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Preparation and Pervaporation Performances of PEA-based Polyurethaneurea and Polyurethaneimide Membranes to Benzene/Cyclohexane Mixture

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Pervaporation is promising in the separation of benzene/cyclohexane mixture for the petrochemical industry. Two kinds of pervaporation membrane materials, including PEA-based polyurethaneurea (PUU) and polyurethaneimide (PUI), were successfully synthesized from the same soft segment of poly(ethylene adipate)diol (PEA) and different hard segments via a two-step method. The hard segment of PUU was prepared from toluene diisocyanate (TDI) and 4,4'-diaminodiphenyl methane (MDA), while that of PUI was from 4,4'-methylene-bis(phenylisocyanate) (MDI) and pyromellitic dianhydride (PMDA). The structures and properties of PUU and PUI were characterized by means of FT-IR, DSC and TGA. During the pervaporation experiment, the PUI membranes had a flux of 12.13 kg $\mu\text{m m}^{-2} \text{h}^{-1}$ and separation factor of 8.25, while the PUU membranes had a flux of 26.35 kg $\mu\text{m m}^{-2} \text{h}^{-1}$ and separation factor of 6.29 for 50 wt% benzene in the benzene/cyclohexane mixture at 40°C. The effects of the structures of hard segments on pervaporation performances were discussed. The investigation of the relationship in molecular structure and PV performances will be helpful for the choice and design of membrane materials in the separation of benzene/cyclohexane mixture.

Keywords: pervaporation membrane; aromatic hydrocarbon; polyurethaneurea; polyurethaneimide

1 Introduction

Separation of aromatic/non-aromatic hydrocarbon mixtures is among the most important and difficult processes in petrochemical industry (1, 2). For example, in the production process of cyclohexane, the unreacted benzene has to be removed for pure cyclohexane recovery. Both benzene and cyclohexane have a similar molecular size, polarity and volatility with only 0.6°C difference. Furthermore, they form close boiling or azeotropic mixtures at the entire range of their compositions, which makes their separation very difficult.

Traditionally, extractive distillation and azeotropic distillation are used for this separation. However, these conventional technologies often suffer from complicated processes and high operation costs. It is a significant incentive to explore new processes for the separation.

Pervaporation (PV) is a promising alternative to the separation of aromatic/non-aromatic hydrocarbon mixtures. It

offers many advantages, such as high separation efficiency, low energy consumption and simple operation (3–6). Furthermore, the separation mechanism of pervaporation is not based on relative volatility but the difference in sorption and diffusion properties of feed components towards a membrane. Therefore, pervaporation is very suitable for the separation of azeotropic and close boiling mixtures such as benzene/cyclohexane system. In the pervaporation process, the membrane material is a key factor for separation efficiency. Thus, it is very important to develop new membrane materials for the pervaporation separation of aromatic/non-aromatic hydrocarbon mixtures.

Polyurethaneurea (PUU) and polyurethaneimide (PUI) are both attractive polymer materials for their good mechanical property and chemical resistance, and they have been widely employed in the fields of architecture, industry and medicine (7–9). Moreover, they are well known as elastomer block copolymers with alternating soft and hard segments depending on the nature and molecular weight of the reagents used for their synthesis. The soft segment is usually an oligomer rubber, while the hard segment is a glassy structure. The thermodynamic incompatibility of soft and hard segments results in the microphase separation and has great effects on their properties.

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Recently, PUU and PUI have found their applications in pervaporation separation owing to the versatile segmented structure and good permselectivity.

It is especially interesting to study the relationships between structure and PV performance for the choice and design of membrane materials (10–14).

Some studies showed that PUU and PUI membranes were promising in the separation of aromatics from alkanes (15). It was proven that the poly(oxytetramethylene)(PTMO)-based PUU membranes showed permselectivity towards benzene in the mixture of benzene and cyclohexane (12, 16, 17), but the separation performances were not satisfactory. On the other hand, the polyester-based PUU membranes, such as poly(ethylene adipate) (PEA)-based, were much more efficient for this kind of separation than PTMO, and they had better selectivity compared with the polyether-based membranes as reported by patents (18, 19, 20). As far as the PUI membranes were concerned, they had good separation performances not only in the pervaporation of alcohol/ether mixtures (13, 14, 21, 22), but also in the removal of aromatic from heavy cat naphtha (23–25).

In this paper, poly(ethylene adipate) (PEA)-based polyurethaneurea (PUU) and polyurethaneimide (PUI) were synthesized. Their chemical structures and properties were characterized by FT-IR, DSC and TGA. The pervaporation performances of the PUU and PUI membranes were investigated for benzene/cyclohexane mixture, and the effects of different hard segment structures on polymer properties and separation performances were discussed. Besides, the pervaporation performances of PUI for benzene/*n*-heptane and benzene/*n*-octane were also investigated.

2 Experimental

2.1 Materials

Toluene diisocyanate (TDI, a mixture of 80% 2,4-TDI and 20% 2, 6-TDI) was supplied by Tianjin Damao Chemical Reagents Factory and used as received. 4,4'-methylenebis(phenylisocyanate) (MDI, 99.9%) was obtained from Yantai Wanhua Polyurethane Co. Ltd. and used as received. Poly(ethylene adipate) diol (PEA, $M_n = 2000$) was obtained from Yantai Huada Chemicals Industry Co. Ltd. and dried under vacuum at 110°C before used. Pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl methane (MDA) were purchased from Beijing Chemical Reagents Company and purified by sublimation. *N,N*-dimethyl formamide (DMF) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å).

2.2 Synthesis of PUU and PUI

The polyurethaneurea (PUU) and polyurethaneimide (PUI) were synthesized by a two-step method including prepolymerization and chain extension reaction as shown in

Figure 1. Initially, the solution of PEA in DMF was placed into a three-neck flask equipped with a reflux condenser and N_2 inlet and then added dropwise with TDI (or MDI) at 70°C (80°C for MDI). The reaction mixture was stirred intensively for 1.5 h for the synthesis of NCO-terminated PUU (or PUI) prepolymer. Then the solution of MDA (or PMDA) as chain extender was added to prepolymer of PUU (or PUI). Finally, the reaction mixtures were heated to 80°C (85°C for PUI) and maintained for another 2 h. The molar ratios of PEA, TDI (or MDI) and MDA (or PMDA) were 1:2:1. Thus the solution of PUU and PUI were obtained.

2.3 Membrane Preparation

The solutions of PUU and PUI were diluted to 15 wt% in DMF and filtered over a 25 μm metal filter to remove impurities. Then, the membranes of PUU and PUI were prepared by casting their solutions in a Teflon mold. After the solvent evaporation (60°C, 1.5 h), the PUU membranes were then cured at 80°C for 10 h to remove the residual solvent, while the PUI membranes were further cured at 150°C for the complete formation of the imide group. Finally, the resulting membranes were stripped from the Teflon mold. The thickness of PUU and PUI membranes was 80–110 μm .

2.4 Characterization of PEA-based PUU and PUI Membranes

The structures of PUU and PUI were characterized by FT-IR spectra, and recorded on a Nicolet IR560 spectrometer with polymer film. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 32 scans at a resolution of 4 cm^{-1} .

$^1\text{H-NMR}$ spectra was used to obtain more information of polymer structures with the solvent of DMSO- d_6 and a Varic ECA-600 spectrometer.

The glass transition temperature (T_g) of PUU and PUI were measured by differential scanning calorimeter (Seiko DSC6200) with a heating rate 10°C/min in the range of –80–200°C under N_2 atmosphere. Thermogravimetric analysis (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20°C/min in N_2 within the temperature range of 30–900°C.

Both PUU and PUI were readily soluble in DMF, DMAc and NMP. The inherent viscosities of PUU and PUI in DMAc solution (conc. 0.5 g/dl) were measured with a Ubbelohde viscometer at 30°C.

The mechanical properties of PUU and PUI membranes were measured on an electronic universal testing machine (WDT-10) at room temperature with film specimens at a rate of 250 mm/min. The contact angles for water on PUU and PUI membranes were determined by OCA20 contact angle system (DataPhysics Co.). The thicknesses of the PUU and PUI membranes were determined by

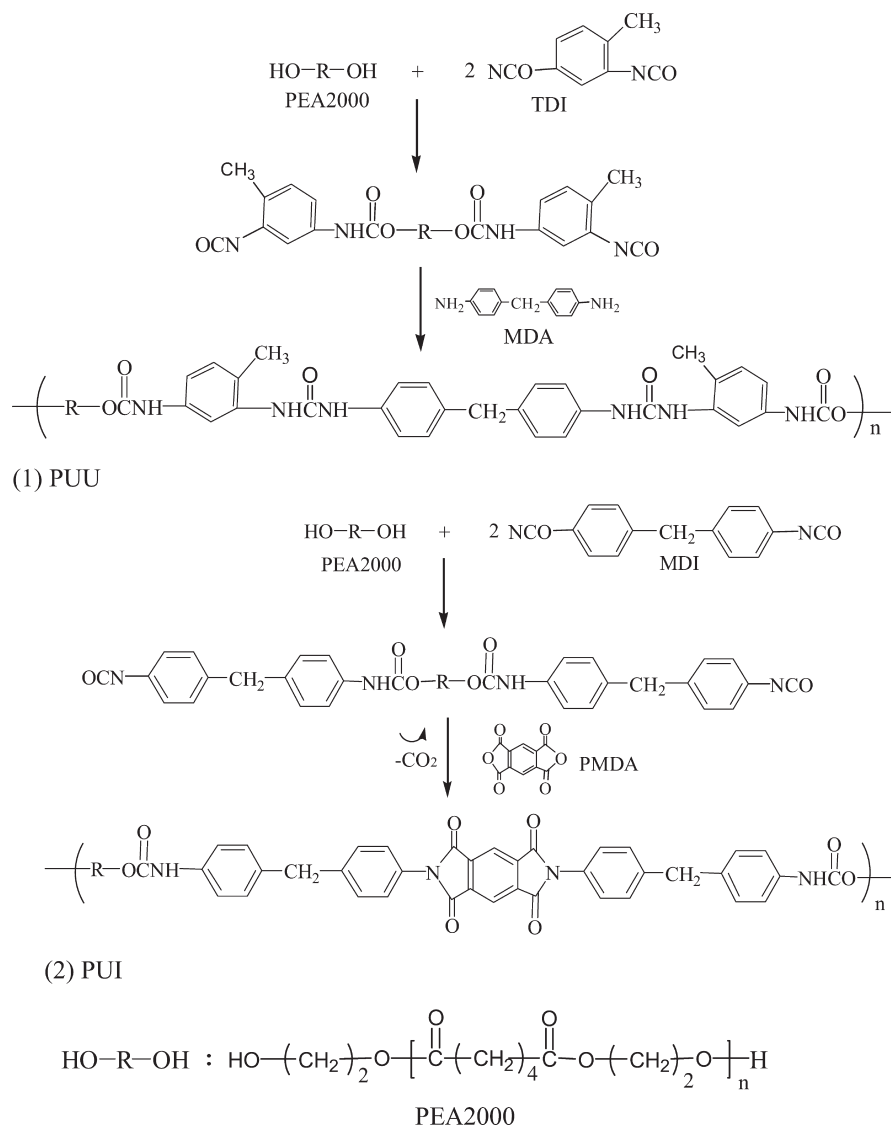


Fig. 1. Synthesis scheme of PEA-based PUU and PUI.

using a micro screw gauge. The density was measured by a floating method using mixtures of ethanol and carbon tetrachloride.

Solubility parameter (δ) is estimated by group contribution method and defined as follows (26):

$$\delta = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2} \quad (1)$$

Where δ_D is the dispersive forces contribution, δ_P is the polar contribution, and δ_H is the hydrogen bonding contribution.

2.5 Swelling Experiment

The swelling experiment was carried out by a weight-gain method. The weighed, dry polymer samples were immersed in benzene/cyclohexane mixtures for 72 h at room temperature. Then the swelled samples were removed from the

solution, wiped with tissue paper to remove the adherent liquid and weighed.

The swelling degree value (Sw) is defined as:

$$Sw = \frac{M - M_0}{M_0} \times 100\% \quad (2)$$

Where M is the weight of the swelled sample and M_0 is the weight of the dry sample.

2.6 Pervaporation Experiments

The pervaporation performances of PUU and PUI membranes were tested by using an apparatus developed in our laboratory as shown in Figure 2. The feed was heated and circulated from the feed tank (volume of $2.5 \times 10^{-3} \text{ m}^3$) through the upstream side of the membrane cell by a pump with an adjustable function of flow rate. A

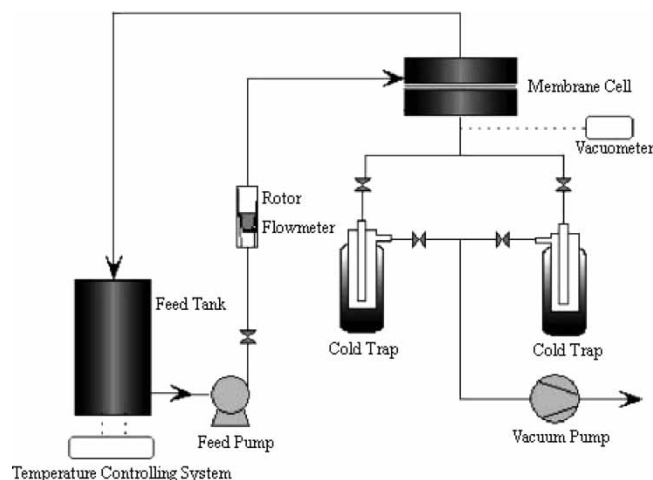


Fig. 2. Pervaporation performances test apparatus.

membrane supported by a porous sintered stainless steel in the permeate side was mounted in the pervaporation cell. The measurements were carried out for aromatic/non-aromatic hydrocarbon mixtures in which the content of aromatic hydrocarbon was 50 wt%. The feed mixture was maintained at a temperature between 35°C and 80°C using a thermostat. The effective area of the membrane was $2.2 \times 10^{-3} \text{ m}^2$. Vacuum on the permeate side was maintained below 400 Pa and monitored with a digital vacuumeter. Two cold traps were set in parallel allowing the collection of permeate without rupture of the vacuum. The concentrations of permeate and feed mixture were analyzed by gas chromatography.

The permeability is evaluated by the normalized flux (J , $\text{kg } \mu\text{m m}^{-2} \text{ h}^{-1}$) as defined in formula 3 to compare pervaporation performances of membranes with different thickness.

$$J = \frac{Q}{A \cdot T} \cdot l \quad (3)$$

where Q (kg) is the total mass of permeate collected through the effective area of membrane (A , m^2) during time T (h), l is membrane thickness (μm).

The selectivity of membrane is estimated by separation factor and defined as:

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \quad (4)$$

where Y_A and Y_B represent the weight fractions of aromatic and non-aromatic hydrocarbons in the downstream permeate, and X_A and X_B represent those in the feed mixture, respectively.

3 Results and Discussion

3.1 Structure Characterization of the PUU and PUI Membranes

The structures of PEA-based PUU and PUI synthesized in this study were shown in Figure 1. They had the same PEA soft segment, while there was great difference in the hard segment. Besides the urethane group, PUI had an imide group instead of a urea group in PUU.

The characteristic peaks of PUU and PUI were tested by FT-IR and shown in Figure 3. In this figure, both FT-IR spectras of

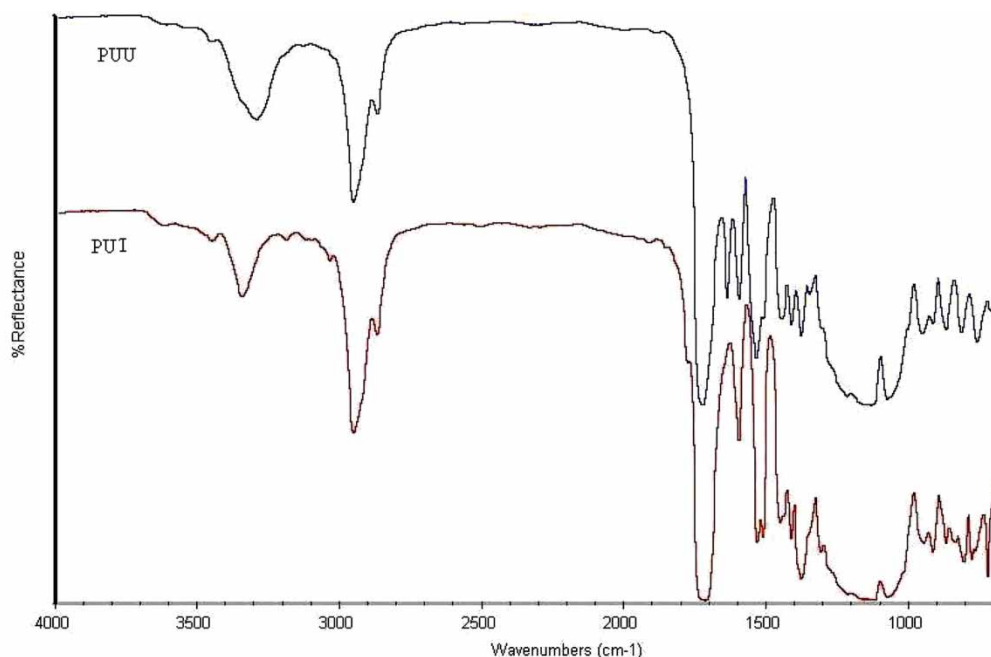


Fig. 3. FT-IR spectra of PEA-based PUU and PUI.

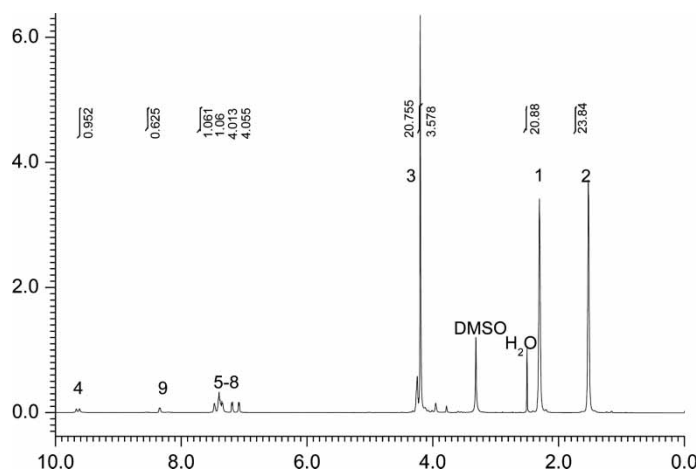


Fig. 4. $^1\text{H-NMR}$ spectra of PEA-based PUI.

PUU and PUI demonstrated the characteristic peaks of PEA and urethane group:

PEA: 2940 cm^{-1} (ν C-H stretch vibration), 1720 cm^{-1} (ν CO), 1220 cm^{-1} (ν COC); Urethane: 3300 cm^{-1} (N-H stretch vibration), 1720 cm^{-1} (amide I), 1510 cm^{-1} (amide II), 1220 cm^{-1} (amide III).

Besides, the spectra of PUI also showed the characteristic bands of imide group: 1780 cm^{-1} (ν C=O), 1720 cm^{-1} (amide I), 1510 cm^{-1} (amide II), 1360 cm^{-1} (ν C-N), 720 cm^{-1} (ring deformation). In addition, no absorption at 2270 cm^{-1} (-NCO) appeared in the spectra, which indicated that -NCO groups in NCO-terminated PUU (or PUI) prepolymer had completely reacted with chain extenders.

The $^1\text{H-NMR}$ spectra of PUI was shown in Figure 4. The aromatic protons were detected around 7.1–8.4 ppm depending on the position in the aromatic ring as expected. All hydrogen peaks in the $^1\text{H-NMR}$ were in good agreement with the proposed polymer structure as indicated in Figure 4.

The physical properties of PEA-based PUU and PUI including inherent viscosity, density, contact angle and mechanical properties were shown in Table 1.

3.2 Thermal Properties of the PEA-based PUU and PUI

The glass transition temperatures of PEA, PUU and PUI were determined by DSC (Figure 5). As shown in DSC curves, two glass transition temperatures (Tg) were found for PUU and PUI. For the PUU membranes, the Tg of PEA soft segment (Tgs) was -34.4°C and that of the TDI-MDA hard segment

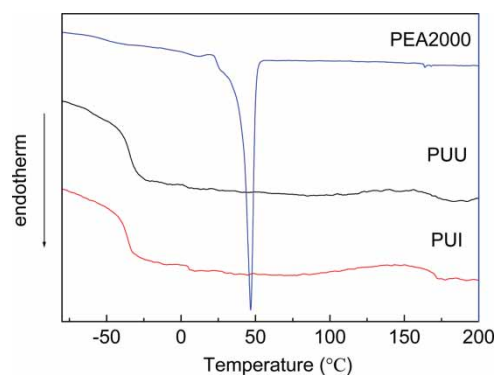


Fig. 5. DSC curves of PEA-based PUU and PUI.

(Tgh) was 171.0°C , while the PUI membranes showed the lower Tgs of -36.0°C and the higher Tgh of 171.9°C . Two Tg suggested the microphase separation structures of the soft and hard micro-domains in PUU and PUI membranes.

The pure PEA also showed an inconspicuous Tg of -49.5°C and an obvious melting peak (Tm) at 46.7°C . It was distinctly found that the Tm of PEA was absent and Tg of PEA was increased when pure PEA became the soft segment of PUU and PUI. The introduction of hard segments resulted in the disrupted chain packing and decreased crystallization of PEA, and the mobility of the pure PEA was also restricted as some hard segments “dissolved” in the soft micro-domain.

Furthermore, the Tgh of PUI was higher than that of PUU. It could be explained from the viewpoint of the chemical structure in hard segments. The hard segment of MDI-PMDA in PUI incorporated not only more aromatic rings in the backbone than TDI-MDA in PUU, but also the cyclic imide group. It made the molecular chain of PUI more rigid than PUU. On the other hand, the high polarity of the imide group probably improved the intermolecular attraction power and made the inner rotation of MDI-PMDA segments more difficult than TDI-MDA.

However, the Tgs of PUI were lower than that of PUU. It was probably due to the effects of hydrogen bonding between soft and hard segments. In the structures of polyurethane-based materials with polyester as soft segments, there were hydrogen bonds with ester -C=O in soft segment as proton-acceptor and urethane N-H in hard segment as proton-supplier. In the structure of MDI-PMDA of PUI, fewer proton-suppliers were found than TDI-MDA of PUU, which would result in smaller density of hydrogen bonds between soft and hard segments. It would decrease the interaction between soft and hard segments, thus the

Table 1. Physical properties of PEA-based PUU and PUI

Materials	Soft segment (wt%)	Hard segment (wt%)	Density (g/ml)	Inherent viscosity (dl/g)	Contact angle	Tensile stress (MPa)	Elongation (%)
PUU	78.5	21.5	1.20	0.31	84.1	16.2	662.1
PUI	73.6	26.4	1.35	0.41	72.1	24.0	580.9

soft segment of PEA in PUI had more flexibility than that in PUU.

The nature of soft and hard segments greatly affected the mechanical properties. As shown in Table 1, PUI obtained the better tensile stress and lower elongation than PUU. Better mechanical properties of PUI were observed in some studies (27, 28), than the related PUU and the incorporation of imide rings would improve the tensile strength greatly. The possible reason was that the rigid hard segment in PUI provided more effective physical crosslink than in PUU.

In Figure 6, the thermal stabilities of PUU and PUI were investigated by TGA. PUU and PUI underwent 5% wt loss at 282°C and 329°C, respectively, the fastest weight loss occurred at 400°C and 425°C. Furthermore, the residual weight fractions at 900°C of PUU and PUI were 0.1% and 12%, respectively. It was obvious that PUI exhibited a better thermal stability than PUU. The better thermal properties of PUI shown by TGA were probably due to the presence of the imide group (29).

3.3 Pervaporation Performances

3.3.1 Effects of Hard Segment Structures on Pervaporation Performances of PUU and PUI to Benzene/Cyclohexane Mixture

The pervaporation performances of PEA-based PUU and PUI membranes to benzene/cyclohexane mixture under different feed temperatures were shown as Figures 7 (a) and 8. As reported by most researchers, the total flux and partial fluxes of PUU and PUI membranes increased and the separation factor decreased with feed temperature. This could be explained from the effects of temperature on the permeates and polymer membranes. With the increased temperature, the enhanced mobility of the individual permeating molecules would facilitate their movement into the membranes. In addition, the increased mobility of the polymer segments provided more free volume for penetrants to occupy, which resulted in the increased degree of swelling of the PUU and PUI membranes.

Furthermore, the dependence of permeability of feed components on temperature was portrayed in Figure 7(b). It was

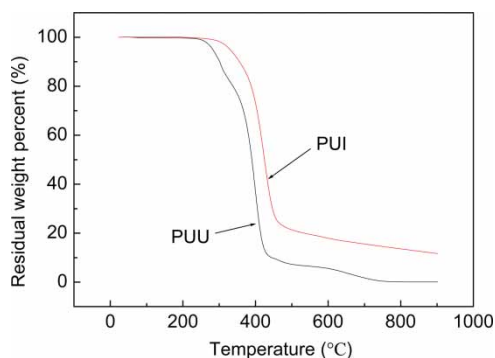


Fig. 6. TGA thermograms of PUU and PUI.

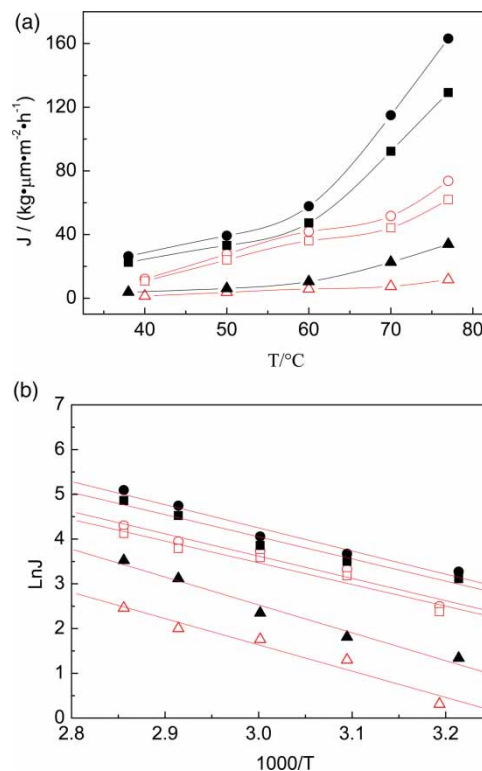


Fig. 7. Effect of feed temperature on permeability of PUU and PUI membranes for benzene/cyclohexane mixture (● Total flux of PUU, ○ Total flux of PUI, ■ Benzene flux of PUU, □ Benzene flux of PUI, ▲ Cyclohexane flux of PUU, Δ Cyclohexane flux of PUI).

found that the permeability of PUU and PUI membranes decreased exponentially with reciprocal feed temperature.

That follows an Arrhenius type relation shown as below:

$$J = J_0 e^{(-Ea/RT)} \quad (5)$$

where J is the flux of membranes, J_0 is the pre-exponential factor, Ea is the activation energy of permeation for feed

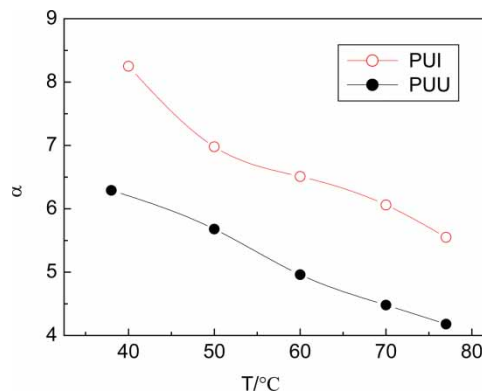


Fig. 8. Effect of feed temperature on selectivity of PUU and PUI membranes for benzene/cyclohexane mixture.

Table 2. Activation energies of feed components (kJ/mol)

Materials	Total	Benzene	Cyclohexane
PUU	43.0	41.2	51.8
PUI	41.4	40.3	48.9

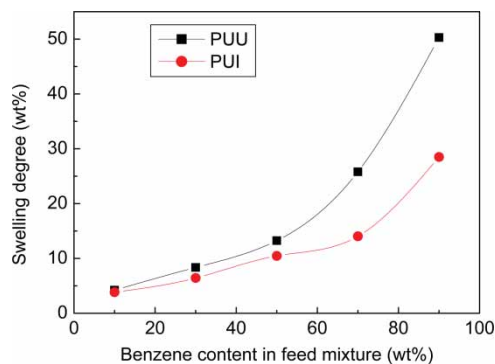
components, T is the feed absolute temperature and R is the gas constant.

The apparent permeation activation energies of feed components were calculated and listed in Table 2. The activation energies of penetrants in PUU and PUI membranes decreased following the order of cyclohexane > mixture > benzene, which implied that the cyclohexane flux was more sensitive to feed temperature and increased more quickly than benzene with an increasing temperature. That would result in the decrease of separation factor as shown in Figure 8.

Some studies (30, 31) found that the diffusion processes of small molecules mainly occurred in the soft domains of polyurethane-based materials with microphase separation structures, while the hard domains served as a physical crosslink and restricted the mobility of soft segments. In this study, the different separation and swelling performances resulted from the different hard segments.

Comparing different membrane materials, the PUU membranes obtained higher flux and lower selectivity than PUI as shown in Figures 7 and 8, and the total and partial fluxes of the PUU membranes were more profoundly affected by temperature as suggested by higher permeation activation energies than PUI as listed in Table 2, which indicated that the PUU membranes were probably more swelled during the pervaporation process than PUI. Furthermore, the results of the swelling experiment (Figure 9) also showed that the PUU membranes had a higher swelling degree than PUI. The swelling degree of PUU membrane was enhanced from 8 to 50 wt%, while the PUI membrane was in the range between 4 and 31 wt% with the content of benzene in feed mixture increasing from 10 to 90 wt%.

From the viewpoint of molecular structure, the TDI-MDA hard block in PUU had a steric hindrance structure induced

**Fig. 9.** Swelling degrees of PUU and PUI membranes in benzene/cyclohexane mixture.

by $-\text{CH}_3$ in TDI (2,4- or 2,6-TDI in this study), which could provide a less aligned interchain structure in the hard domain than the MDI-PMDA. The hard segment of MDI-PMDA in PUI was a regular and symmetric structure, which was advantageous to form dense chain packing. The polar imide group would especially increase the interaction between hard segments. All this made the hard domain of MDI-PMDA in PUI provide more effective crosslink for the polymer, which indicated that PUI membranes had a more rigid network and would resist the swelling of solvents better.

On the other hand, the soft PEA in PUU seemed to have less flexibility in “dry” membranes, which was shown by higher T_g s (Figure 5) than PUI. But during the PV and swelling experiment, the PEA segment in PUU would probably obtain more mobility as the hydrogen density between soft and hard segments could be weakened in swelled PUU membranes. That was another possible reason for the higher flux and swelling degree of PUU than PUI.

Furthermore, the solubility parameter (δ) of PEA segment ($21.5 \text{ (MPa)}^{1/2}$) was closer to benzene ($18.6 \text{ (MPa)}^{1/2}$) than cyclohexane ($16.8 \text{ (MPa)}^{1/2}$) as shown in Table 3. It was in agreement with the fact that the PEA-based PUU and PUI both showed good selectivity to benzene. Besides, the greater difference of solubility parameters between soft

Table 3. Solubility parameters (δ) of feed components, PEA, PUU and PUI

Compound	σ_{LJ} 32	V_d (cm^3/mol)	Solubility parameter ($(\text{MPa})^{1/2}$)			
			δ_D	δ_P	δ_H	δ
Benzene	6.2	89.4	18.4	0.0	2.0	18.6
Cyclohexane		108.7	16.8	0.0	0.2	16.8
n-Heptane	7.9	147.5	14.8	0.0	0.0	14.8
n-Octane	8.5	163.6	14.9	0.0	0.0	14.9
PEA		132.6	18.1	5.2	10.3	21.5
TDI-MDA (PUU)		331.3	25.7	4.3	10.5	28.1
MDI-PMDA (PUI)		318.4	28.9	6.5	11.0	31.6

σ_{LJ} : Lennard–Jones collision diameters of different penetrants (nm); V_d : van der Waals volume; δ : Hansen solubility parameter, δ_D : dispersive forces contribution, δ_P : polar contribution, δ_H : hydrogen bonding contribution.

(21.5 (MPa)^{1/2}) and hard segments (31.6 (MPa)^{1/2}) was found in PUI than PUU. It could be speculated that the PUI membranes tended to yield more incompatibility phenomenon and revealed the higher degree of microphase separation. The more aggregation of hard segments implied more physical crosslink in PUI membranes, which would make the swelling of membranes better suppressed than PUU with the increased feed temperature in PV and increased benzene content in swelling experiment as shown in Figures 7 and 9.

In addition, the polymer materials with more polarity were generally considered to have better affinity to aromatic molecules. The surfaces of PUI membranes had more polarity, which could be proved by smaller contact angle data (Table 1) of PUI than PUU. The more polarity of materials in membranes would facilitate the process of sorption and solution of benzene molecule in PUI membranes. It also could support the better selectivity of PUI membranes in pervaporation besides the more restricted swelling of membranes.

3.3.2 Pervaporation Performances of PUI to Aromatic/Aliphatic Hydrocarbon Mixtures

Besides aromatic/alicyclic hydrocarbon mixtures such as benzene/cyclohexane, the pervaporation performances of PUI to aromatic/aliphatic hydrocarbon mixtures such as benzene/n-heptane and benzene/n-octane were investigated as shown in Figures 10 and 11, respectively. With feed temperature developing, the flux increased and the separation factor decreased, which was the same trend as observed in benzene/cyclohexane mixture.

Furthermore, the PUI membranes obtained higher selectivity to aromatic/aliphatic hydrocarbon mixtures than benzene/cyclohexane mixture under the same feed temperature and benzene content in feed mixtures. That could be explained in terms of solubility parameter. As shown in Table 3, the solubility parameter of cyclohexane (16.8 (MPa)^{1/2}) was higher than n-heptane and n-octane, and it was closer to the PUI membranes. This meant that

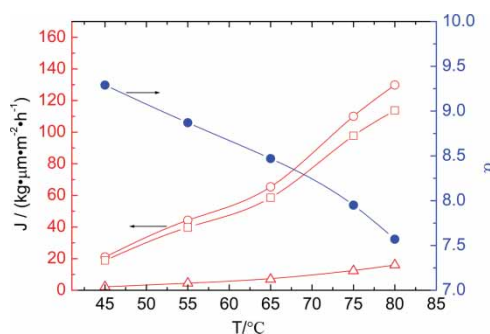


Fig. 10. Effect of feed temperature on pervaporation performance of PUI membranes for benzene/n-heptane mixture (○ Total flux, □ Benzene flux, ● n-heptane flux, ● Separation factor α).

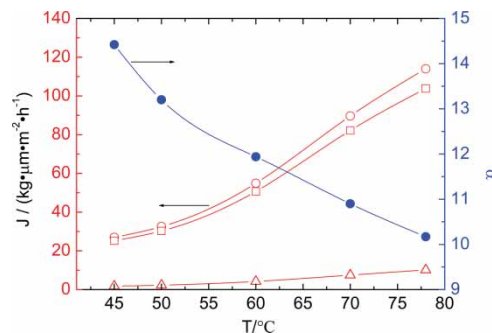


Fig. 11. Effect of feed temperature on pervaporation performance of PUI membranes for benzene/n-octane mixture (○ Total flux, □ Benzene flux, ● n-octane flux, ● Separation factor α).

cyclohexane had relatively better affinity to membranes and would dissolve in them more readily than n-heptane and n-octane. Since there was less difference between benzene and cyclohexane in affinity to membranes than benzene and n-heptane (or n-octane), lower separation factor was obtained in pervaporation of benzene/cyclohexane mixture than benzene/n-heptane and benzene/n-octane.

The higher separation factor for benzene/n-octane than benzene/n-heptane could be attributed to molecular size of penetrants. Although the slightly larger solubility parameter (14.9 (MPa)^{1/2}) of n-octane than n-heptane (14.8 (MPa)^{1/2}) was disadvantageous to the separation of benzene (18.6 (MPa)^{1/2}), the larger size of n-octane with higher collision diameters (see σ_{LJ} in Table 3) would result in the slower diffusion than n-heptane. Furthermore, the “size effect” seemed to be a predominant factor, thus the much higher separation factor was obtained from benzene/n-octane ($\alpha = 10.17 \sim 14.42$) than benzene/n-heptane ($\alpha = 7.57 \sim 9.29$).

4 Conclusions

The PEA-based polyurethaneurea (PUU) and polyurethane-imide (PUI) were successfully synthesized via a two-step method. The PUU and PUI thus obtained were revealed the microphase separation structures by DSC. The PUI membranes exhibited the better thermal stability than PUU. Both membranes of PUU and PUI showed selective permeation towards benzene in pervaporation separation of benzene/cyclohexane mixtures. The PUU membranes obtained the higher flux and the lower selectivity and more easily swelled than PUI. For 50 wt% benzene in the benzene/cyclohexane mixture at 40°C, PUI membranes had a flux of 12.13 kg $\mu\text{m m}^{-2} \text{h}^{-1}$ and separation factor of 8.25, while PUU membranes had 26.35 kg $\mu\text{m m}^{-2} \text{h}^{-1}$ and 6.29. The increasing feed temperature resulted in higher flux and lower separation factor of PUU and PUI membranes. Furthermore, the PUI membranes obtained better performances to aromatic/aliphatic hydrocarbon mixtures than benzene/cyclohexane.

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