Properties and pervaporation performances of crosslinked HTPB-based polyurethane membranes

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Abstract

Hydroxyl-terminated polybutadiene (HTPB), 4,4′-dicyclohexyl methane diisocyanate (H12MDI) and 1,4-butane diol are used to synthesize polyurethane (PU) solutions by a two-stage process. PU S with different equivalent ratios of NCO/OH from 1.0 to 1.5 are prepared. Thermal degradation temperature, tensile strength and contact angle of membranes are all increased with the increase of NCO/OH ratio. While the elongation of membranes is also increased with the increase of NCO/OH ratio, they are then decreased disruptly when NCO/OH ratio equals to 1.5. These PU membranes are used for the separation of ethanol/water, isopropanol/water solution by pervaporation test. Membranes with NCO/OH = 1.3 ratio possess the largest (36,713 g/(m² h)) pervaporation separation index (PSI), while the ethanol concentration in the feed on the separation factor has different effect than that of IPA/water solution.

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1. Introduction

Presently, the dehydration of organic mixtures is the most important application for pervaporation [1–3]. Research efforts have been directed to the selection of proper membrane materials. A good pervaporation membrane material should have high permeation flux and separation factor for the pervaporation dehydration of organic mixtures. Whereas pervaporation has been recognized as an important technique to separate organic compounds produced in chemical industries [4–8], there are many polymers being used for pervaporation studies of organic mixtures, for example, cellulose acetate [9], polyvinyl alcohol [10], chitosan [11], asymmetric Nylon 4 [12], the IPN of PU membranes [13] and PVA/PAA [14]. And the principle of the pervaporation membrane separation process is relatively simple. The minor component of the liquid mixture is preferentially separated with phase change through polymeric dense membranes at efficiencies considerably better than those obtained in other separation processes such as distillation, adsorption and fractional crystallization processes. The advantages are particularly apparent when azeotropic mixtures are to be separated [15].

Polyurethane possesses good membrane formation and chemical resistance. HTPB is used in this study because it possesses low temperature flexibility and lower surface energy, which induces superhydrophobic surface of a PU polymer [16]. The HTPB soft segments will easily migrate toward the surface of the PU membrane. This is due to the subsequent change of composition on the air–polymer interface of these PUs and polymer chains of HTPB-based PU at the air–polymer interface are in an unsymmetrical environment in comparison with those within the polymer [17]. HTPB-based PU exhibits low tensile strength and a breaking strength at room temperature and has been used as a membrane for pervaporation studies [18,19].

In this article, polyurethane membranes were used for pervaporation separation of water/ethanol and water/isopropanol mixtures, respectively. The purpose of this study was to prepare the crosslinked HTPB-based PU membranes for the pervaporation separation process. The crosslinking between polymer chains was prepared with the increase of NCO/OH ratio (e.g. hard segment content) for the study of the effects on water selectivity, thermal stability and tensile properties. The effects of NCO/OH ratio, kinds of alcohol feed, feed compositions and feed temperature on the pervaporation performances were studied. Measurements of tensile properties by DMA, infrared spectra by FTIR-ATR and thermal degradation behaviors by TGA were reported.
2. Experimental

2.1. Materials

The chemicals used for this study were 4,4’-dicyclohexylmethane disiocyanate (H_{12}MDI, Desmodie W of Mobay Co.), hydroxyl-terminated polybutadiene (HTPB, equivalent weight 1333 g, average functionality of 2.2, R-45M of ARCO Co.), 1,4-butane diol (1,4-BD) used as chain extender and dibutyltin dilaurate (DBTDL) used as catalyst. Toluene (Tedla Co.), ethanol (Tedla Co.), isopropyl alcohol (Tedla Co.) and N-methyl-2-pyrolidone (NMP) from Tedla Company were dehydrated with molecular sieves and used as solvents for the polymerization of the PU solution. Aqueous solutions with 70, 80 and 90 wt% ethyl alcohol or isopropyl alcohol content were used for the feed of pervaporation studies.

2.2. Preparation of polyurethane membranes

PU solutions with different equivalent ratios of H_{12}MDI/HTPB/1,4-BD with NCO/OH from 1.0 to 1.5 were synthesized by a two-stage process. The two-stage PUs were polymerized first by an –NCO terminated prepolymer at 80 °C, and the chain extended with 1,4-BD under 30 wt% solid content after the theoretical –NCO content was reached. It was diluted to 20 wt% solid content after extended reaction had proceeded for 30 min, and the reaction was terminated. After the PU membranes were prepared by knife-coating on glass plates, all these PU membranes were then put in an oven under vacuum and step-heated at 50 and 70 °C for 12 and 36 h, respectively. Finally, all these PU membranes under study were with 90–100 μm thickness in a dried state.

2.3. Characterization and properties measurements

Infrared-ATR spectra of polyurethanes were obtained by using a FTIR Nicolet-320 spectrometer. It is found that the peak due to bonded C═O stretching is centered at 1698 cm\(^{-1}\) and due to free C═O stretching is centered at about 1716 cm\(^{-1}\). The infrared absorption bands of butadiene soft segment are the \(\text{trans-1,4}\) form at 970 cm\(^{-1}\), \(\text{trans-1,2}\) form at 912 cm\(^{-1}\) and \(\text{cis-1,4}\) form at 685 cm\(^{-1}\). The infrared absorbance of the total carbonyl groups detected by FTIR-ATR was calculated by the addition of the respective hydrogen bonded C═O absorbance and free hydrogen bonded C═O absorbance. The C═O/C═C ratio on the surface is the ratio of total C═O absorbance with \(\text{trans-1,4}\) form C═C absorbance. A larger value of this ratio indicates that larger hard segment content is present on the surface of the membrane.

The contact angle of the PU membranes was measured using a contact angle meter, and shapes of droplets on PU membranes were photographed. Thermogravimetric analysis was performed by a Du Pont TA system equipped with a 951 TGA module. The TGA thermograms were measured in the temperature range between 50 and 600 °C at a heating rate of 20 °C/min in nitrogen flow rate of 50 ml/min. Eight to 10 mg of all samples were used. The tensile property was measured by a TA Instrument DMA 2980 at 25 °C and 3–18 N/min.

2.4. Pervaporation measurements

The pervaporation measurement was carried out by using the apparatus described in a previous publication [20]. A normal vacuum pervaporation apparatus consists of a cell made of stainless steel with circulation of the liquid over the membrane. The feed solution is in direct contact with the membrane. The effective membrane area in contact with the feed solution was 7.07 cm\(^2\). The membrane was supported by filter paper on a sintered stainless steel disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg, and the permeate was collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography. The permeate rate was determined by the weight of the permeate. The feed temperature was studied in the range of 30–60 °C. The compositions of the feed and the permeate were measured by gas chromatography (Agilent Technologies 6890N Network GC System). The separation factor was determined by the following equation:

\[
\alpha_{\text{water/alcohol}} = \left( \frac{X_W}{X_A} \right) \left( \frac{Y_W}{Y_A} \right)
\]

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

3. Results and discussions

3.1. Characterization

Fig. 1 shows that all the HTPB-based PU membranes possess characteristic absorption peaks. The absorption peak is at 970 cm\(^{-1}\) for the C═C double bond of HTPB soft segment and the carbonyl absorption peak splitting into two peaks. The peak at 1698 cm\(^{-1}\) is assigned to the hydrogen bonded C═O stretching, while the peak at 1716 cm\(^{-1}\) is for free bonded C═O stretching. According to Coleman et al. [21], hydrogen bonded carbonyl bands correspond to those groups that are in the interior of the hard segments, whereas the free bands may correspond to those groups in the hard segment domains or in the soft domains or at interface. In the butadiene-containing polyurethanes, hydrogen bonding occurs only between urethane segments of the N–H and C═O group, since the carbonyls in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors.

While the extent of C═O groups participating in the hydrogen bonding is expressed by the hydrogen bonding index [22], which is defined as the relative absorbencies of the two C═O group peaks, i.e., \(HBI = \frac{A_{\text{C═O, bonded}}}{A_{\text{C═O, free}}}\), where \(A_{\text{C═O, bonded}}\) and \(A_{\text{C═O, free}}\) are the absorbencies of bond and free C═O groups, respectively. Table 1 also shows that the HBI values change from 1.198 to 1.216. The larger HBI values indicate stronger intermolecular hydrogen bonding, which is increased as the NCO/OH ratio increased.

On the other hand, as discussed in the previous reports [23,24], infrared absorption frequency shift has been used as a measure of the average strength of intermolecular interactions. Table 1 shows that wavenumber of C═O group shifts from 1698 to 1693 cm\(^{-1}\) for hydrogen bonding and 1716 to 1712 cm\(^{-1}\) for
Fig. 1. FTIR-ATR spectra of the HTPB-based polyurethane membrane with different NCO/OH ratio.

free bonding. The reason is that intermolecular hydrogen bonding and crosslinked allophanate structure will be increased as the NCO/OH ratio increased from 1.0 to 1.5. And the wavenumber of absorption peak will shift to lower frequency with the increase of intermolecular hydrogen bond and crosslinked structure.

Table 1

<table>
<thead>
<tr>
<th>NCO/OH ratio</th>
<th>C=O bonded (cm⁻¹)</th>
<th>C=O free (cm⁻¹)</th>
<th>HBI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1698</td>
<td>1716</td>
<td>1.198</td>
</tr>
<tr>
<td>1.1</td>
<td>1698</td>
<td>1716</td>
<td>1.197</td>
</tr>
<tr>
<td>1.2</td>
<td>1697</td>
<td>1716</td>
<td>1.207</td>
</tr>
<tr>
<td>1.3</td>
<td>1695</td>
<td>1714</td>
<td>1.212</td>
</tr>
<tr>
<td>1.5</td>
<td>1693</td>
<td>1712</td>
<td>1.261</td>
</tr>
</tbody>
</table>

The surface composition of these HTPB-based PU membranes were measured by FTIR-ATR and represented as the C=O/C=C ratio, which can be regarded as the ratio of hard/soft segment content on the surface. The variation of surface composition with respect to NCO/OH ratio is shown in Fig. 2. The reason is that HTPB soft segment possesses lower surface energy and will easily migrate toward the surface of the PU membranes. With the increase of NCO/OH ratio, the intermolecular attraction will be increased due to the much more hard segment content and the allophanate crosslinkage formed. The latter two components are with higher surface energy and will disperse more within the bulk of the polymer. While the HTPB segment will easily migrate to the air–polymer interface as the NCO/OH ratio increased, the C=O/C=C ratio is slightly decreased and then increased with the increase of NCO/OH ratio. The explanation is that the increase of NCO/OH ratio will enhance the aggregation of hard domain and the separation between hard/soft domains will increase. So that more soft segment content, which possesses C=C groups, will migrate to the surface of membranes. As the NCO/OH ratio increased further, the increasing hard segment content will induce more allophanate crosslinkage formation and then the whole PU composition will be more homogeneous. On the other hand, the detection region of FTIR-ATR is between surface and the bulk, which can be expressed as near surface. Consequently, these may be the reason for the increase of C=O/C=C ratio in the near surface as the NCO/OH ratio of membranes is larger than 1.2.

3.2. Contact angle measurements

Contact angle analysis provides information on the surface of hydrophobicity or hydrophilicity and molecular mobility at the air–water–solid interface [25]. High contact angle values, included between 70° and 90°, indicate high hydrophobic surfaces such as silicone or fluorocarbon polymers, while low contact angle values (0–30°) indicate highly hydrophilic surfaces such as glass or mica [26]. The hydrophobicity or hydrophilicity of PU membrane’s surface can be characterized by contact angle.

Table 2 shows that the values of contact angle change from 82.4 to 90.4 as the NCO/OH ratio of PU membranes vary from...
1.0 to 1.5. This phenomenon is due to the fact that HTPB is the soft segment with lower energy component, while the hard segment, H12MDI and 1,4-BD, possesses higher energy. During the membrane’s preparation period, the soft segment with lower energy will migrate to the surface and the hard segment with higher energy then migrate to the bulk of membrane. The amount of hard segment content in the higher NCO/OH values of membranes is large in comparison to the amount of hard segment content in the lower NCO/OH values of membranes due to stronger intermolecular hydrogen bonding and hence the hard segment will cluster more closely and strongly. Then there are harder segment contents that will disperse in the bulk of membrane. On the other hand, the amount of HTPB soft segment migrating to the surface/polymer interface increased. This induces the hydrophobicity of membrane’s surface more as the NCO/OH value increased.

3.3. Thermal properties

A three-step degradation curve was observed. In the first step, the weight loss is less than 5%. The quantity of gaseous components, mainly water released in this step, is relatively small. Decomposition temperatures of steps 2 and 3 are at approximately 300 and 450 °C. The main quantity of gaseous components, e.g., carbon monoxide and methane, is split off in these two steps. Decomposition of step 2 corresponds to urethane-bond (i.e., hard segment) breaking, and step 3 is the polyl decomposition [27].

The decomposition results are shown in Table 3. The decomposition temperature of second step and the residue increase are from 271.86 to 277.80 °C and from 4.90 to 11.22%, respectively, as the NCO/OH ratio of membranes increase from 1.0 to 1.5. This was attributed to the increase of hard segment content in the polyurethane. The increase of NCO/OH ratio will increase the hard segment content and crosslinkage, which will increase the intermolecular bonding and hence needs more energy to decompose the membrane. Whereas the ring structure of H12MDI and hard segment content are increased as the NCO/OH ratio increased. This will induce the difficulty of reaction with air to form CO2, H2O, and then more carbon residues will be produced.

3.4. Mechanical properties

Tensile properties of these membranes are measured by DMA. Table 4 indicates that the tensile strength and young’s modulus of membranes are all increased with the increase of NCO/OH ratio. This phenomenon is the same as that reported by Zdrahala et al. [28,29]. The reason is due to the increase of hard segment content and the rigidity of hard segment.

On the other hand, the elongation at break is also increased as the NCO/OH ratio increased and then decreased as the NCO/OH ratio reached 1.5. PU will change from soft-toughness rubber with low hard segment content to high elongation elastomer as the hard segment content increased and then change to rigid glassy type plastic as membranes with high hard segment content [30]. As the NCO/OH ratio is larger than one, the three-dimensional allophanate crosslinks [31] will be formed and the number of urethane groups increased. The introduction of chemical allophanate crosslinks has a detrimental effect on the hard domains. The increase of chemical crosslinking leads to a change in morphology [32] and affects the mechanical properties [33]. The existence of three-dimensional allophanate restricts the mobility of molecular chain. And the increase of intermolecular attraction of hard-to-hard segments by the increase of NCO/OH ratio tends to increase tensile property, while the elongation also increase due to the increase of three-dimensional allophanate crosslinking between hard segments. This can diminish the intermolecular entanglement of HTPB soft segment and enlarge the elongation. As the crosslinking increases to a large extent such as NCO/OH = 1.5, the elongation disrupts to 905%. It is obvious that lower crosslinking density will increase the elongation and larger crosslinking density then change the membrane to glassy type and break at lower elongation.

3.5. Pervaporation results

In a pervaporation separation process it is desirable to have the characteristics of high permeation through polymer films combined with good selectivity for a polymer film. In order to obtain good permeability and high degree of separation for liquid mixtures, it is essential to choose the right membrane as

<table>
<thead>
<tr>
<th>NCO/OH ratio</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>E’ at 50% (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.98</td>
<td>1289</td>
<td>0.52</td>
</tr>
<tr>
<td>1.1</td>
<td>4.63</td>
<td>1544</td>
<td>0.71</td>
</tr>
<tr>
<td>1.2</td>
<td>5.73</td>
<td>1581</td>
<td>0.87</td>
</tr>
<tr>
<td>1.3</td>
<td>7.84</td>
<td>1750</td>
<td>1.13</td>
</tr>
<tr>
<td>1.5</td>
<td>11.22</td>
<td>1009</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Young’s modulus: E’.
well as the optimum operating conditions. The major purposes of this study are to measure the permeability and separation factor of different NCO/OH ratio membranes for ethanol and isopropanol aqueous solutions by pervaporation, and to investigate the dependence of permeation behavior on the feed composition as well as the operating temperature.

3.5.1. Effect of NCO/OH ratio

The membranes used in this pervaporation study were dipped in the feed with 90, 80 or 70 wt% of alcohol content, respectively, for 1 day. Fig. 3 shows the permeability and separation factor of an ethanol/water mixture of 90 wt% ethanol content diffusing through membranes with different NCO/OH ratios. The permeability only slightly increased, and the separation factor increased with the increase of NCO/OH ratio.

The high permeability of PU membrane is due to the diffusion through HTPB soft segment of membrane, whereas the HTPB segment is a hydrophobic component and has strong affinity with ethanol and swell by ethanol [34–36]. Meanwhile, there are harder segments contained in PU membrane, as the increase of NCO/OH ratio will increase the segregation between non-polar HTPB soft segment and polar hard segment. This is due to fewer polar carbonyl groups being freely dispersed in the soft segment and the enlargement of hard segment aggregation. On the other hand, the increase of NCO/OH ratio will increase the intermolecular hydrogen bonding and hence decrease the permeability. These two contradictory explanations may be the reasons for the slight increase of permeability as the NCO/OH ratio increased.

When the membranes are immersed in the ethanol/water mixtures, the ethanol molecules absorbed in the membranes are selectively absorbed upon the polymer chain of the HTPB soft segment owing to the hydrophobic HTPB polymer chain, which interacts with the hydrophobic moiety of the ethanol and the –OH groups of ethanol exposed on the surface. This hydrophilization of the somewhat hydrophobic membrane by the ethanol is probably responsible for the selectivity of water. In addition, the water molecules are smaller than those of ethanol and hard segment is in a hydrophilic component. Then the separation factors of these membranes are increased as the NCO/OH ratio increased. The membranes are very hydrophobic as shown by the contact angle data; surprisingly, the membranes selectively permeate water. Apparently, the high selectivity of water permeation does not agree with the high hydrophobicity of the membranes.

The pervaporation separation index (PSI) [37] was determined by the following equation:

$$\text{PSI} = \frac{P}{\alpha}$$

where $P$ and $\alpha$ are the permeability and separation factor, respectively. Fig. 4 indicates that PU membrane with NCO/OH ratio equal to 1.3 possesses the largest pervaporation separation index (36,713 g/(m² h)). The high PSI values for dehydration may indicate the good performance of these membranes. Then PU membrane with NCO/OH = 1.3 is selected for the following three sections of pervaporation tests.

3.5.2. Effect of feed concentration

Fig. 5 shows the effect of feed ethanol concentration on the permeability and the separation factor through PU membrane with NCO/OH ratio equal to 1.3 ratio. The permeability increases and separation factor decreases from dilute ethanol aqueous solution to concentrated solution. The reason is that when the membranes
are immersed in water–ethanol mixture, the ethanol molecules are absorbed on the polymer chains of HTPB soft segment. The swelling degree increases with the increase of ethanol content in the feed concentration as shown in Fig. 6. This may be the reason for the increase of permeability with respect to the increase of ethanol content in the feed.

While the ethanol molecules are absorbed into the HTPB segment, the water or ethanol molecules may be absorbed into the first layer of ethanol molecules to form double layer adsorbants. For the ethanol concentrated feed, more double layer of ethanol molecules are absorbed on the first layer of ethanol molecules and hence membrane’s surface change to hydrophobic property. Then hydrophilic water molecules diffuse through the membranes with difficulty. This may be the reason for the decrease of separation factor with the increase of ethanol content in the feed.

3.5.3. Effect of feed temperature

For the NCO/OH = 1.3 membrane, the permeability increases and the separation factor decreases with the increase of feed temperature as shown in Fig. 7. These results are due to the fact that a higher feed temperature, causing an increase in chain mobility and the swelling of membrane matrix and hydrogen bonds decay with the increase of feed temperature, induces a higher permeability of crosslinked PU membranes [22]. On the other hand, the increase of feed temperature will increase the free volume and softness of polymer chain, which will induce the decrease of separation factor [36]. When the feed temperature reaches 50–60°C, the free volume of membrane largely increases and hence the permeability and separation factor change appreciably.

3.5.4. Effect of different feed alcohol/water solution

Figs. 8(a) and 9(a) show the permeability as a function of feed concentration for membranes with different NCO/OH ratio and alcohol/water solution, respectively. The permeabilities are all increased with the increase of NCO/OH ratio or the increase of alcohol content in the feed. These phenomena can be explained with the increase of swelling ratio and sorption ability on the membrane’s surface, which has been discussed in the former section.

The permeability of IPA/water solution through membranes is slightly lower than those of corresponding ethanol/water solution present. This is due to the fact that sorption of IPA into the membrane’s surface and the swelling behavior of membranes are all larger than those of ethanol. The reason is that IPA is more hydrophobic than ethanol and has more affinity with HTPB soft segment. This will induce larger permeability of IPA/water solution through membranes. On the other hand, the steric structure
of IPA molecules, which are absorbed on the membrane’s surface, will hinder the permeation of feed through the membrane. The competition of these two contradictory effects on the permeabilities may be the reason for the slightly lower permeability of IPA/water solution through the membranes.

Figs. 8(b) and 9(b) show the effects of NCO/OH ratio and alcohol concentration on the separation factor, respectively. The separation factors of ethanol/water solution are all increased with the increase of NCO/OH ratio, while it is decreased with the increase of ethanol content in the feed. The reason may be that the increase of hydrophilic hard segment content will increase the separation factor, while with the membrane immersed in the feed with high alcohol content, there may be double layer absorption on the membrane’s surface and high swelling ratio formed and induce the increase of separation factor, which has been discussed in the former sections.

On the other hand, the separation factors for IPA/water solution through membranes are increased with the increase of IPA content in the feed. With the double layer absorption of IPA molecules on the membrane’s surface, there will be more free volume formed. Then the water molecules are easily permeated through the above free volume because the size of water molecules is lower than that of IPA molecule. This may be the reason for the increase of separation factor with the increase of IPA content in the feed.

4. Conclusion

The characteristic absorption peaks of C=O bond and C=O free groups shift to lower frequency with the increase of NCO/OH ratio. The contact angles of these HTPB-based PU membranes are between 80° and 90°. The contact angle, HBI value, tensile strength, modulus are all increased with the increase of NCO/OH ratio. While elongation also increased and then decreased as the NCO/OH value equalled 1.5, the permeabilities are all increased with the increase of NCO/OH ratio or the increase of alcohol content in the feed. The separation factors of ethanol/water solution permeating through membranes are all increased with the increase of NCO/OH ratio, while it decreased with the increase of ethanol content in the feed. On the other hand, the separation factors of IPA/water solution through membranes are increased with the increase of IPA content in the feed.

References


