split off. Decomposition of step 2 corresponds to the urethane bond breaking and step 3 is the polyol decomposition.³³ Almost complete decomposition was observed at $\sim 500^\circ\text{C}$.

Table II shows the decomposition temperature of the second and third steps as well as the weight percentage of residue. The decomposition temperature of these three types of cobalt metal-complexed membranes are higher than those of uncomplexed membranes. Membranes of tightly complexed structure require more energy for the decomposition. Decomposition temperature of the second step (i.e., urethane bonding breaking) increases as the cobalt chloride content increases for all three types of membranes with different composition. The addition of cobalt chloride enhances the intermolecular attraction between hard segments. This attraction increases as the cobalt chloride content increases.

The decomposition temperature of the third step (i.e., polyol decomposition) increases as the cobalt chloride content increases also. The addition of cobalt chloride might cause complexation

Table II Decomposition Temperature and Residue of Thermogravimetric Analysis

| Composition | Decomposition Temperature (°C) | | Residue (wt %) |
|---------------|--------------------------------|--------|----------------|
| | Step 2 | Step 3 | |
| 143 | 425 | 472 | 15.0 |
| 143-1 : 4Co | 431 | 480 | 15.1 |
| 143-1 : 3Co | 438 | 489 | 15.2 |
| 187 | 412 | 462 | 14.0 |
| 187-1 : 4Co | 417 | 468 | 14.6 |
| 187-1 : 3Co | 423 | 475 | 14.8 |
| 11211 | 355 | 459 | 13.3 |
| 11211-1 : 4Co | 358 | 464 | 14.0 |
| 11211-1 : 3Co | 363 | 468 | 14.3 |

between hard segments of shorter length, which disperses in the soft segment region. This implies that the soft segment of these complexed PUs are aggregated more tightly than those of uncomplexed PUs.

All these PUs have nearly the same residue. Membranes with low hard segment content have the higher residue due to the lower oxygen and nitrogen atom content in the molecular structure of lower hard segment content. However, with the addition of cobalt chloride the residue increases. The reason may be that cobalt metal cannot release gaseous components during thermal decomposition.

Stress and Strain Measurements

The effects of hard segment content and cobalt chloride content on the stress and strain at break behavior of the prepared membranes are shown in Figures 6 and 7. The stress at break increases as the hard segment content increases; on the contrary, the strain at break decreases.³⁴ The increase of hard segment content increases the hydrogen bonding between hard segments and results in the increase of intermolecular attraction.

There is a disruption of the stress and strain properties as the hard segment content exceeds 50 wt %. With the extension of these nonpolar HTPB-based PU membranes, the repulsion between nonpolar soft segment and polar hard segment increases. The effect of this repulsion force decreases when PU possesses high hard segment content. Meanwhile, if the diisocyanate content is

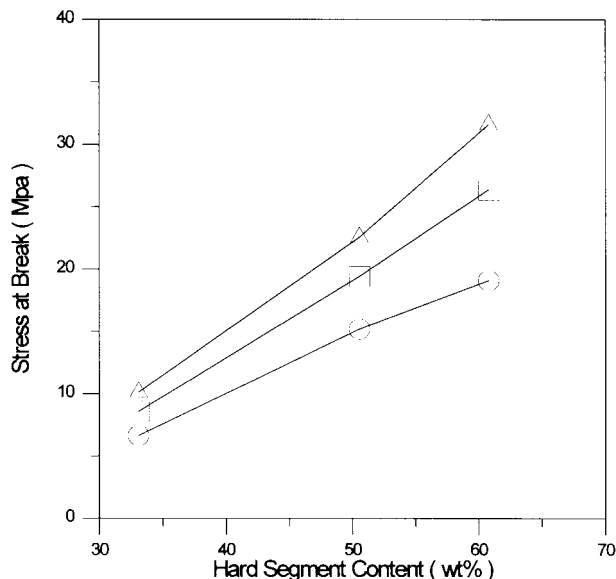


Figure 6 Effect of hard segment content on the property of stress at break of membranes with different CoCl_2 content. (○) 0, (□) 1 : 4, (△) 1 : 3 molar ratio of cobalt chloride complexed.

higher than 38 wt %, both soft and hard segments will show crystallization.³⁵ This may contribute to the increase of stress and slow decrease of strain property as the hard segment content exceeds 50 wt %.

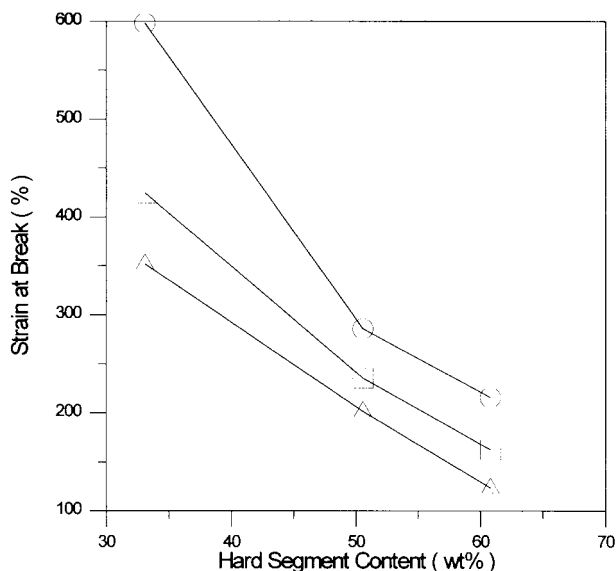


Figure 7 Effect of hard segment content on the property of strain at break of membranes with different CoCl_2 content. (○) 0, (□) 1 : 4, (△) 1 : 3 molar ratio of cobalt chloride complexed.

The stress and strain behavior of these complexed membranes was affected by the cobalt chloride content. The stress at break of membranes increased as the cobalt chloride content increased, while the strain at break decreased. The increase of cobalt chloride content enhances the complexation between hard segments and hence, increases the intermolecular attraction.

Effect of Hard Segment Content on Gas Permeability

Figures 8 and 9 show that regardless of cobalt chloride content, the higher the hard segment content was, the lower was the gas permeability and the higher was the separation factor. These results of HTPB-based PU membranes are contradictory to those of conventional polyol-based PU membranes reported by Hsieh, Tsai, and Tseng.²

There are two effects of hard segment content on the gas permeability. One effect was the enlargement of hard segment aggregate and the other was the restriction of the movement of soft segments. The former effect can be evidenced by the increase of HBI values as the increase of hard segment content. This could be explained by there being more hydrogen-bonded N—H groups in PU membranes with a higher hard segment content, as shown in Figure 1. The increase of HBI values

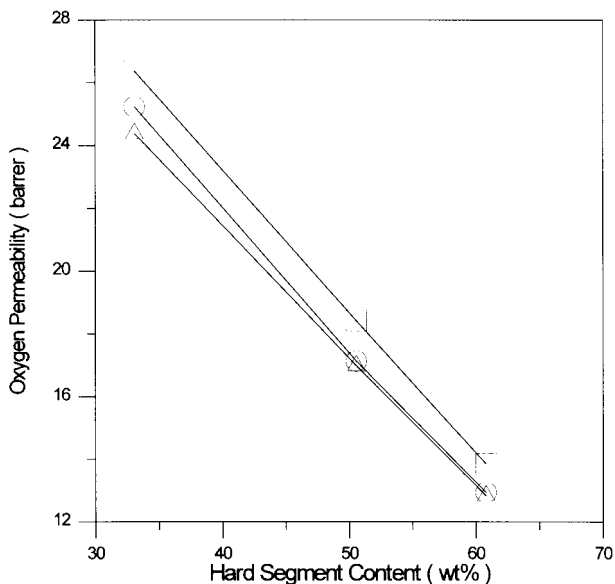


Figure 8 Effect of hard segment content on the oxygen permeability of membranes with different CoCl_2 content. (○) 0, (□) 1 : 4, (△) 1 : 3 molar ratio of cobalt chloride complexed.

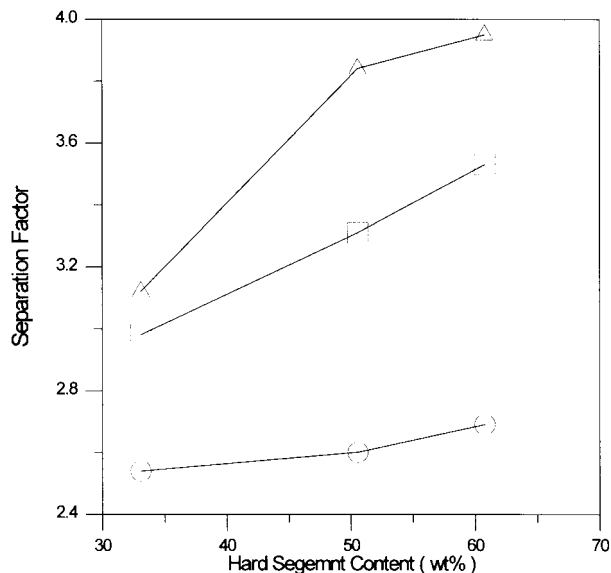


Figure 9 Effect of hard segment content on the separation factor of membranes with different CoCl_2 content. (○) 0, (□) 1 : 4, (△) 1 : 3 molar ratio of cobalt chloride complexed.

indicated that the intermolecular attraction between hard segments increased and the area of hard segment domain enlarged. Figure 3 shows that the area enlargement of the hard segment could be indicated by the increase of T_{gh} as the increase of hard segment content. On the other hand, the decrease of flexibility in soft segments may be explained by the increase of T_{gs} , which is shown in Figure 4, as the hard segment content increased. The increase of T_{gh} indicated that the increase of hard segment content increased the intermolecular attraction between hard segments, while the increase of T_{gs} indicated the decrease of soft segment mobility. These discussions may explain why the gas permeability decreased as the hard segment content increased.

Effect of Cobalt Chloride Addition on Gas Separation

Figure 8 shows that oxygen permeability of membranes containing 1 : 4 CoCl_2 /MDEA molar ratio were higher than those of zero cobalt chloride content. However, the membranes with 1 : 3 molar ratio of cobalt chloride had nearly the same permeability. Since the cobalt ion interacts with the tertiary amine of MDEA as well as the cobalt and secondary amine in urethane linkage, a suitable amount of cobalt ion addition may enhance the

binding between hard segments, and subsequently enlarge the void volume in soft segment domains. As the CoCl_2 dispersed in the soft segment, the repulsion between soft segment increases and causes higher segregation. These may explain why gas permeability of complexed PUs increased after 1 : 4 molar ratio of cobalt chloride was added. As the cobalt chloride content increased, excess cobalt chloride filled up the void space and decreased the flexibility of soft segment. This may contribute to the decrease in gas permeability of membranes containing 1 : 3 molar ratio of cobalt chloride.

Cobalt ion has high oxygen affinity and therefore the introduction of cobalt ion can enhance the separation factor of O_2/N_2 .¹¹⁻¹⁷ Figure 9 shows that membranes containing either 1 : 4 or 1 : 3 $\text{CoCl}_2/\text{MDEA}$ molar ratio has higher separation factors than the ones without CoCl_2 addition. There is a remarkable change of separation factor as the hard segment content exceeds 50 wt %. The aggregation of the hard segment is enlarged, which can be evidenced by the disruption in increase of HBI values as the hard segment content exceeds 50 wt %. Meanwhile, the gas transports through soft segment only. Hence, the oxygen affinity decreases due to the lower hard segment content dispersing in soft segment and slight decrease of separation factor of membrane occurs at hard segment content exceeding 50 wt %.

CONCLUSIONS

The gas permeabilities of membranes with 1 : 4 molar ratio of cobalt chloride are higher than those without cobalt chloride, while the gas permeability of membranes containing 1 : 3 molar ratio of cobalt chloride remain nearly the same. The separation factors of these complexed membranes are all higher than those of uncomplexed ones. By manipulating the composition, the amount of cobalt addition, a separation factor of 3.95 and oxygen permeability of 12.83 barrers can be obtained by 11211-1 : 3 Co membrane. The T_{gh} and T_{gs} of membranes are all increased as the cobalt chloride content increased, while the ΔT_g decreased. Wavenumbers of bonded N—H group absorption shift to higher frequency, and frequency difference ($\Delta\nu$) decreased as the cobalt chloride content increased. Properties of stress at break are increased as the cobalt chloride

content is increased, while the strain at break decreased.

All the above results can be explained by the flexibility of soft segments and the aggregation of hard segments. The decrease in size and the disruption in packing of hard segment aggregation would increase the gas permeability. A small amount of hard segments dispersed in soft segment would increase the segregation of soft segment and increase the oxygen permeability. As the amount of hard segments and cobalt chloride dispersed in soft segment increased, the mobility of soft segment would decrease and subsequently reduce the gas permeability.

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