Properties and Pervaporation Separation of Hydroxyl-Terminated Polybutadiene-Based Polyurethane/Poly(methyl metharcylate) Interpenetrating Networks Membranes

Mei-Hui Tsai, Shih-Liang Huang, Po-Hsueh Chang, Chiou-Jey Chen

Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 41111, Taiwan, Republic of China

ABSTRACT: Hydroxyl-terminated polybutadiene (HTPB), 4,4′-dicyclohexyl methane diiscyanate (H$_{12}$MDI), and 1,4-butane diol are used to synthesize polyurethane (PU) solutions by two-stage process. Interpenetrating networks (IPNs) of HTPB-based PU and poly(methyl methacrylate) (PMMA) with HTPB/MMA (wt/wt % ratio) = 2.0, 1.5, 1.0, 1.5, 0.8, and 0.6, which are designated as IPN1 to IPN5, respectively, are synthesized by sequential polymerization technique. Thermal properties, tensile strength, and contact angle of membranes increase with the increase of MMA content, while the elongation of membranes show the reverse trend. Characterization of membranes are investi-gated by C=C/C=O absorption ratio and infrared absorption frequency shiftment. These PU and IPN membranes are used for the separation of ethanol/water and isopropanol/water solution by pervaporation test. IPN3 membrane possesses the largest pervaporation permeability and the separation factor. The pervaporation results of ethanol/water feed has the same trend as that of isopropyl alcohol (IPA)/water solution. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4277–4286, 2007

Key words: hydroxyl-terminated polybutadiene; PU; IPN; mechanical properties; pervaporation separation

INTRODUCTION

Polyurethane (PU) is well known for its wear resist-ance and high toughness, but it has a low modulus and poor heat resistance. HTPB is used for the polyol of PU, because HTPB possesses low tempera-ture flexibility and lower surface energy, which induces a superhydrophobic surface of the PU poly-mer on the surface of the PU membrane.[1] HTPB-based PU exhibits low tensile strength and a break-ing strength at room temperature and has been used as a membrane for pervaporation studies.[2,3]

Poly(methyl methacrylate) (PMMA) has excellent solvent and oil resistance, low temperature proper-ties, and a good optical and adhesive nature. How-ever, if PU is modified by poly(methyl methacrylate) (PMMA) through interpenetrating network (IPN), the heat stability and the strength of resulting poly-mers will be obviously improved. IPNs are unique class of polymer alloys consisting of two (or more) crosslinked polymers.[4,5] These crosslinked polymers are held together by permanent entanglements, which are produced by homocrosslinking of two or more polymer systems. On the other hand, better compatibility, enhancement of mechanical properties, and resistance to degradation may be achieved by IPN synthesis. The concept of the IPNs may be applied to combine two polymers with different hydrophilicity. There are many IPN studies of PU-PMMA system. Kim[6] studied the structural mor-phology and Jin et al.[7] reported the polymerization kinetics.

Pervaporation is a membrane separation process, which can be used to separate liquid mixtures. Per-vaporation process is potentially useful in the areas where conventional distillation techniques are diffi-cult to be applied, such as the fractionation of azeo-tropic or isomeric mixtures. Separation mechanism of the pervaporation processes is basically due to so-lution–diffusion mechanism.[8] Presently, the dehydra-tion of organic mixtures is the most important appli-cation for pervaporation.[9–11] However, too much hydrophilicity often leads to excessive swelling of the membrane in contact with the aqueous feed solu-tions, and results in a loss of the mechanical and selective properties of the membrane. To avoid such defects, several methods of membrane preparation

TABLE I
IPNs Composition

Polymer code	Sample code	Contents of HTPB (wt %)	Contents of prepolyurethane (wt %)	Contents of MMA (wt %)
PU[a]	–	81	100	–
HTPB/MMA[b]				
2.0	IPN1	67	71	29
1.5	IPN2	60	65	35
1.0	IPN3	50	55	45
0.8	IPN4	44	50	50
0.6	IPN5	38	43	57

[a] NCO/OH = 1.0, equivalent ratio of $H_{12}MDI$/HTPB/1,4-BD = 2/1/1.
[b] Weight ratio.

may be used: modification of the membrane surface by introducing the hydrophilic polymer on the hydrophobic substrate, introduction of the crosslinking, block or graft copolymerization, and by polymer blending.

Therefore, a good pervaporation membrane material should have high permeation flux and separation factor for the pervaporation dehydration of organic mixtures and the ideal material for the pervaporation membrane should have a fine balance of the affinity and swelling capacity as well as good mechanical properties.

Several attempts were made to utilize multicomponent polymers for pervaporation membranes with different hydrophilicity and swelling capacity for controlling the hydrophilic nature and permeation characteristics. For example, block[12,13] or graft[14–16] copolymers of hydrophilic/hydrophobic constituents have been tested for use as high performance membranes. Lee et al.[17,18] studied the pervaporation using IPN membranes, because the physical interlocking between the polymer components can restrict the phase separation usually observed in polymer blends owing to the incompatibility of the polymers. One of the disadvantages of the pervaporation process using IPN membranes is the low permeation rate especially with highly selective membranes.[19–21]

In this article, PU/PMMA IPNs are synthesized by the simultaneous polymerization process. Measurements of the characterization by FTIR-ATR, thermal degradation behaviors by TGA, and tensile properties by DMA will also be reported. The effects of the different MMA content, kinds of alcohol feed, and feed compositions on the pervaporation performances are studied.

EXPERIMENTAL

Materials

The chemicals used for this study are hydroxyl-terminated polybutadiene (HTPB, equivalent weight 1333 g, average functionality of 2.2, R-45M of ARCO Co.,

USA), 4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$, Desmodue W of Mobay Co., Germany), 1,4-butane diol (1,4-BD; used as chain extender), and dibutyltin dilaurate (DBTDL; used as catalyst). Methyl methacrylate (MMA) monomer and 2,2′-Azobis-isobutyronitrile (AIBN) were obtained from Showa Company (Japan). Toluene, ethanol, isopropyl alcohol, and N-methyl-2-pyrrolidone (NMP) from Tedia Company are dehydrated with molecular sieves. Aqueous solutions with 70, 80, and 90 wt % ethyl alcohol and isopropyl alcohol content are used as the feed for pervaporation studies.

Synthesis of IPN membrane

PU solutions with equivalent ratio of $H_{12}MDI$/HTPB/1,4-BD = 2/1/1 and NCO/OH ratio equal 1.0 are synthesized by two-stage process. IPNs of HTPB-based PU and PMMA with HTPB/MMA (wt/wt % ratio) = 2.0, 1.5, 1.0, 1.5, 0.8, and 0.6, which are designated as IPN1 to IPN5, respectively, are synthesized by sequential polymerization technique. Calculated weight percentage of MMA monomer and 1 wt % AIBN are dissolved in MMA monomer and then charged into a three-necked round-bottomed flask, which contains the PU polymer. The mixture was stirred at room temperature for 30 min to form a homogeneous solution. While membranes are prepared by knife-coating on cleaned glass plates and then put in an oven under vacuum keeping at 30°C for 24 h and slowly raise to 80°C for 24 h. Finally, all these PU/PMMA IPN membranes under study have a thickness of 90 to 100 μm in a dried state. Compositions of the prepared IPNs are depicted in Table I.

Characterization and measurements

Infrared-ATR spectra of PU/PMMA IPN membranes are obtained by using a FTIR Nicolet-320 spectrometer. The physical properties such as tensile strength and percentage elongation at break are measured using a TA Instrument DMA 2980 at 25°C and 3–18 N/min. The stress–strain property is measured using

test pieces with 30 mm in length, 3 mm in width, and 0.09–0.1 mm in thickness. Dynamic mechanical analysis is carried out by a TA Instrument DMA 2980 at a frequency of 1 Hz. The size of test pieces is 45 mm in length, 5 mm in width, and 0.09–0.1 mm in thickness. The operating temperature ranged from −100°C to 120°C with a heating rate of 5°C/min. Thermogravimetric analysis is performed by a Du Pont 9900 TA system equipped with a 951 TGA module. The TGA thermograms are measured in the temperature range between 50 and 550°C at a heating rate of 20°C/min in nitrogen flow rate of 50 mL/min. All sample weight of 8–10 mg is used. The contact angle of the membranes are measured using a contact angle meter; shapes of droplets on membranes are photographed.

Swelling experiments

The swelling experiment is carried out using test pieces with 10 mm in length, 10 mm in width, and 0.09–0.1 mm in thickness. A piece of membrane is immersed in a water–alcohol mixture solution at room temperature for 24 h. When sorption reached equilibrium, the membrane is rapidly removed from the solution and wiped with filter paper to remove the surface droplets and then weighed. The swelling ratio DS is defined as:

$$DS = 100(W_S − W_d)/W_d$$

where W_d and W_S denote the weight of dry and swollen membrane, respectively.

Pervaporation measurements

The pervaporation measurements are carried out by using the apparatus described in a previous publication.[22,23] The effective membrane area in contact with the feed solution is 7.0686 cm^2. The membrane is supported by filter paper on a sintered stainless steel disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg, while permeate is collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography. The permeability is determined by the weight of permeate. The feed temperature studied is kept at 30°C. The compositions of the feed and the permeate are measured by gas chromatography (Agilent Technologies 6890N Network GC System). The separation factor is determined by the following equation:

$$\alpha_{\text{Water/Alcohol}} = (Y_W/Y_A)/(X_W/X_A)$$

where X_W and X_A, and Y_W and Y_A are the weight fractions of water and alcohol in the feed and permeate, respectively.

RESULTS AND DISCUSSION

Characterization

Figure 1 shows the characteristic absorption peaks of HTPB-based PU membrane and all IPN membranes. The characteristic absorption peak at 970 cm^{-1} for the C=C double bond of HTPB soft segment, while the carbonyl absorption peak splitting into two peaks. The peak at 1698 cm^{-1} is assigned to the absorption frequency of hydrogen-bonded C=O stretching, while the peak at 1716 cm^{-1} is for the absorption frequency of free-bonded C=O stretching.[24] The spectrum (3800–2600 cm^{-1}) of the all the IPNs show the characteristic absorption peak in the region of 3600–3100 cm^{-1}, which corresponds to N—H stretching. The absorption peak intensity corresponding to N—H stretching peak decreases,
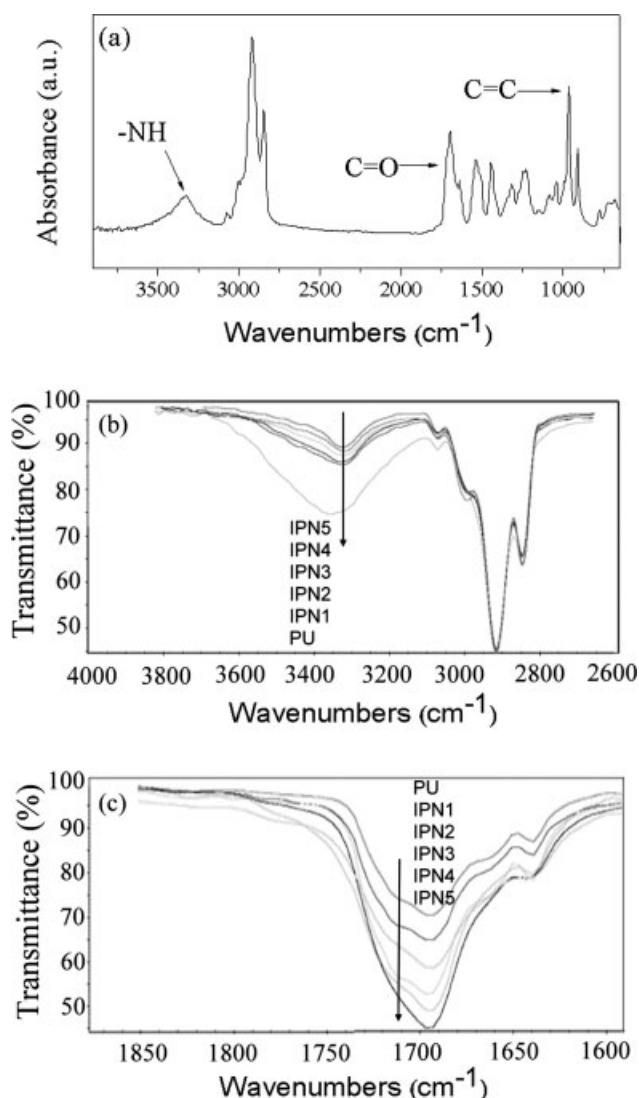
Figure 1 FTIR spectrum of PU and PU/PMMA IPNs in the wave number regions of (a) 800–4000 cm^{-1}; (b) 2600–3800 cm^{-1}; (c) 1600–1850 cm^{-1}.
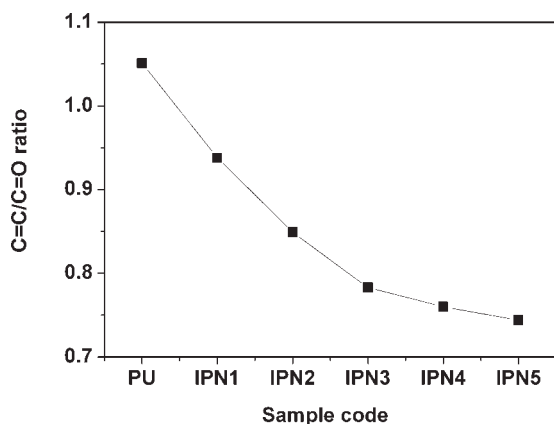
Figure 2 Effect of MMA content of membranes on the C=C/C=O absorbance peak ratio of surface.

while the C=O peak intensity increases as the increase of PMMA content increased in the IPNs as shown in Figure 1(b,c), respectively. The addition of MMA component, which possesses C=O groups, will enhance the hydrogen bonding with N—H group of IPN membranes and then decrease the intensity of N—H group. While the increase of C=O component, the C=O peak intensity increases as the increase of MMA component due to the free-hydrogen bonded part of C=O group increased.

On the other hand, as discussed in the previous reports,[25,26] infrared absorption frequency shiftment has been used as a measure of the average strength of intermolecular interactions. The wavenumber of hydrogen-bonded C=O group shifts from 1698 to 1693 cm^{-1} and hydrogen-bonded N—H group shifts from 3330 to 3308 cm^{-1} with the increase of MMA content. The increase MMA content (i.e. C=O group content) will enhance the hydrogen-bonding with N—H groups. Upon the increase of hydrogen bonding, the energy and force constant of the bonded C=O or N—H group absorption decreases, and the absorption band shifts to a lower frequency.

The surface composition of these HTPB-based PU membrane and PU/PMMA IPN membranes are measured by FTIR-ATR and represented as the C=C/C=O ratio, which can be regarded as the ratio of soft/(hard segment plus PMMA content) on the surface. The variation of C=C/C=O ratio decreased sharply with the increase of MMA content and is shown in Figure 2. There are two explanations for the above phenomenon: One is that the HTPB soft segment possesses lower surface energy and will easily migrate toward the surface of the PU/PMMA IPN membranes.[27] The other is that the addition of MMA monomer to the PU solution, most of the MMA monomer will disperse to the HTPB soft segment due to the nearly solubility parameter of these two components and the structure morphology of

HTPB soft segment is loose than that of hard segment possesses. The C=C group of MMA monomer may interact with the C=C group of HTPB segment and then form intermolecular crosslinkage structure which dispersed in the membrane's surface. Then, part of the C=C group of HTPB segment disappears and the C=O group of MMA monomer content increased, which may be the reason for the sharp decrease of C=C/C=O ratio with the increase of MMA content (i.e. from PU to IPN5). As the MMA monomer further increased (i.e. from IPN3 to IPN5), part of the MMA monomers react to form PMMA homopolymer. Then the PMMA homopolymer will disperse into the intermolecular space of HTPB/ PMMA-crosslinked molecules due to the compatibility between HTPB and PMMA. This may be the reason for the further decrease of C=C/C=O ratio with the increase of MMA content.

Contact angle measurements

Contact angle analysis provides information on the hydrophobic or hydrophilic surface at the air–water–solid interface.[28] High contact angle values, between 70° and 90°, indicate strong hydrophobic surfaces such as silicone or fluorocarbon polymers, while low contact angle values (0–30°) indicate highly hydrophilic surfaces such as glass or mica.[29] The hydrophobicity or hydrophilicity of PU/PMMA IPN membrane surface are characterized by contact angle. Table II shows that the values of contact angle change from 82.4° to 73.9° as the membrane's composition varies from PU to IPN5. The surface composition of pure PU membrane will be HTPB-rich, which is a lower energy component and will easily migrate to the air–polymer interface of the membrane. With the addition of MMA monomer, part of MMA monomers copolymerize with HTPB segment and form a crosslinkage structure, and the other part of MMA monomers react to form a homopolymer. Then part of the HTPB component on the membrane's surface will be replaced by the MMA component. This may be the reason for the decrease of contact angle of these IPN membranes.

TABLE II
Contact Angle of PU-PMMA IPNs

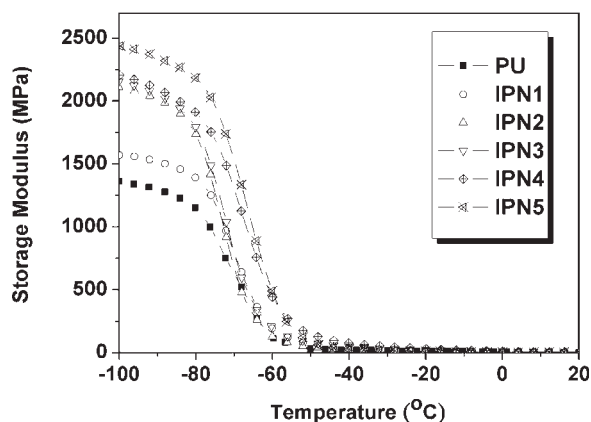| Sample	Contact angle
PU	82.4
IPN1	79.2
IPN2	78.5
IPN3	76.9
IPN4	75.6
IPN5	73.9
PMMA	65.6

TABLE III
Mechanical Properties of PU-PMMA IPNs

Sample	Tensile strength (MPa)	Elongation at break (%)	E' at 50%[a] (MPa)
PU	1.98	1289	0.52
IPN1	23.51	396	20.51
IPN2	28.16	340	23.72
IPN3	34.64	253	29.54
IPN4	40.85	217	32.96
IPN5	48.91	185	40.02

[a] Young's modulus : E'

Mechanical properties

The stress–strain results of the PU/PMMA IPN membranes are measured by DMA 2980 and presented in Table III. It indicates that the tensile strength and Young's modulus of membranes increase with the increase of MMA content, while the elongation at break decreases from 1289% to 185%. The reason is that PMMA is benefit to increase the strength of the polymer and may be attributed to the enhanced interlocking of polymeric chains on IPN formation. There are three phenomena that may affect the IPN's morphology as the addition of MMA monomer. One is the crosslinkage structure formed between HTPB soft segment and MMA monomer. The other is that the increase of hydrogen bonds originating between —NH groups of PU and C=O groups of PMMA. The third effect is that, with the MMA content further increased, there exists a phase conversion. Part of the IPN converts from the continuous phase to the disperse phase, which acts as enhancer to the membrane's mechanical properties.[30] The phase conversion verifies that by increasing the MMA content, the tensile strength of the polymers increases, while the elongation at break decreases. The IPNs with more crosslinked structure and stiffness possess higher tensile strength than that of the PU and because of the chemical crosslink-

ing and physical tangling effect, the tensile strength of IPN5 is the highest. These may be the reasons for the increase of tensile strength and the decrease of elongation at break of IPNs with the increase of MMA content.

Dynamic mechanical analysis

Figure 3 shows the temperature dependence of storage modulus (E') of PU to IPN5. The IPN5 has superior storage modulus compared with the other samples, which is also the result of the stronger cohesive properties between hard segments caused by the hydrogen bonding, as revealed in the FTIR-ATR result. The crosslinkage structure and rigidity of the IPNs increase as the MMA content changes from PU to IPN5 as discussed in the previous section. These may be the reasons for the increase of storage modulus of membranes from PU to IPN5.

The glass transition temperature of HTPB soft segment (T_{gs}) and hard segment (T_{gh}) in the maximum of the loss modulus curves (E'') are shown in Figure 4. The T_{gs} and T_{gh} are all increased as the compositions change from PU to IPN5 and are depicted in Table IV. The other glass transition temperatures of
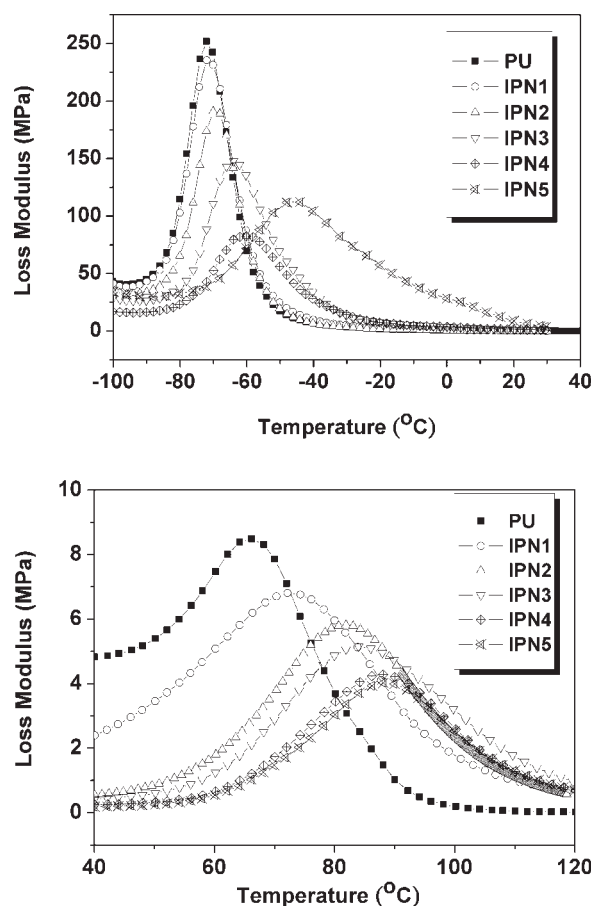
Figure 4 Temperature dependence of the loss modulus (E'') of PU/PMMA IPN membranes.

Figure 3 Temperature dependence of the storage modulus (E') of PU/PMMA IPN membranes.

TABLE IV
Dynamic Mechanical Analysis of PU-PMMA IPNs

Sample code	Storage modulus E' (MPa)[a]	T_{gs} (°C)[b]	T_{gh} (°C)[c]
PU	1360	−72.06	65.69
IPN1	1570	−71.01	72.95
IPN2	2109	−69.06	81.72
IPN3	2156	−64.00	83.95
IPN4	2205	−60.12	87.80
IPN5	2438	−44.49	88.36

[a] Storage modulus of IPN membranes are measured at −100°C.
[b] The maximum in loss modulus curve between −100 to 40°C is designated as glass transition temperature of soft segment.
[c] The maximum in loss modulus curve between 40 to 100°C is designated as glass transition temperature of hard segment.

PMMA at about 105°C are not observed in Figure 4. This may indicate that all PMMA are compatibly dispersed into the PU and the glass transition temperature of PMMA disappeared. As discussed in the former sections, the MMA monomers are almost introduced into the HTPB soft segment and form crosslinkage structure or PMMA homopolymer and dispersed into the HTPB soft segment. The PMMA contents look as hard segment, and the increase of PMMA content results in the enhancement of rigidity and glass transition temperature (T_{gs}). This may be the reason for the increase of T_{gs} from PU to IPN5.

On the other hand, T_{gh} values increase from 65.69°C to 88.36°C from PU to IPN5. The explanation is that part of PMMA dispersed into hard segment will induce two effects. One is that the clustering of hard segment will be somewhat disrupted. The other is that the compatibility induced by the increase of hydrogen bonding between C=O and N—H groups through the introduction of C=O group of PMMA component is enhanced. The competition of the above two reverse effects indicates that the latter hydrogen bonding possesses superior influence on the hard segment and hence increases the T_{gh} value.

The intensities of membranes are also decreased with the increase of MMA content. This indicates that the mobility of polymer network is reduced from PU to IPN5. The increase of MMA content will increase the intermolecular crosslinkage, rigidity, and hydrogen bonding of membrane and hence reduce the intensity of membranes from PU to IPN5.

Thermal gravimetric analysis

The TGA scans are taken in the temperature range 50–550°C at a heating rate of 20°C/min in nitrogen as shown in Figure 5. A three-step degradation curves are observed and the TGA thermogram of PU/PMMA IPNs is stable up to 300°C and completely degrade around 500°C. In the first step, the

weight loss is less than 3 wt %. The quantity of gaseous components, mainly water released in this step, is relatively small.

Decomposition temperatures of steps 2 and 3 are at ∼ 300°C and 500°C. Step 2 corresponds to the urethane bond-breaking and step 3 is the polyol decomposition.[31] The decomposition temperatures of these IPN membranes are all slightly higher than that of pure PU membrane and increased with the increase of MMA content. However, it is interesting to note that these IPNs follow similar degradation behavior as that of PU up to 400°C, and above 400°C, the IPNs show a slight enhancement in weight retention in comparison to PU (400–550°C). There is an explanation by the hypothesis that unzipped MMA monomer produced during thermal degradation may act as a free radical scavenger for PU degradation product.[32] Crosslinked molecular structures are more thermal-resistant than those of uncrosslinked structures.[23,33] It has been reported that aromatic ethers usually exhibit good thermal stability.[34] This suggests that the thermal stabilities of IPN membranes are all larger than that of pure PU. Obviously, membrane of tight IPN structure requires more energy for the decomposition. The hydrogen bonding and crosslinkage between PU and PMMA will be enhanced by MMA addition as expressed in the above section and increase as the MMA content increased. This may be the reason for the increase of thermal degradation temperature with the increase of MMA content.

The residues of all these IPN membranes are all larger than that of pure PU membrane and increases, from pure PU to IPN5, with the increase of MMA content. Membranes with low hard segment content (i.e. with high HTPB and MMA content) possess more carbon atom content and crosslinkage structure in the polymer molecules. Moreover, due to the crosslinkage structure, the decomposition of membrane cannot be completely attained. The rates of
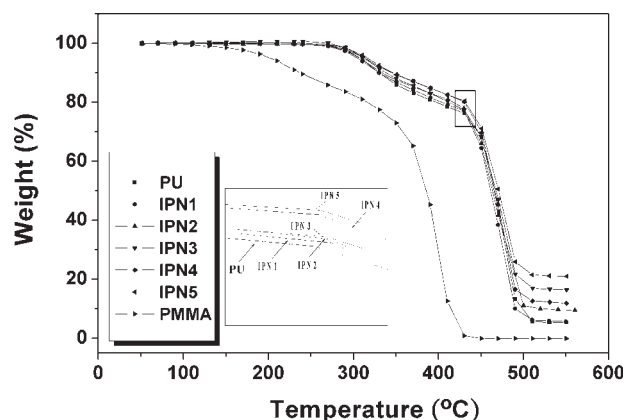
**Figure 5** TGA thermograms of the different PU/PMMA IPNs systems.
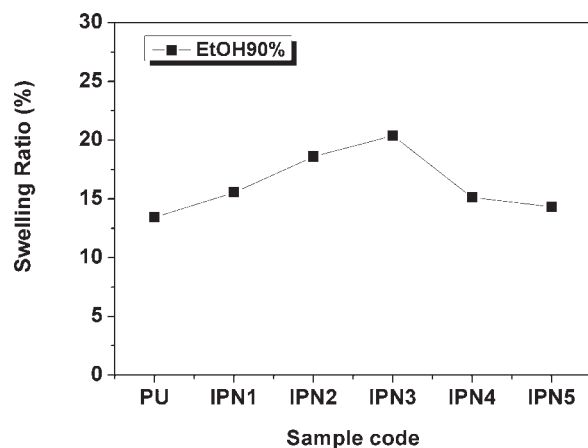
Figure 6 Swelling ratio of PU-PMMA IPN membranes as dipped in 90 wt % ethanol solution.

degradation are much lower for polymers with crosslinkage because of ring formation of the transient species.[23,34] These may be the reasons for the higher residues that remained after thermal treatment of the membranes with the increase of MMA content.

Pervaporation results

Swelling measurements

The swelling ratios increased from PU to IPN3 and then slightly decreased from IPN3 to IPN5 as shown in Figures 6 and 7. For membranes from PU to IPN3, there are three aspects to explain the above phenomena. One is that HTPB and MMA compositions are much affinitive to the ethanol or IPA when dipping in the aqueous solution with 90 wt % alcohol content. As the MMA content increased in the IPN membranes, the swelling ratios will be increased. The second reason may be that the MMA monomer reacted with C=C group of HTPB soft
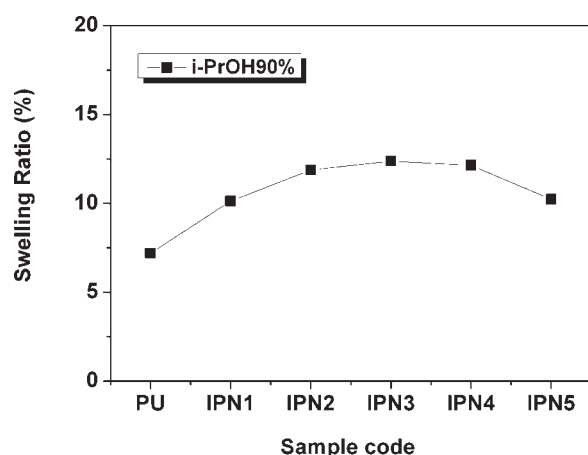
segment to form the crosslinked structure, which will enlarge the intermolecular space of soft and entangled HTPB segment and hence increase the adsorption of feed solution and the swelling ratio. On the contrary, the third reason is that the increase of crosslinked structure will decrease the sorption of ethanol solution. The former two aspects may possess superior effects on the increase of swelling ratio from PU to IPN3. Then the swelling ratios are increased from PU to IPN3.

As the MMA content is further increased from IPN3 to IPN5, the increased MMA content may be polymerized to form PMMA homopolymers and inserted into the intermolecular space of HTPB soft segment. The crosslinking of membranes from IPN3 to IPN5 are not increased and the space for the sorption then decreased. By the way, the alcohol sorption ability of MMA component is much less than that of HTPB segment. These may be the reasons for the decrease of swelling ratio as the composition changes from IPN3 to IPN5.

On the other hand, the swelling ratios of membranes dipped in IPA solution are all lower than those of corresponding membranes dipped in ethanol solution. The explanations are the steric structure of IPA solution to the membrane's surface. The steric structure of IPA component will induce that the adsorption amount with IPA is less than that with ethanol (i.e. decreases the swelling ratio). The former may possess superior effect on the lower swelling ratio of IPA solution than that of ethanol solution.

Effect of PU/PMMA ratio

The major amount of permeability of PU membrane is due to the diffusion through HTPB soft segment of membrane. Figure 8 shows that the permeabilities of IPN membranes are all higher than that of pure PU membrane and increased from PU to IPN3 and

Figure 7 Swelling ratio of PU-PMMA IPN membrane as dipped in 90 wt % IPA solution.
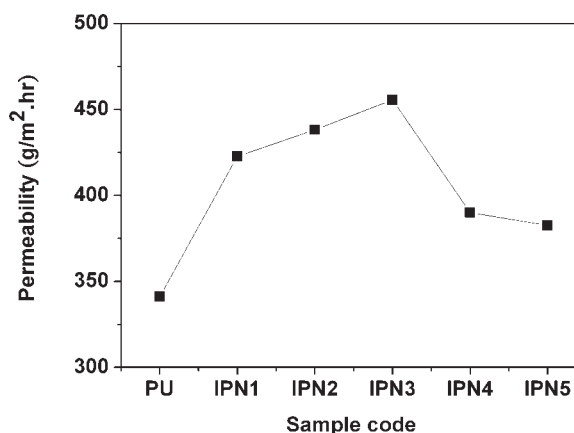
Figure 8 Permeability curves of PU and PU/PMMA IPN membranes at 30°C operating temperature and 90 wt % aqueous ethanol solution.
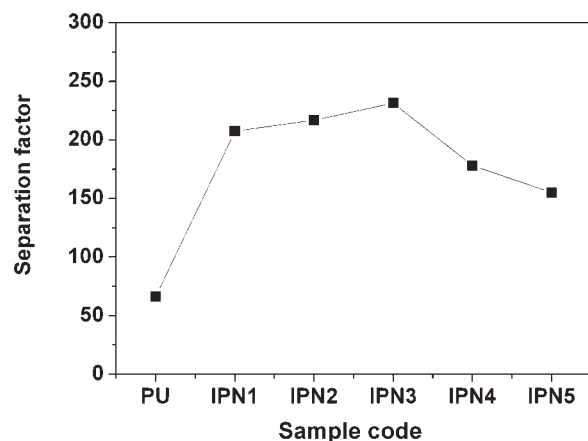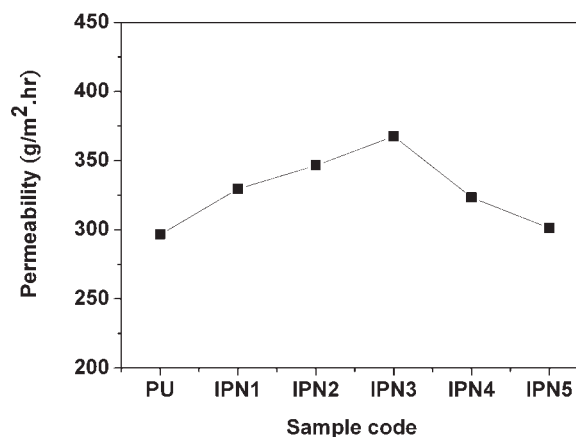
Figure 9 Separation factor curves of PU and PU/PMMA IPN membranes at 30°C operating temperature and 90 wt % aqueous ethanol solution.

Figure 10 Permeability curves of PU and PU/PMMA IPN membranes at 30°C operating temperature and 90 wt % aqueous isopropanol solution.

then decreased from IPN3 to IPN5. The reason is the crosslinkage between MMA and C=C group, which will enlarge the intermolecular space and hence increase the permeability from PU to IPN3, as described in the former section. On the other hand, further MMA monomer addition may form PMMA polymer, which is rigid, inserting into the HTPB segment's space. This will decrease the permeability from IPN3 to IPN5.

The membranes are very hydrophobic as shown by the data of contact angle, surprisingly the membranes selectively permeate water. When the membranes are immersed in the ethanol/water mixtures, the ethanol molecules absorbed on the membranes are selectively absorbed upon the polymer chain of the HTPB soft segment or MMA component. Owing to the hydrophobic HTPB polymer chain or less hydrophobic MMA component, which may interact with the hydrophobic moiety of the ethanol group of ethanol/water solution and then the —OH groups of ethanol group exposed on the surface of membrane's pore. This hydrophilization of the somewhat hydrophobic membrane by the ethanol is probably responsible for the selectivity for water. In addition, the water molecules are smaller than those of ethanol and hard segment of PU is a hydrophilic component, which will induce the permeation to water. The above two explanations may be the reasons for the increase of separation factor from PU to IPN3. While on the other hand, the intermolecular spaces are increased from PU to IPN3 and then the separation factors of these membranes will be decreased with the increase of MMA content. The competition of these three contradictory effects indicates that the former two effects have superior influence on the increase of separation factor from PU to IPN3, as shown in Figure 9.

While as the MMA content further increased from IPN3 to IPN5, these MMA will react to PMMA and

inserted into the HTPB segment's spaces and induce the decrease of intermolecular space, and the water molecules are smaller than those of ethanol. This will increase the separation factor of membrane. By the way, the inserted PMMA is less hydrophilic than HTPB and the hydrophilization phenomenon of the somewhat hydrophobic membrane by the ethanol is not obvious than HTPB. Then the selectivity to water will be decreased. The latter effect may possess superior effect on the decrease of separation factor from IPN3 to IPN5.

The same trends occurred for the permeability and separation factor of IPA solution with respect to ethanol solution as shown in Figures 10 and 11. The values of permeability and separation factor of IPA solution are all lower than those of corresponding membranes with ethanol solution. The permeability of IPA/water solution through membranes is slightly lower than those of corresponding ethanol/water solution present. Because of the sorption of
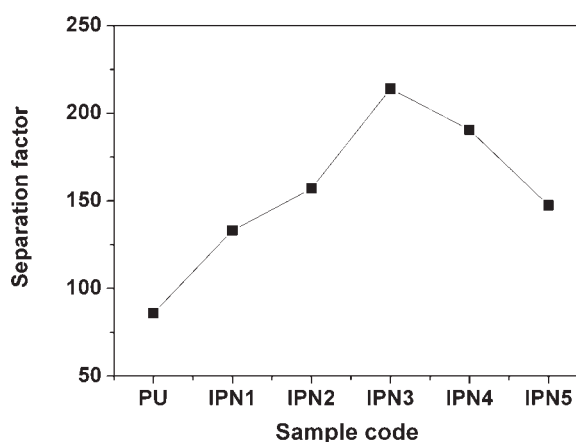
Figure 11 Separation factor curves of PU and PU/PMMA IPN membranes at 30°C operating temperature and 90 wt % aqueous isopropanol solution.
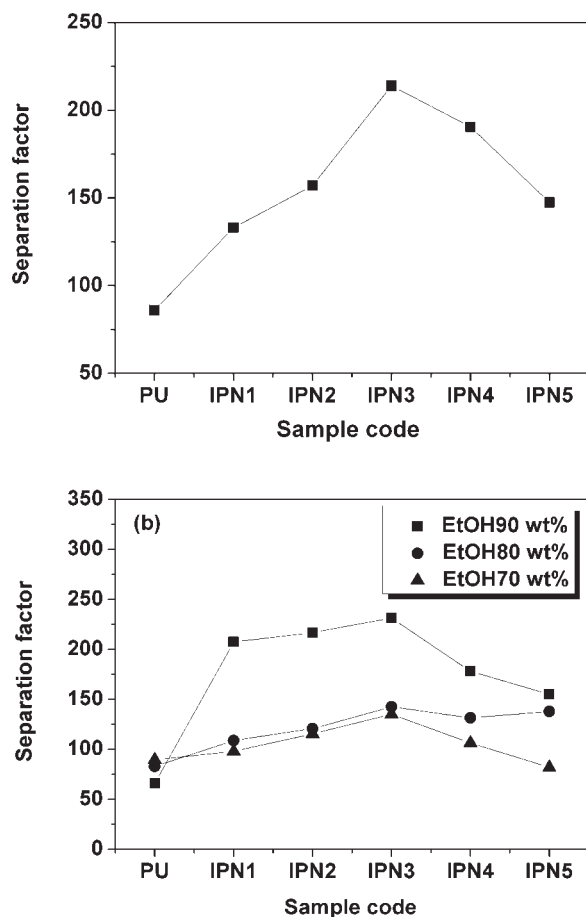
Figure 12 Pervaporation curves of PU/PMMA IPN membranes at 30°C operating temperature and different concentration of ethanol aqueous solution: (a) permeability; (b) separation factor.

IPA on the membrane's surface, the swelling behaviors of membrane are all lower than those of ethanol. This will induce lower permeability of IPA/water solution through membranes.
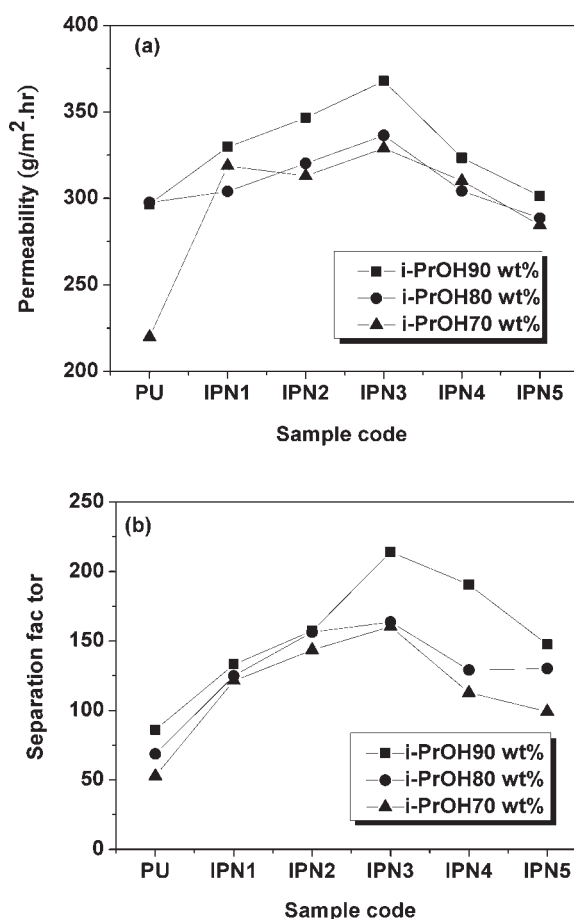
On the other hand, the steric structure of IPA molecules, which are adsorbed on the membrane's surface, will hinder the permeation of feed through the membrane. The above two effects on the permeabilities may be the reason for the slightly lower permeability of IPA/water solution through the membranes.

While as the membrane immersed in the feed with IPA solution, there may be that the double layer absorption on the membrane's surface. This induces the membrane's surface changes from hydrophobic HTPB to hydrophobic IPA again and then the membrane's surface changes from affinitive to IPA not water. On the other hand, the permeation activation energy of IPA through membrane is larger than that of ethanol and then the selectivity of IPA/water solution decreased. The above two explanations may be the reasons for the separation factors of IPA solution are lower than those of ethanol solution.

Effect of feed concentration and alcohol solution

Figures 12(a) and 13(a) show the permeability as a function of feed concentration for membranes with different MMA content and alcohol/water solution, respectively. The permeabilities are all increased as the feed composition changes from 70, 80, to 90 wt % of ethanol or IPA content. The reason is that the soft segment of HTPB or MMA content of IPNs are hydrophobic compositions, which are affinitive to the ethanol or IPA. This is not consistent with the general comment that the increase of hydrophilic property will result in an increase in swelling properties and the permeabilities.

The permeabilities are all increased with the increase of MMA content and then decreased. The reason of this phenomenon is the same as that has been discussed in the former section. The permeabilities are also increased with the increase of alcohol content in the feed. The reason is that the increase of swelling ratio and sorption ability on the membrane's surface will be increased with the increase of alcohol content in the feed.

Figure 13 Pervaporation curves of PU/PMMA IPN membranes at 30°C operating temperature and different concentration of isopropanol aqueous solution: (a) permeability, (b) separation factor.

The permeabilities of IPA/water solution through membranes are slightly lower than those of corresponding ethanol/water solution present. The reason is that the steric structure of IPA molecules, which are absorbed on the membrane's surface, will hinder the permeation of feed through the membrane. This may be the reason for the slightly lower permeability of IPA/water solution through the membranes.

Figures 12(b) and 13(b) show the effect of MMA content and alcohol concentration on the separation factor, respectively. The separation factors of ethanol/water solution are all increased with the increase of MMA content and then decreased. The reason may the intermolecular space and hydrophilization phenomenon as described in the previous section. The separation factors are slightly increased as the increase of ethanol content in the feed. The reason is that as the membrane immersed in the feed with high alcohol content, the hydrophilization phenomenon will be more obvious and then induce the increase of separation factor as the increase of alcohol content in the feed. The separation factors for different composition of IPA/water solutions permeating through membrane are also increased as the increase of IPA content in the feed.

CONCLUSIONS

The characteristic absorption peaks of C=O and N—H-bonded groups shift to lower frequency with the increase of MMA content. The contact angle, tensile strength, and modulus are all increased with the increase of MMA content. The permeabilities and separation factors of alcohol solutions are all increased as the increase of MMA content and then decreased and all are increased as the increase of alcohol content in the feed. The permeabilities and separation factors of IPA/water solution through membranes are all lower than that of corresponding ethanol solution presented.

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