Synthesis and properties of poly(urethane-imide) interpenetrating network membranes

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Abstract

Poly(urethane-imide) (PUI) membranes are prepared by blending polyurethane (PU) prepolymer with different ratio of poly(amide acid) (PAA). PU prepolymer are synthesized by two-stages process with hydroxyl-terminated polybutadiene (HTPB), 4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$) and 1,4-butane diol (1,4-BD). While 4,4′-diaminodiphenyl ether (ODA) and 3,3′–4,4′-benzophenonetetracarboxylic dianhydride (BTDA) are reacted to forming the polyimide (PI) oligomer solution of poly(amide acid) (PAA). IPN structures are formed through reaction between PU prepolymer and PAA and unsaturated C=C double bond between different HTPB segment of PU. All PUI membranes show three steps of weight loss curves and PI shows one step weight loss curve by thermogravimetric analysis (TGA). Compositions lower than 50 wt.% of PU content (0.5-PUI) possess better compatibility between PU and PI and the glass transition temperature of PU hard segment (Tgh) of PUI membranes disappeared. The Tgh values, maximum degradation temperature and char yield of PUI membranes are increased as the increase of PI content. The gas permselectivities of 0.5-PUI are 12 times than that of pure PI.

Keywords: Polyimide; Polyurethane; Poly(urethane-imide); DMA; TGA; Morphology; Gas separation

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1. Introduction

Polyimide materials possess superior heat durability, chemical stability, mechanical strength, dielectric properties and many usages in semi-conductor industries. Others are ultra thinning film formation and high gas separation properties, which is an important aspect of gas separation's materials [1–5]. While the low gas permeability of polyimide due to its densed structure and cannot provide economical usage. HTPB used as the polyol of PU because HTPB possesses low temperature flexibility and lower surface energy, which induces a superhydrophobic surface of very soft PU polymer [6–9]. HTPB-based PU exhibits low tensile strength and a breaking strength at room temperature. PU material possesses superior viscolasticity, tenacity and abrasion resistance. In general, the gas perme-abilities of PU materials are high. While the gas selectivity, mechanical properties and thermal stability of PU membranes are low and cannot be used for the separation performances [10–12]. For the combination of these two materials' superiority, add PI to PU to expand their respective characteristics and expect the best separation performances to be obtained. We hope that the prepared PI/PU hybrids can be suited to separating gases and increasing the economical efficiency. There are many reports on the PI/PU hybrid membranes for the studies of heat, mechanical properties and phase separation [13–20], while rarely study on the HTPB-based PU and gas separation. In this study, series of PI/PU hybrid membranes are prepared and studies on the phase separation, thermal stability and O_2/N_2 gas separation performance.

2. Experiment

2.1. Materials

4,4′-Diaminodiphenylether (ODA, 98%) from Lancaster is dried in a vacuum oven at 125°C for 24 h prior to use. 3,3′–4,4′-Benzophenone-tetracarboxylic dianhydride (BTDA) from Acros Organics is purified by recrystallization from acetic anhydride and then dried in a vacuum oven at 125°C overnight. Hydroxyl-terminated polybutadiene (HTPB) (equivalent weight 1333 g, average functionality of 2.2, R-45 of Arco Co.), 4,4′-dicyclohexylmethane diisocya-nate ($H_{12}MDI$) (Desmodue W of Mobay Co.), and 1,4-butane diol(1,4-BD) are used to synthe-size PU prepolymer. N-methyl-2-pyrrolidone (NMP) from Tedia Company is dehydrated with molecular sieves.
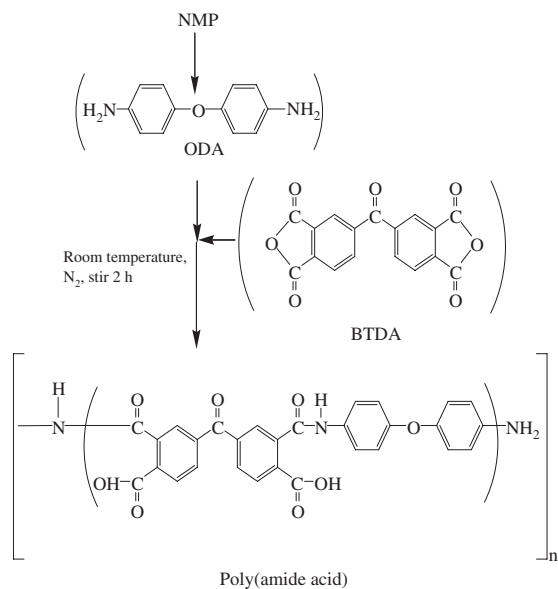
2.2. Preparation of membranes

2.2.1. Synthesis of poly(amide acid)

Purified ODA and suitable amount of NMP are added to the three necked bottle and purged with N_2 gas and stirring at room temperature. After thoroughly dissolved, then BTDA is added in three sequences and the addition of every sequence must be dissolved homogeneously. Continuing stirring for 2 h and then put in the refrigerator. The preparation procedure is worked out in Scheme 1.
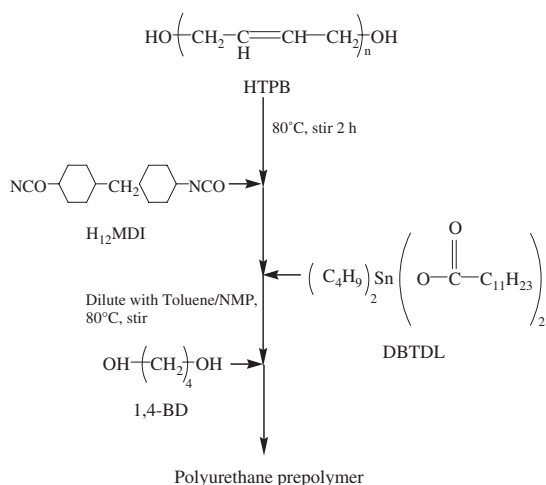
2.2.2. Synthesis of PU-prepolymer

One equivalent weight of HTPB is added to the three necked bottle and stirred for 2 h to remove the residual water. Two equivalent weight of $H_{12}MDI$ and small amount of DBTDL are added the above reactor and stirred thoroughly. Then suitable ratio of NMP and toluene are added to 80 wt.% solid content and stirred reac-tion at 80°C as the NCO% reaching theoretical value. The stoichiometric amount of chain extender (1,4-BD) and solvent (NMP + toluene) are then added and reacted for the theoretical NCO% (5 wt.%) reached. The final PU solution is with 20 wt.% solid content and the preparation procedure is presented in Scheme 2.

Scheme 1. The flow chart of the procedures to prepare the poly(amide acid).

2.2.3. Preparation of PUI solutions

Different weight ratio, 0.9:0.1, 0.8:0.2, 0.5:0.5 and 0.2:0.8, of PU-prepolymer and poly(amide acid) are blended respectively, which are expressed as 0.9-PUI, 0.8-PUI, 0.5-PUI and

Scheme 2. Flow chart of the procedures to prepare polyurethane prepolymer.

0.2-PUI, and stirred for 2 h purging with N_2 gas and then stored at refrigerator for usage.

2.2.4. Preparation of PUI membranes

Pour the above PUI solutions to the glass plate, respectively and knife coating to obtain 160 μm thickness film and then put on the vacuum oven at 50°C for 2 h. After most of solvent is removed and then put in circulation oven with increasing temperature programming. Through four steps of heating, thermal treatment, for imidization reaction of PI and reaction between PU and PI at 100°C (2 h), 150°C (2 h), 175°C (2 h) and 200°C (2 h), golden and semi-transparent solid films are obtained.

2.3. Measurements

Fourier transfer infrared spectrophotometer (FT-IR) absorption spectra are recorded between 4000 and 400 cm^{-1} by Nicolet PROTEGE-460. It is found that the peak due to bonded C=O stretching is centered at about 1698 cm^{-1} and that due to free C=O stretching is centered at about 1716 cm^{-1}. The infrared absorption bands of butadiene soft segment are the trans-1,4 form at 970 cm^{-1}, trans-1,2 form at 912 cm^{-1} and cis-1,4 form at 685 cm^{-1}. The infrared absorbance of the total carbonyl groups ($U_{C=O}$) detected by FTIR is calculated by the addition of the respective hydrogen bonded C=O absorbance and free hydrogen bonded C=O absorbance. The $U_{C=O}/U_{C=C}$ absorption peak ratio is the ratio of total C=O absorbance with trans-1,4 form C=C absorbance. A larger value of this ratio indicates that larger C=O functional groups presents on the membrane. Thermogravimetric analysis (TGA) is performed from 60 to 800°C with Du Pont TGA-950 at a heating rate of 20°C/min and under nitrogen. The dynamic mechanical analysis (DMA) is carried out by means of thermal analyzer DMA-2980 from 60 to 300°C, at a frequency of 1 Hz and heating rate of 3°C/min.

Oxygen and nitrogen (mixed) permeabilities of the hybrid films are determined by using the Yanaco GTR-10 gas permeability analyzer. The data of gas permeabilities are the average of at least three measurements. Experiments are carried out by measuring air gas flows through the membrane under constant membrane pressure equal to 38 cm Hg. The gas permeation area is 15.6 cm^2 and the gas permeability is evaluated by the following equation:

$$P = \frac{ql}{(P1 - P2)A}$$

where P is the N_2 or O_2 gas permeability [cm^3 (STP) cm/(cm Hg cm^2 s)], q is the volumetric flow rate of gas permeation [cm^3 (STP)/s], l is the film thickness(cm), P_1 and P_2 are the upstream and downstream pressures (cm Hg) and A is the effective film area (cm^2). While gas selectivity is named as the ratio of P_{O_2}/P_{N_2} and permselectivity is the product of P_{O_2} and selectivity.

3. Results and discussions

3.1. Infrared spectra

The Fourier transfer infrared spectrophotometer spectra of pure PU, 0.8-PUI and pure PI membranes are shown in Fig. 1. The characteristic PI absorption peaks are imide asymmetrical stretching (1780 cm^{-1}), C=O symmetrical stretching of imide (1720 cm^{-1}), C–N stretching of imide (1380 cm^{-1}) are presented. While those of PU absorption peaks are N–H stretching (3200–3500 cm^{-1}), CH$_2$ stretching (2900–2930 cm^{-1}), and C=O symmetrical stretching (1730–1700 cm^{-1}). Fig. 2 shows the FT-IR spectra of 0.8-PUI hybrid membrane after different thermal treatment temperature. The absorption peak, 1680 cm^{-1}, of amide acid group decreases after 175°C thermal treated. While the absorption peaks, at 1380, 1720, 1780 cm^{-1}, of imide functional group have no any changes, which can
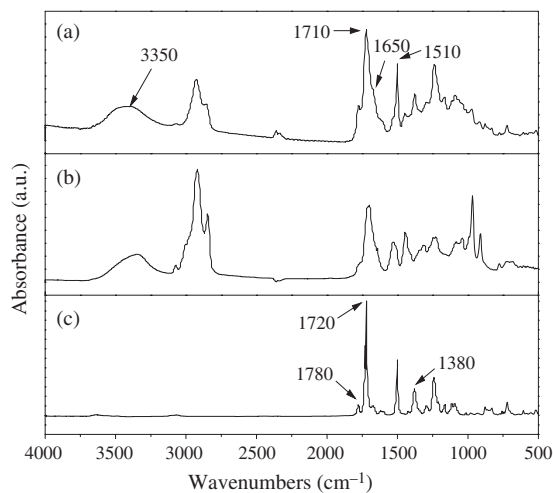

Fig. 1. FT-IR spectra of (a) pure PU, (b) 0.8-PUI and (c) pure PI membranes.

evidence that the imidization reaction has been attained completely.

While the absorption peak, at 2920 cm^{-1}, of CH$_2$ group of PU composition has a little changes. Fig. 3 shows that the $U_{C=O}/U_{C=C}$ absorption
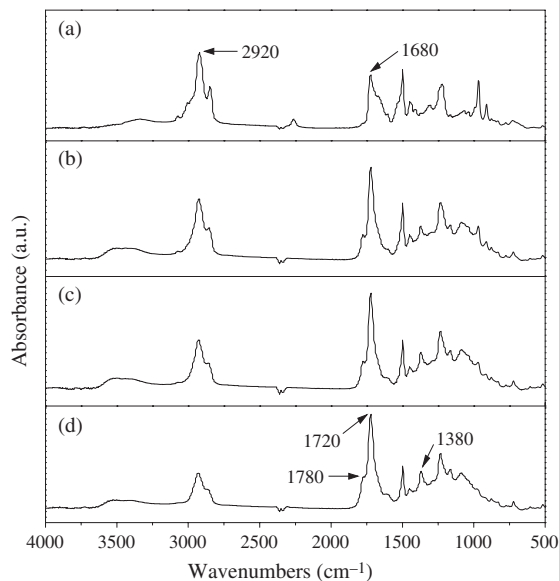

Fig. 2. FT-IR spectra of 0.8-PUI hybrid membrane at different thermal treatment temperature: (a) 100°C, (b) 150°C, (c) 175°C and (d) 200°C.
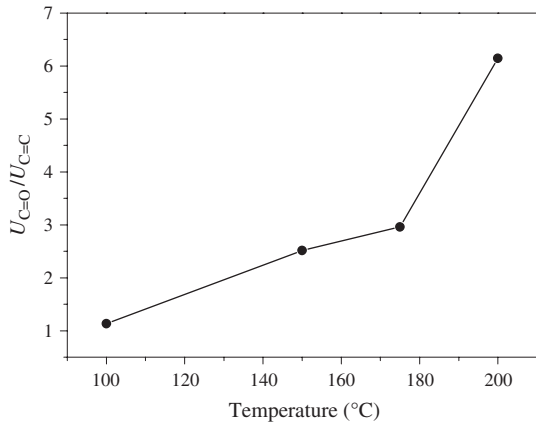
Fig. 3. Relationship between absorption ratio $U_{C=O}/U_{C=C}$ and thermal treatment temperature of 0.8-PUI membrane.

peak ratios of 0.8-PUI membrane are increased as the increase of imidization temperature and the other PUI membranes present the same trend as well. The reason is that the oxidation or broken reaction of the unsaturated C=C double bond of HTPB polyol will be produced to form carbonyl groups or crosslinked together between different HTPB segment and hence the C=C absorption peak decreased. Then the $U_{C=O}/U_{C=C}$ absorption peak ratios are increased as the increase of thermal treatment temperature.

3.2. Thermal gravimetric analysis (TGA)

A three-step degradation curves are observed. In the first step, the decomposition temperature corresponds to urethane-bond (i.e., hard segment) breaking and step 2 is the polyol decomposition (i.e., HTPB soft segment) [21,22], while step 3 corresponds to PI decomposition [23]. The thermogravimetric profile and maximum degradation temperature of PUI membranes are shown in Figs. 4 and 5 .

All the PUI hybrid and pure PU membranes show three steps weight loss and PI shows one step weight loss as shown in Fig. 4. The decomposition temperatures (T_d) are listed in Table 1.
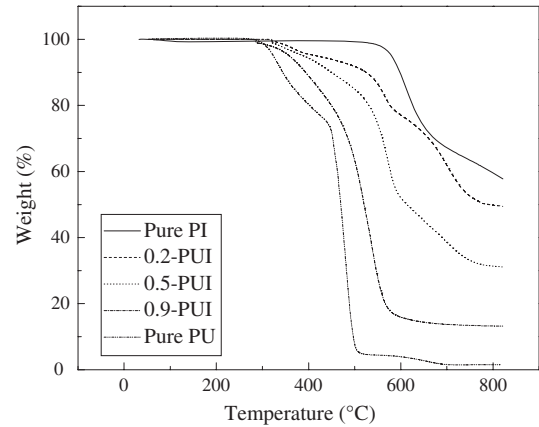

Fig. 4. Thermogravimetric curves of PUI membranes.

The 1st step decomposition temperatures of PUI membranes are nearly lower than that of pure PU. The reason may be that part of PU with free NCO content, which reacts with –NH group of amide (–CO–NH–) chain or with carboxylic acid of PI segment and hence the hydrogen bonding between PU hard segment decreased, which can be explained for the decrease of 1st decomposition temperatures. On the other hand, the 2nd step decomposition temperatures of PUI membranes are all nearly higher than that of pure PU. The explanation is that the oxidation or broken reaction of the unsaturated double
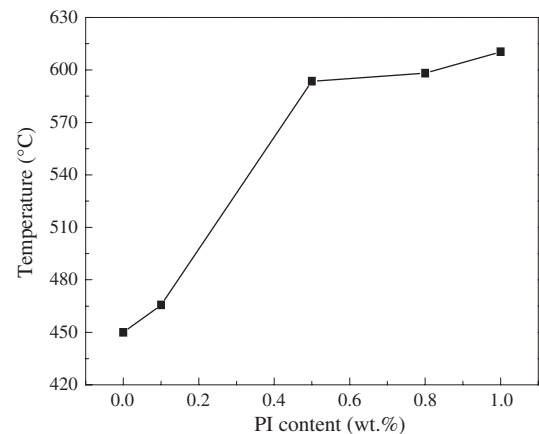

Fig. 5. Relationship between maximum degradation temperature and PI content.

Table 1
Thermal gravimetric analysis

Compound code	First step decomposition temperature (°C)	Second step decomposition temperature (°C)	Third step decomposition temperature (°C)	Char yield (%)
Pure PU	300	450	–	0.2
0.9-PUI	302.75	448.74	465.71	14
0.5-PUI	229.23	463.45	593.57	30
0.2-PUI	260.88	462.32	598.10	50
Pure PI	–	–	610.43	60

bond of HTPB polyol will be produced to form carbonyl groups and forming intermolecular bonding between PI and PU. Meanwhile, the unsaturated C=C double bond between different HTPB segments may be brokened and cross-linked together and then the decomposition temperature of HTPB polyol increased. Meanwhile, the 3rd step decomposition temperatures of PUI membranes are all lower than that of pure PI. The reason is that the numbers of imide ring structures of PUI are decreased, which is due to part of PU with free NCO content reacted with –NH group of amide (–CO–NH–) chain or with carboxylic acid of PI segment. Then the 3rd step decomposition temperatures increase as the increase of PI content as shown in Fig. 5. Table 1 depicts that the residual after 800°C degradation increases as increasing the PI content also. The increase of PI content will increase the ring structures and hence needs more energy to decompose the membrane and then the residual increased. The above three decomposition temperatures changes can be collaterally used as an indication of PU dispersed in PI chain and will be discussed in Section 3.4.

3.3. Dynamical mechanical analysis (DMA)

The dynamic mechanical properties of PUI membranes as a function of temperature are shown in Figs. 6 and 7 and the results are summarized in Table 2. Fig. 6 shows the storage modulus of pure PI, 0.2-PUI, 0.8-PUI and 0.9-PUI membranes. It shows that the storage modulus of 0.8-PUI and 0.9-PUI, which are all with high PU content, are largely lower than pure PI and decreased to lower than 500 MPa.

While the storage modulus of PUI with high PI content at 225°C, such as 0.2-PUI, maintains larger than 1000 MPa. Fig. 7 shows the tan δ curves of pure PI, 0.2-PUI, 0.5-PUI, 0.8-PUI and 0.9-PUI membranes. Aiming at T_g value of PU, the tan δ peaks shift to higher temperature as the increase of PI content. While for the tan δ peaks of PI then shift to lower temperature and the peak intensity increased as the increase
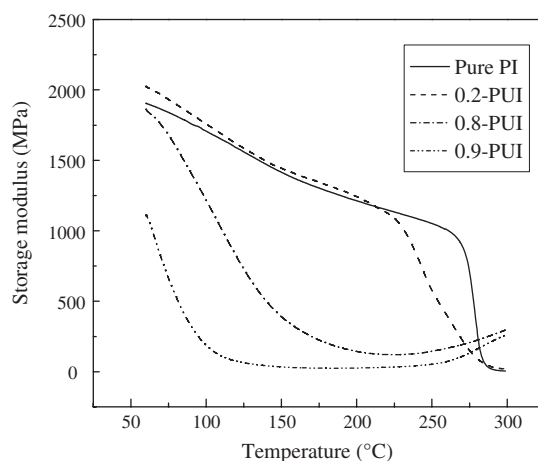

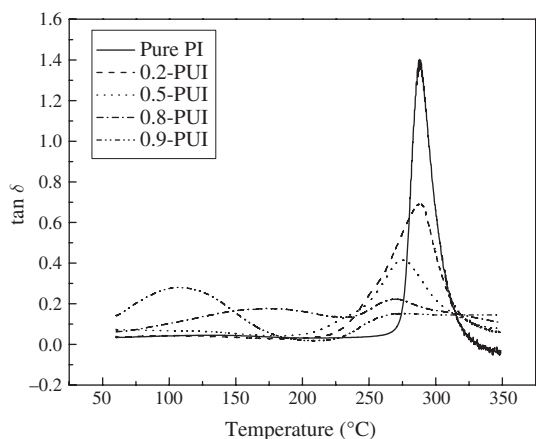Fig. 6. Dynamic mechanical analysis of storage modulus curves.

Fig. 7. Dynamic mechanical analysis of tan δ curves.

of PU content. The storage modulus are largely decreased as the temperature is higher than T_g value and the tan δ curves present disrupt decrease of damping loss peak.

This indicates that the damping loss peak of PUI is lower than that of pure PI membrane. The T_g values of PI part are decreased as the increase of PU content, while that of PU part are increased as the increase of PI content and disappeared from 0.5-PUI, 0.2-PUI to pure PI. The latter result may mean that the compatibility between PU, lower than 50 wt.% content, and PI is good.

3.4. Morphology and order between PU and PI

The PU content in PUI hybrid may be dispersed into two parts: one is mixed with PI chain as the PU content is lower than 0.5-PUI. And as the PU content is higher than 50 wt.%, the excess part of PU is not mixed with PI and may be dispersed on the membrane's upper layer. The explanation is that the addition of 5 wt.% NCO content of PU prepolymer to the polyamic acid (PAA), the free NCO content may react with –NH group of amide (–CO–NH–) chain to form allophanate (–CO–N(CO–NH–)–) crosslinkage at elevated temperatures (100°C or above).

The other reaction of isocyanate may with carboxylic acid of PAA proceeds usually with the formation of anhydride (–NH–CO–O–CO–) followed by decomposition, yielding the corresponding amide (–NH–CO–) with liberation of carbon dioxide at elevated temperatures (100°C or above).

The free NCO content of PU prepolymer may react with –NH group of amide (–CO–NH–) chain or with carboxylic acid of BTDA chain as the PU content is low as 0.2-PUI and 0.5-PUI. And then the PU polymer chains will be dispersed or entangled with the BTDA segment of PI chain, which can be evidenced from the disappearance of tan δ temperature of 0.2-PUI,

Table 2
Dynamical mechanical properties of PUI membranes

Compound code	Storage modulus (MPa)[a]	tan δ of PI (°C)	tan δ of PU (°C)
Pure PU	–	–	90
0.9-PUI	1113	264.5	107.6
0.8-PUI	1864	273.8	112.4
0.5-PUI	1939	275.1	b
0.2-PUI	2019	287.4	b
Pure PI	1901	287.8	b

[a]Storage modulus are measured at 60°C.
[b]Peak of PU disappeared.

0.5-PUI as depicted in Table 2. While as the PU content increased from 0.5-PUI to 0.9-PUI, part of PU content is not mixed with PI and may be dispersed on the membrane's upper layer. The above two phenomena may be collaterally evidenced from the 1st step decomposition temperatures of PUI membranes are nearly lower than that of pure PU and the 3rd step decomposition temperatures of PUI membranes are all lower than that of pure PI.

On the other hand, the unsaturated C=C bond of HTPB may be oxidized, broken or crosslinked together at elevated temperatures (100°C or above). There have many reports about the low oxidized stability of unsaturated double bond (C=C) of HTPB segment through thermal treatment. Chiu and coworkers [24,25] have reported that the oxidation or broken reaction of the unsaturated double bond (C=C) of HTPB-based PU, under 60°C, 30 days, does not happened. While the oxidation or broken reaction of the unsaturated double bond of HTPB will be produced to form carbonyl groups at temperature higher than 100°C. Meanwhile, the unsaturated double bond between different HTPB segments may be crosslinked together through oxidation or broken reaction. As part of PU may be reacted with –NH group of amide (–CO–NH–) chain or with carboxylic acid of PI segment. The other part of PU may be oxidized or broken between different HTPB segments to form crosslinkage. This can be collaterally evidenced from the 2nd step decomposition temperatures of PUI are all nearly higher than pure PU. Then the interpenetrating networks (IPNs) between PU and PI are formed.

3.5. Gas separation performances

The O_2/N_2 separation performances of HTPB-based PU membranes are all different from those of PI presented. HTPB-based PU membranes are with high gas permeability and low selectivity, while PI membranes possess the reverse results.

This study tries to blend two polymers and expects to obtain superior permeation performances.

Gases permeating through membrane are mainly through soft segment of polymer chain. From PI's chemical structure, gases are permeating through soft segments of –C(O)– group between two imide groups and –O– group between two benzene group. As the blend of PU and PI, the free group –NCO group may react with –NH group of amide chain or with carboxylic acid of BTDA chain and then disrupt the rigid imide chain. Then gases may permeate through the disrupted imide chain and then the gas permeability through the PI chain changed.

Table 3 depicts that the gas permeabilities of O_2, N_2 are all increased as the increase of PU content, while the selectivities of O_2/N_2 present the reverse trend. The O_2, N_2 gas permeability of 0.5-PUI membrane are 23, 51 times than that of pure PI membrane, respectively, while the selectivity of O_2/N_2 is only 1/2 times lower than PI membrane. As the PU content is higher than 50 wt.%, 0.8-PUI and 0.9-PUI, the gas permeabilities and selectivities are all nearly the same as pure PU membrane. The explanations are that the free NCO content of PU prepolymer may react with –NH group of amide (–CO–NH–) chain or with carboxylic acid of BTDA chain as the PU content is low as 0.2-PUI and 0.5-PUI. And then the PU polymer chains will be

Table 3

O_2, N_2 permeabilities and O_2/N_2 selectivity of pure PI, PU and PUI membranes at 35°C

Compound code	P_{O_2} (Barrer)	P_{N_2} (Barrer)	P_{O_2}/P_{N_2}
Pure PU	22.8	11.9	1.92
0.9-PUI	20.1	10.2	1.97
0.8-PUI	17.2	7.82	2.20
0.5-PUI	3.65	1.07	3.41
0.2-PUI	0.25	0.054	4.63
Pure PI	0.16	0.021	7.62

dispersed or entangled with the BTDA segment of PI chain. While as the PU content increased from 0.5-PUI to 0.9-PUI, the imide chain of PI will be entangled and destructed more seriously. Then the gas permeabilities and selectivities of 0.5-PUI–0.9 PUI membranes are nearly the same as that of PU membrane. This may be the reason for there has a disrupt change at 0.5-PUI for the gas permeability and selectivities.

4. Conclusion

The absorption peak, 1680 cm^{-1}, of amide acid group of PI chain decreases after 175°C thermal treated. The $U_{C=O}/U_{C=C}$ absorption peak ratios of 0.8-PUI membrane are increased as the increase of imidization temperature due to the oxidation reaction of the unsaturated double bond (C=C) of HTPB segment and the other PUI membranes present the same trend as well. The 1st step decomposition temperatures of PUI membranes are nearly lower than that of pure PU. On the other hand, the 2nd step decomposition temperatures of PUI membranes are all nearly higher than that of pure PU. Meanwhile, the 3rd step decomposition temperatures of PUI membranes are all lower than that of pure PI. While the residual after 800°C degradation increases as increasing PI content. The T_g values of PI part are decreased as the increase of PU content, while T_{gh} of PU part are increased as the increase of PI content and disappeared from 0.5-PUI, 0.2-PUI to pure PI. The latter result may mean that the compatibility between PU and PI is good as the PU content is lower than 50 wt.%. As part of PU may be reacted with –NH group of amide (–CO–NH–) chain or with carboxylic acid of PI segment. The other part of C=C groups of PU may be oxidized or broken between different HTPB segments to form crosslinkage. Then the interpenetrating networks (IPNs) between PU and PI are formed. PU content may be dispersed into two parts: one is mixed with PI chain as the PU content is lower than 0.5-PUI. The other is

that as the PU content is higher than 0.5-PUI, part of PU is not mixed with PI and may be dispersed on the membrane's upper layer.

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