ELSEVIER

Polymer 40 (1999) 6089–6097

polymer

Design of polypropylene oxide/polybutadiene bi-soft segment urethane/urea polymer for pervaporation membranes

Chun-tian Zhao, Maria Norberta de Pinho*

Departamento de Engenharia Quimica, Instituto Superior Tecnico, 1096 Lisbon Codex, Portugal

Received 2 June 1998; received in revised form 4 September 1998; accepted 12 November 1998

Abstract

Novel cross-linked urethane/urea polymers with two soft segments, polypropylene oxide and polybutadiene, were prepared by extending polypropylene oxide-based isocyanate-terminated triol prepolymer with polybutadiene diol. Infra-red spectra indicated that with increasing polybutadiene content in the polymers, the hydrogen bonding of urethane/urea groups among hard segments became weaker. This was interpreted as an improvement of freedom of urethane/urea groups and their mixing with polypropylene oxide. The dynamic mechanical thermal analysis indicated that the two soft segments were highly dispersed, and could lead to a molecularly mixed phase. The swelling experiments with ethanol aqueous solutions indicated a preferential sorption of ethanol and a decrease of the swelling degree with increase of polybutadiene content in the polymer films. The preferential permeation of ethanol is confirmed by the pervaporation results. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bi-soft segment urethane/urea polymer; Polypropylene oxide; Polybutadiene

1. Introduction

Urethane/urea polymers usually consist of hard segments, namely urethane/urea groups and/or low molecular weight chain extenders, and one kind of soft segment, ordinarily being polyether/polyester. Depending on the type of hard and soft segments and on the processing parameters, the hard and soft segments of the resulting polyurethane can be totally mixed or phase-separated to different degrees [1–3]. The literature [4,5] relative to polybutadiene diol as a soft segment of polyurethane reported a complete phase separation between hard and soft segments. The versatility of structure design of urethane/urea polymers is an important asset on the tailoring of permeation selectivity of pervaporation membranes. Despite that and the fact that the synthesis, structure and properties of this group of segment copolymers has been extensively investigated, there are no significant developments on their use for membrane preparation.

Polyether, typically polypropylene oxide, based urethane/urea polymers have been used as pervaporation membrane materials [6–8] to extract or remove organics from aqueous solutions. However, in pervaporation, the preferential permeation of organics is often diminished by the hydrophilicity of urethane/urea groups and the weak interaction between polypropylene oxide and water [9]. Also the lack of polymer structure design is another factor responsible for the unsatisfactory characteristics of pervaporation membranes, specially in ethanol/water pervaporation process. On the other hand, the use of crosslinked polybutadiene for pervaporation membranes yielded rather high organophilic selectivity but very low flux [10,11].

The objective of this work is the optimisation design of the chemical and physical structure of urethane/urea polymers in order to prepare pervaporation membranes with enhanced permeation performance. Novel cross-linked urethane/urea polymer materials with two soft segments, polypropylene oxide and more hydrophobic polybutadiene, were prepared by extending a polypropylene oxide-based tri-isocyanate-terminated prepolymer with polybutadiene diol. The urethane/urea polymers were characterised with infra-red spectroscopy, dynamic mechanical thermal analysis and solvent swelling measurements. The ethanol/water pervaporation characteristics of these membranes were also tested.

2. Experimental part

2.1. Materials

The polypropylene oxide-based prepolymers with

---

* Corresponding author. Tel.: 841-7259-308-951.

PII: S0032-3861(98)00833-7

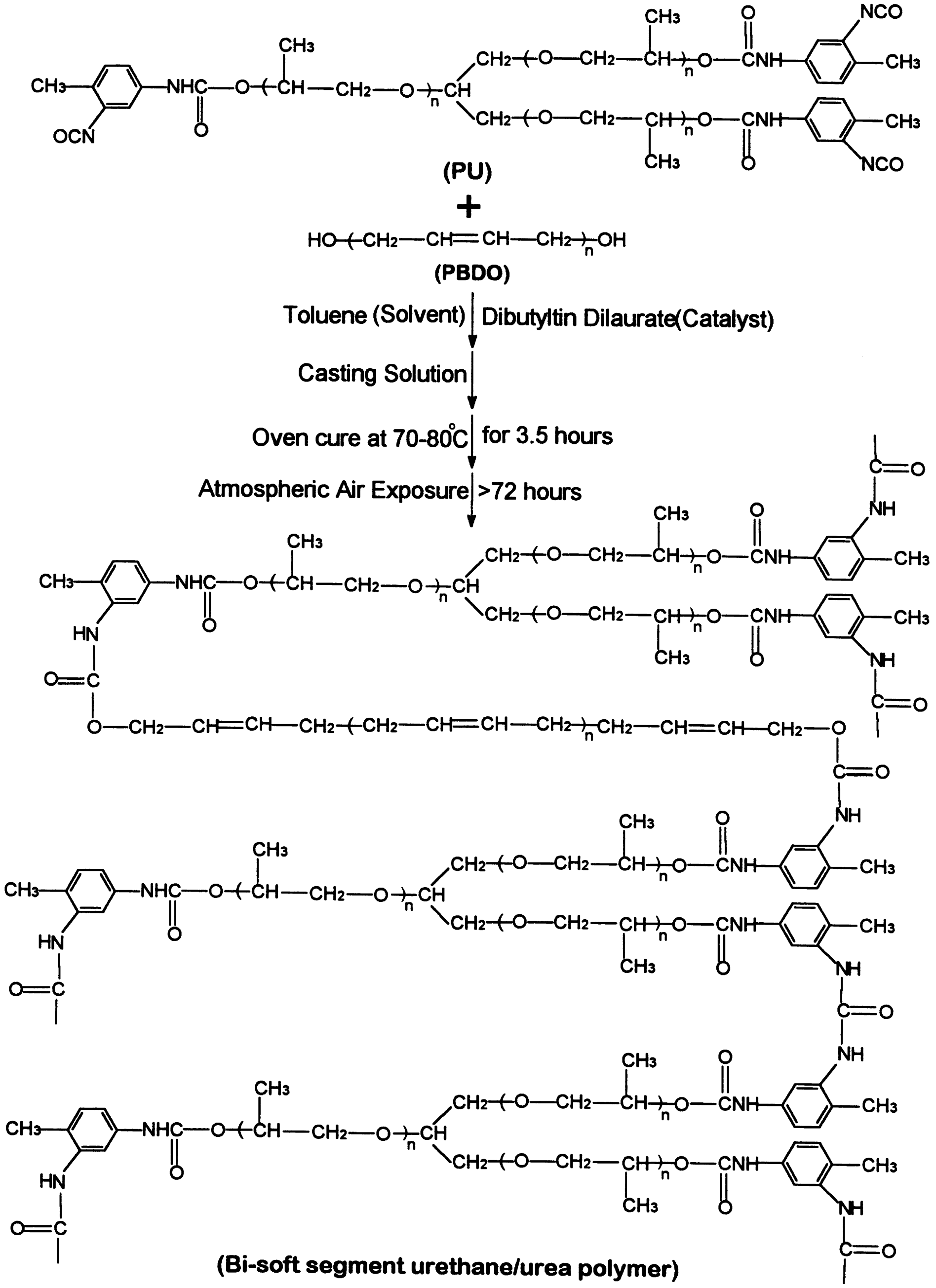

Fig. 1. Preparation of polypropylene oxide/polybutadiene bi-soft segment urethane/urea polymer membranes.

three isocyanate terminal groups were designated as PU. They were supplied by Portugese Hochest, S.A. Fig. 1 shows its chemical structure. The molecular weight was approximately 3500. The polybutadiene diol (PBDO) supplied by Aldrich has a number average molecular weight of 2800 and contains 20–30 wt.% vinyl, 10–25 wt.% *cis*-1,4 and 50–60 wt.% *trans*-1,4 isomers. The dibutyltin dilauryate (DBTDL) supplied by Aldrich was used as a catalyst. The pro-analysis toluene supplied by Merck was used as a solvent.

2.2. Membrane preparation

In our laboratory, highly cross-linked membranes have been previously prepared through a non-catalysed reaction of the isocyanate groups with water [7]. In the present work, the reaction of the isocyanate groups of PU with the hydroxyl groups of PBDO are catalysed by DBTDL at 70–80°C (Fig. 1). The ratio of PU and PBDO was varied to yield cross-linked polymers with different compositions. For comparison purposes, PU membranes were prepared by moisture reaction with isocyanate groups.

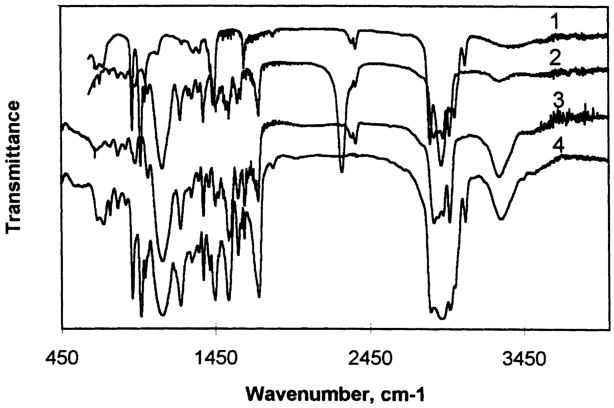

Fig. 2. Infra-red spectra of: (1) polybutadiene diol; (2) polypropylene oxide-based tri-isocyanate-terminated prepolymer; (3) moisture-cured tri-isocyanate-terminated membrane; and (4) bi-soft segment urethane/urea polymer membrane with 60% polybutadiene.

2.2.1. Bi-soft segment urethane/urea polymer membranes

PU and PBDO prepolymers were co-dissolved in toluene, and 1–2 drops of DBTDL were added. The solid content of the solutions was about 40 wt.%. The solutions were cast onto a glass plate at room temperature with a 0.25 mm Gardner knife. After being cured in an oven at 70–80°C for 3.5 h, the films were exposed to air and continued curing for at least 72 h by atmospheric moisture.

For the purpose of polymer characterisation, thinner and thicker films were also prepared from casting solutions with prepolymer concentration of 10 and 60 wt.%, respectively.

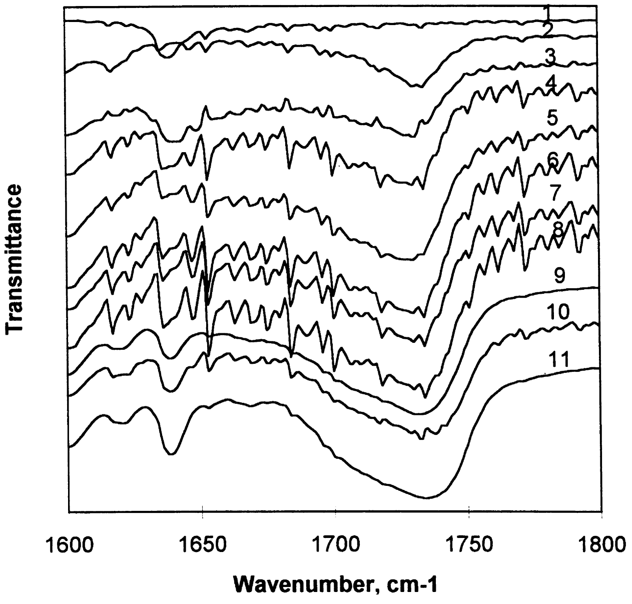

Fig. 3. Infra-red spectra in the range 1600–1800 cm^{-1}, showing the carbonyl stretching bands of: (1) polybutadiene diol; (2) tri-isocyanate-terminated prepolymer; (3) moisture-cured tri-isocyanate-terminated membrane and bi-soft segment urethane/urea polymer membrane with a polybutadiene content of: (4) 10%; (5) 20%; (6) 25%; (7) 33.3%; (8) 50%; (9) 60%; (10) 66.7%; and (11) 75%.

2.2.2. PU membranes

The casting solutions were prepared by dissolution of 40 wt.% PU prepolymers in toluene and spread over a glass plate with a 0.25 mm Gardner knife. The membranes were afterwards exposed to air for at least 72 h.

2.3. Characterisation

Infra-red spectra of P_2O_5 dried urethane/urea polymers and membranes were recorded with a Perkin Elmer 1600 IR spectrometer. The samples were scanned 64 times at a resolution of 2 cm^{-1}.

The dynamic mechanical thermal properties of the polymers were measured with a PL-I spectrometer in bending mode at a frequency of 1 Hz. The temperature was increased at 2°C min^{-1} from −100°C to +20°C.

The swelling degree of the membranes were measured by immersion in ethanol/water solutions After a 24 h immersion period, the sample was removed and the surface solution was wiped out with filter paper. The percentage of membrane weight gain, D_w, was determined as:

$$D_w = (W_s - W_d)/W_d \times 100\% \quad (1)$$

where W_d and W_s are, respectively, the weight of the membrane before and after immersion.

2.4. Pervaporation

The experiments were carried out with a flat sheet cell of four compartments in series and a total effective membrane area of 62.68 cm^2. The ethanol/water solution was fed at 25, 35, 40 and 50°C, and the permeate pressure was kept between 3.5–4.5 mbar. The permeate was condensed with liquid nitrogen and was analysed with a 85A Dohrmann Carbon Analyser. The pervaporation rates were determined by weighing the condensed permeates. The ethanol selectivity factor, $\alpha_{\text{ethanol/water}}$, was defined by:

$$\alpha_{\text{ethanol/water}} = (Y_{\text{ethanol}} \cdot X_{\text{water}})/(X_{\text{ethanol}} \cdot Y_{\text{water}}) \quad (2)$$

where X_{ethanol}, X_{water}, Y_{ethanol} and Y_{water} are, respectively, the weight fractions of ethanol and water in the feed and the permeate.

3. Results and discussions

3.1. Infra-red spectra of the urethane/urea polymers

Fig. 2 displays the infra-red spectra of the two prepolymers, cured pure PU film and membranes of urethane/urea polymers containing 60% polybutadiene. The ν(NCO) band at 2270 cm^{-1} was very obvious in the spectra of the prepolymer PU. This band was hardly detectable in the spectra of urethane/urea polymer films. Instead the appearance of the $\nu(C=O)$ band of urea group and an enhancement of the $\nu(C=O)$ band of the urethane group were observed, indicating the reaction of almost all original isocyanate groups.

Table 1
Characteristics of ν(CO) and ν(NH) bands

Polybutadiene in polymers (%)	Wavenumber (cm^{-1}) of ν(CO)urea[a]	Wavenumber (cm^{-1}) of ν(CO)urethane[a]	A_{1734}/A_{1700}[b]	ν(NH) band wavenumber (cm^{-1})
Polybutadiene diol				
PU prepolymer		1732		
0	1642, 1647	1696, 1700, 1715, 1734	1.1446	3291
10	$1647 < 1653$, 1663, 1669, 1675, 1684	1696, 1700, 1718, $1734 < 1730$	1.2583	3292, 3447
20	$1647 < 1653$, 1663, 1669, 1675, 1684	1696, 1700, 1718, 1730	1.4919	3299, 3447
25	$1647 < 1653$, 1663, 1669, 1675, 1684	1696, 1700, 1718, $1734 > 1730$	1.3518	3299, 3447
33.3	$1647 < 1653$, 1663, 1669, 1675, 1684	1696, 1700, 1718, $1734 > 1730$	1.5530	3309, 3447
50	$1647 < 1653$, 1663, 1669, 1675, 1684	1696, 1700, 1718, 1734	1.5275	3311, 3447
60		1731	1.9189	3301, 3453
66.7		1732.6	1.9884	3309, 3453
75		1734	2.4893	3309, 3453

[a] Strength comparison between some bands is also given.

[b] $A_{1734} = \ln(T_{1800}/T_{1734})$, $A_{1700} = \ln(T_{1800}/T_{1700})$, T = transmittance, A = absorbance.

There is a vast amount of literature related to the infra-red spectroscopy of urethane/urea polymers. In the revision of this literature [9,12–19], the assignment of urethane/urea carbonyl and amine bands is fairly consistent for different polymers and for different authors, despite the well-established fact that the localised vibrations including the N–H or C = O stretching vibrations are very sensitive to the perturbation of hydrogen bonding. The formation of hydrogen bonds will alter the electronic distribution associated with the N–H bond [20] and add to the contribution of transition dipole–dipole coupling for the C = O stretching vibration [21]. Both frequency shift and intensity changes characterise the specificity or magnitude of the hydrogen bonding. Assigned in accordance with the literature, the N–H or C = O stretching bands are analysed in this work.

Fig. 3 gives the stretching bands of carbonyl of prepolymers and urethane/urea polymers with different compositions. The spectra of bi-soft segment polymers, specially the polymers containing 10–50% polybutadiene were very complex. A series of $\nu(C = O)$ bands appeared, corresponding to the diversified environment of carbonyl groups. The good reproducibility of these bands was verified among different samples and among repeated measurements for the same sample. The $\nu(C = O)$ of urea groups was distributed in three ranges of 1617–48, 1653–69 and 1675–91 cm^{-1}, respectively, representing the hydrogen bonded ordered, disordered and free urea carbonyl [19]. In the spectra of cured pure PU film, the bands of 1642 and 1648 cm^{-1} were far stronger than the others, indicating that most urea carbonyls were hydrogen bond ordered. In the spectra of urethane/urea polymers with 10–50% of polybutadiene, the 1653 cm^{-1} band was the strongest, denoting that more urea groups were hydrogen bond disordered; the free urea carbonyl band at 1684 cm^{-1} also became much stronger, comparable with the 1653 cm^{-1} band. When the polybutadiene content was higher than 60%, the urea $\nu(C = O)$ bands became hardly detectable.

The enhancement of the urethane $\nu(C = O)$ band increased with polybutadiene content in the polymers. With increasing polybutadiene content in the films, there was a tendency for the peak of the urethane $\nu(C = O)$ to shift slightly to higher wavenumber. The quite wide asymmetric $\nu(C = O)$ urethane band consisted of two regions, 1717–1734 and 1696–1715 cm^{-1}, representing free and hydrogen bonded urethane carbonyl, respectively. The so-called free urethane carbonyls were accepted to correspond to those carbonyls not hydrogen bonded with amine hydrogen. The work of Coleman et al. [16] and Strikovsky et al. [18] revealed that the carbonyls in the form of the urethane group associated with the ether group, in the soft segment domains or at the interface and absorbed infra-red light at 1729 or 1733 cm^{-1}. The carbonyl band of truly free urethane [18] should be at a higher wavenumber, e.g. 1738 cm^{-1}. In the spectra of all the films, the 1717–1734 cm^{-1} region was stronger than the region corresponding to hydrogen bonded carbonyl. The literature [17] suggested that the efficient absorptivity of hydrogen bonded carbonyl is larger than that of non-hydrogen bonded carbonyl. So the difference in band intensity indicated that most urethane carbonyls were not hydrogen bonded.

A preliminary experiment was conducted by acquiring the infra-red spectra of these urethane/urea polymer films after immersion in *n*-propanol. The shape of the asymmetric urethane carbonyl band changed, with the centre of the strongest area shifting below 1715 cm^{-1}. This resulted from the formation of hydrogen bonds of originally free carbonyls with the hydroxyls of *n*-propanol, confirming, in one respect, the correctness of the band assignment of hydrogen bonded carbonyl and the existence of non-hydrogen bonded carbonyl in dry urethane/urea polymers. These experiments need to be further improved and analysed.

An attempt to simulate the stretching band of urethane carbonyl turned out to be unsuccessful because of the complexity of the spectra. Here we adopt a characterisation method similar to that of the literature [12,15]. The ratio of the absorbance of the peaks around 1734 and 1700 cm^{-1},

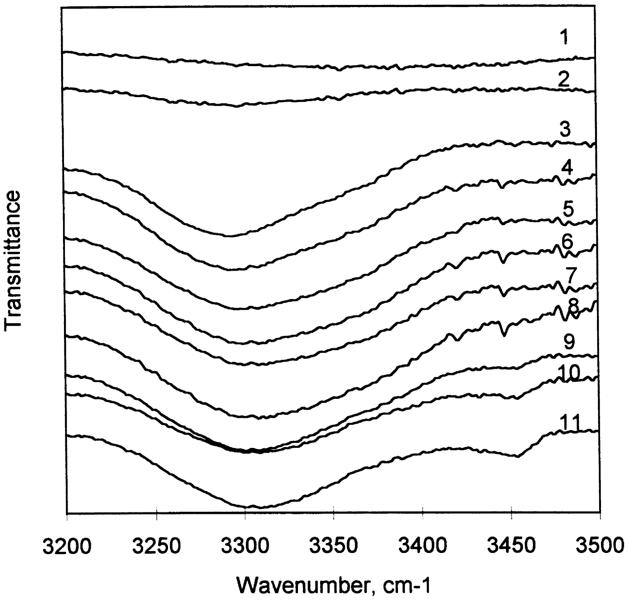

Fig. 4. Infra-red spectra in the range 3200–3500 cm^{-1}, showing the amine stretching bands of: (1) polybutadiene diol; (2) tri-isocyanate-terminated prepolymer; (3) moisture-cured tri-isocyanate-terminated membrane and bi-soft segment urethane/urea polymer membrane with a polybutadiene content of: (4) 10%; (5) 20%; (6) 25%; (7) 33.3%; (8) 50%; (9) 60%; (10) 66.7%; and (11) 75%.

A_{1734}/A_{1700}, was used as an indication of hydrogen bonding of the urethane groups among hard segments. The higher the ratio, the greater the number of urethane groups that are free or associated with polypropylene oxide. Since the thickness of the infra-red samples was not exactly controlled, the transmittance at 1800 cm^{-1} was selected as an internal standard in calculating absorbance:

$$A_\nu = \ln(T_{1800}/T_\nu) \quad (3)$$

where T_ν and T_{1800} were, respectively, the transmittance at wavenumber of ν and at 1800 cm^{-1}, A_ν was the absorbance at wavenumber ν. The values of the ratio of A_{1734}/A_{1700} are listed in Table 1. Globally, this ratio increases with the content of polybutadiene in the polymer films. That signifies an increase of the fraction of free urethane groups or those mixed with polypropylene oxide.

Fig. 4 gives the stretching bands of amine groups. The main ν(N–H) band was located at 3293–3313 cm^{-1}. This relatively strong and broad band qualitatively indicated that many, maybe most, –NH groups were hydrogen bonded. The peak shifted to higher wavenumbers with an increasing content of polybutadiene in the films (Table 1). By incorporation of polybutadiene, another small band appeared at 3447 or 3453 cm^{-1}. The band strength increased with polybutadiene content. That band was considered to be a ν(NH) band representing free –NH. The real fraction of free NH can be higher than that created by the band strength difference, since the efficient absorptivity of hydrogen bonded –NH is far bigger than that of non-hydrogen bonded –NH. The quantitative analysis of hydrogen bonding by –NH stretching bands is not recommended because of the possible large error [16,17].

Hydrogen bonding among urethane/urea groups is an indication of mixing between hard and soft segments of urethane/urea polymers. The infra-red spectra analysis in this work suggested that, with increasing polybutadiene content in the bi-soft segment urethane/urea polymers, the hydrogen bonding between urethane/urea groups became weaker. This can be interpreted as an improvement of freedom of urethane/urea groups and their mixing with polypropylene oxide. In cured pure PU films, there were only polypropylene oxide and hard segments. The hard segments consisted of two urethane groups linked by two toluene and one urea groups. These hard segments were short, meaning low melting points of possible aggregates, and were highly influenced by the soft polypropylene oxide segments because of chemical linkage. The hydrogen bond, which is sensitive to geometry, might have difficulty fully forming among hard segments, especially the urethane parts. Though there existed some micro-ordered aggregates of urea linkages, as shown by the infra-red bands of 1642 and 1648 cm^{-1}, to a certain extent, the hard segments, or parts of hard segments, were mixed with polypropylene oxide. This explains the low degree of hydrogen bonding of urethane carbonyls and, on the contrary, the high degree of hydrogen bonding of the amine groups. The mixing was also indicated by the high transparency and amorphous morphology of these polymer films.

The introduction of polybutadiene yielded a decrease of the number of urea linkages. On the other hand, more hard segments were formed between polypropylene oxide and polybutadiene. These hard segments consisted of two urethane groups linked by one toluene group. Due to the hydrophilic character of the hard segments, one would expect a segregation tendency from the very hydrophobic polybutadiene. However, these hard segments were shorter than the hard segments between two polypropylene oxide segments so that they were more mobile and highly influenced by the soft segments. And the occurrence of segregation would not mean an effective decrease of thermodynamically unfavourable hard segment/polybutadiene contact due to the fact of the hard segments being too short and chemically linked to polybutadiene. As a result, the hard segment might have a greater opportunity to mix with polypropylene oxide, or even to be free because of the influence of a one-ended chemical linkage with polybutadiene.

3.2. Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal analysis curves of cured PU and bi-soft segment urethane/urea polymer films are given in Fig. 5. In the spectrum of cured pure PU film, one peak at −25°C appeared to correspond with the glass transition of the polypropylene oxide segment. This glass transition temperature was higher compared with that of the

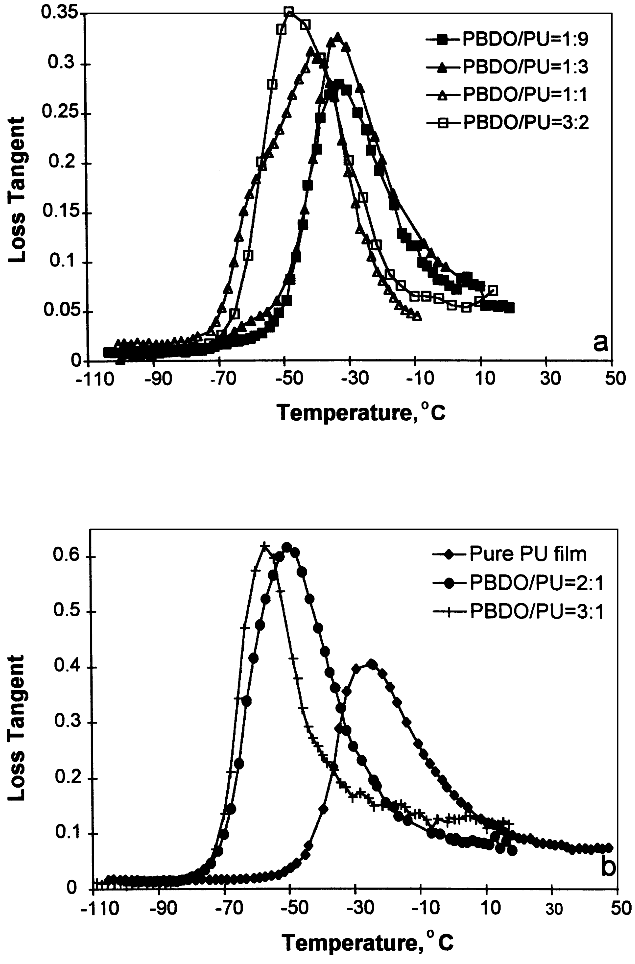

Fig. 5. Dynamic mechanical thermal analysis curves of moisture-cured PU (isocyanate-terminated triol) film and bi-soft segment urethane/urea polymer film with different compositions.

bulky polypropylene oxide (−75°C) [22], and those of films cured from polyurethane prepolymers with higher molecular weight polypropylene oxide in our previous work (−42.5°C, −46°C) [7]. This result could be partly attributed to the mixing of polypropylene oxide segments with hard segments and their high degree of cross-linking, by both triol itself and the urea aggregates. The dynamic mechanical thermal properties of urethane/urea polymers had strong stoichiometry dependence. When the polybutadiene content in the films was less than 50%, two peaks appeared in the DMTA spectra, corresponding to the glass transitions of polybutadiene and polypropylene oxide segments, respectively. Though the polybutadiene were mixtures of vinyl-, *cis*-1,4 and *trans*-1,4 isomers, only one glass transition of polybutadiene was obviously detected as a peak shoulder at lower temperatures with a low loss tangent; to a greater degree assigned to the *trans*-1,4 isomer. As a reference, one can find in the literature [23] the glass transition temperatures of bulky *cis*-1,4, *trans*-1,4 and isotactic vinyl-polybutadiene as being −108, −78 and −4°C, respectively. The glass transition of the polypropylene oxide segment appeared at higher temperatures with a high loss tangent. The glass transition temperatures of the two soft segments are plotted against the content of polybutadiene in bi-soft segment copolymers (Fig. 6). The two transitions got closer to each other with increasing polybutadiene content. The degree of peak shift increased in tendency with increasing content of polybutadiene. When the polybutadiene content in the films was equal to or higher than 60%, only one transition was observed for the whole polymer. The corresponding temperature decreased with increasing content of polybutadiene.

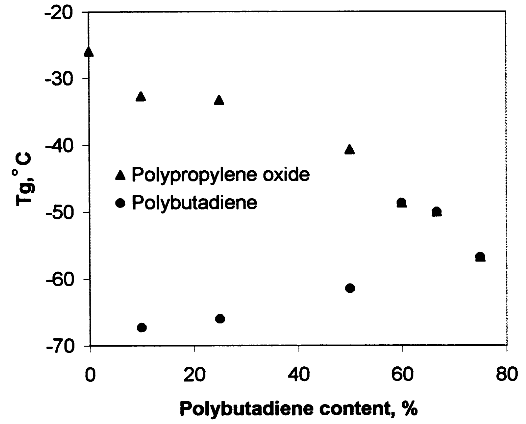

Fig. 6. Dependence of glass transition temperatures of polypropylene oxide and polybutadiene in the bi-soft segment urethane/urea polymers.

When polybutadiene content in the films was less than 60%, the loss tangent or the area of the transition peaks were quite low, indicating a high degree of cross-linking of the materials. When the polybutadiene content reached 66.7 or 75%, the peak loss tangent was relatively high, denoting a lower degree of cross-linking of the two films. This result was in accordance with the ratio of molecular weight of the two original prepolymers. The functionality of the PBDO and PU were, respectively, 2 and 3. So, when the PBDO/PU ratio was lower than 3:2, the amount of hydroxyl groups was equal to or lower than that of thte isocyanate groups, and the resulting films were still relatively highly cross-linked. With an increase in PBDO content, a few hydroxyl groups were left unreacted, leading to a decrease in the degree of cross-linking.

The blend of polypropylene oxide and polybutadiene was reported as displaying an upper critical solution temperature behaviour [24]. In the present case, as illustrated by DMTA, polybutadiene and polypropylene oxide were, in principle, thermodynamically immiscible below room temperature, though their molecular weights are not very high. The two soft segments favoured the formation of separate microphases. The two phases in these cross-linked copolymers, however, were very finely dispersed within each other, so that the interfacial interaction by chemical linkage or physical contact was very striking. In response, the glass transitions of the two soft segments approached each other. With increasing polybutadiene content, the mixing of the two soft

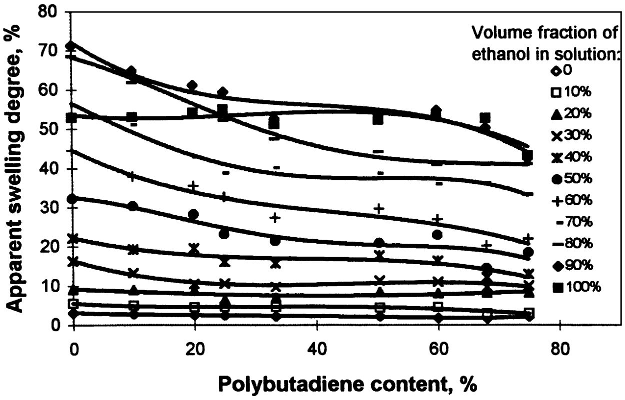

Fig. 7. Apparent swelling degree of the PU part in moisture-cured PU film and the bi-soft segment urethane/urea polymer films immersed in an ethanol/water solution.

segments increased, and the chemical cooperativity remarkably improved. Finally, polybutadiene and polypropylene oxide were molecularly mixed so that only one glass transition was detected.

The phase structure was also denoted by the transparency of the membranes. The atmospheric moisture-cured pure PU film was very clear. With incorporation of polybutadiene, the urethane/urea films became slightly translucent, indicating microphase separation to some degree. However, with increasing polybutadiene content to above 50%, the membrane transparency became clearer again, suggesting an improvement of the phase mixing degree.

3.3. Ethanol/water solution swelling behaviour

The urethane/urea polymer film could be regarded as the cured blend of two prepolymers, one part originated from PU, another part originated from PBDO. It is well known that the swelling degree of polybutadiene in an ethanol/water solution is very low. Consequently, the swelling degree of the bi-soft segment urethane/urea polymers was obviously lower than that of the cured pure PU films. We assumed that all the swelling of the urethane/urea polymers was due to the PU contribution. The apparent swelling degree, D_{pu}, was defined as:

$$D_{\mathrm{pu}} = D_{\mathrm{w}}/f \tag{4}$$

where f is the weight fraction of PU in the original prepolymer blend.

Fig. 7 shows the apparent swelling degree varying with the content of polybutadiene in the polymers at room temperature. When applied to the swelling in pure water and in ethanol aqueous solutions, the value of D_{pu} relative to the bi-soft segment polymer films, were remarkably lower than the ones relative to the cured pure PU film. As a trend, the higher the polybutadiene content, the more pronounced the decrease of D_{pu}. In other words, the introduction of polybutadiene decreased the swelling ability of the other part of the polymer. In contrast, the value of D_{pu} relative to immersion in pure ethanol decreased obviously only for the urethane/urea polymer with polybutadiene content over 68%.

The swelling degree of the cured pure PU film was rather high and showed a maximum with an ethanol content of 90% v/v. The difference between this maximum and the swelling degree in pure ethanol was rather remarkable and leads to the conclusion that the preferential sorption towards ethanol is low. The bi-soft segment polymer films displayed lower swelling degrees than the ones of the cured pure PU films. When polybutadiene content in polymers was less than 60%, the difference between the values of D_{pu} for solutions of 90% v/v ethanol content and the value of D_{pu} for pure ethanol became smaller. Moreover, when the polybutadiene content was higher than 60%, the value of D_{pu} monotonously increased with the ethanol content of the immersion solution. The results indicated an improvement of ethanol sorption selectivity with the incorporation of polybutadiene in the films.

Due to the hydrophilicity of urethane/urea groups and the weak ability of water sorption of polypropylene oxide, the swelling degree of cured PU films in ethanol/water solutions was quite high despite the low sorption selectivity towards ethanol. In the bi-soft segment urethane/urea polymers, the polypropylene oxide and hard segments rather than polybutadiene assumed swelling or liquid sorption. Because of the finely dispersed phase structure of bi-soft segment urethane/urea polymers, the polypropylene oxide and hard segments were highly influenced by polybutadiene. The sorption would change the phase structure and induce the thermodynamically unfavourable interaction with hydrophobic polybutadiene. In response, the polybutadiene would suppress the ethanol/water sorption and, in particular, the water sorption.

The increase of polybutadiene content also decreased the cross-linking degree of the whole polymer and even led to a few non-reacted hydroxyl groups when the PBDO content was higher than 60%. However, this had little effect on swelling, since the distribution density of the hydroxyl groups would be very low and, in one sense, especially when the polymers were swollen, the polybutadiene or its microphase acted as a cross-link of the polypropylene oxide and hard segments. So, for the components which sorbed liquid, the cross-linking degree did not decrease significantly. It was their fine mixing with polybutadiene that played a major role in affecting the swelling. The overall result was that the higher the content of polybutadiene, the more striking the decrease of ethanol/water swelling.

3.4. Ethanol/water pervaporation

We have tested the ethanol/water pervaporation characteristics of two membranes with 44.2 and 68.1% polybutadiene, designated as membrane I and II, respectively. Figs. 8 and 9 give the total flux and selectivity factor of the membranes at different temperatures and ethanol

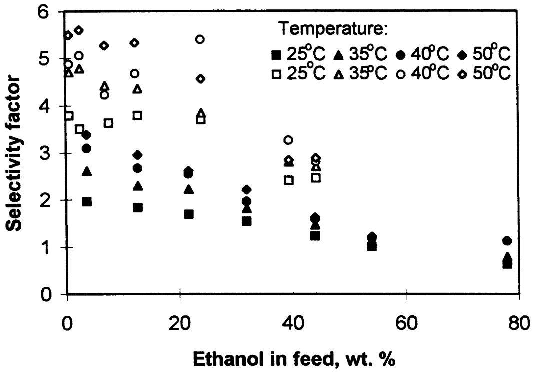

Fig. 8. Ethanol pervaporation selectivity of the bi-soft segment urethane/urea polymer membrane I with 44.2% polybutadiene (filled points) and membrane II with 68.1% polybutadiene (unfilled points) at different temperatures, feed: ethanol/water.

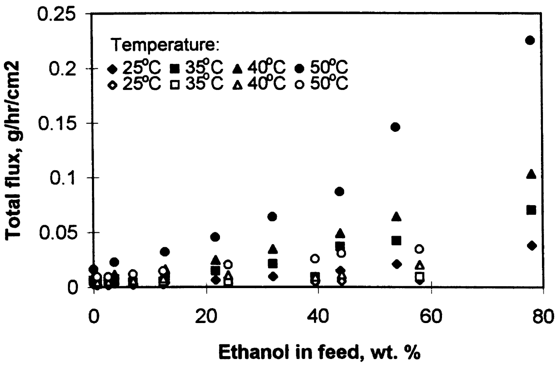

Fig. 9. Total pervaporation flux of bi-soft segment urethane/urea polymer membrane I with 44.2% polybutadiene (filled points) and membrane II with 68.1% polybutadiene (unfilled points) at different temperatures, feed: ethanol/water.

concentrations. The selectivity factor decreased with increasing ethanol feed concentration or decreasing feed temperature. The total flux displayed an opposite tendency. With increasing polybutadiene content in polymers, the total flux decreased, but the selectivity, on the contrary, increased.

The enhancement of pervaporation selectivity towards ethanol could be partly attributed to the improvement of ethanol sorption selectivity according to the solution–diffusion model [25,26]. According to this model, the pervaporation is governed by a sorption–diffusion–desorption mechanism. For the ethanol/water feed mixtures, the diffusion step would not introduce a significance differentiation between the fluxes of the two components and the global process would be controlled by the sorption step. In fact, the hydrophilicity/hydrophobicity characteristics of the membrane polymer is the major parameter determining the preferential sorption towards ethanol and setting up the membrane selectivity. The present situation of a bi-soft segment polymer with two soft blocks highly mixed would enhance the membrane hydrophobicity, favouring polybutadiene/polypropylene oxide interactions with ethanol and therefore lead to a membrane displaying preferential sorption towards ethanol.

Table 2 compares the ethanol/water pervaporation characteristics of the two membranes with those of membranes reported in the literature. The ethanol selectivity of bi-soft segment polymer membranes was lower, but the total flux was far higher than that of cross-linked polybutadiene membranes, even considering the influence of the membrane thickness. The total pervaporation flux with bi-soft segment urethane/urea polymer membranes could be comparable with that of poly(ether block amide) (PEBA) membranes, however the ethanol selectivity was higher than that of the PEBA membrane.

4. Conclusions

Cross-linked bi-soft segment urethane/urea polymers were prepared. The two soft segments were highly dispersed in each other, and could even be molecularly mixed. The urethane/urea groups tended also to be more distributed. Consequently, the sorption and pervaporation selectivity towards ethanol for ethanol/water solution was improved, without a great flux reduction. The concept of bi-soft segment urethane/urea polymer used in this work is a strong asset on the tailoring of structure and properties in polymers and polymeric membranes.

Acknowledgements

C.T. Zhao gratefully acknowledges the financial support of the Institute of Science and Engineering of Materials and Surfaces (ICEMS)-Instituto Superior Tecnico. The authors gratefully acknowledge Prof. A. Diogo and Mr E. Baptista

Table 2
Membrane performance in ethanol/water pervaporation

Membrane	Feed	Membrane thickness	Selectivity factor	Total flux, g hr^{-1} cm^{-2}
Cross-linked polybutadiene [11]	10% ethanol, 25°C	∼ 300 μm	∼ 4.9	∼ 0.00012
Membrane I	ibid	∼ 60 μm	∼ 1.9	∼ 0.025
Membrane II	ibid	ibid	∼ 3.7	> 0.004
Membrane I	1% ethanol, 50°C	ibid	∼ 3.5	∼ 0.019
Membrane II	ibid	ibid	∼ 5.6	∼ 0.0094
Poly(ether block amide) [6]	ibid	50 μm	3.22	0.019

for the total accessibility to DMTA equipment and the scientific support and discussions relative to the DMTA experiments.

References

[1] Cooper SL, Tobolsky AV. J Appl Polym Sci 1966;10:1837.
[2] Blackwell J, Gardner KH. Polymer 1979;20:13.
[3] Fridman ID, Thomas EL. Polymer 1980;21:388.
[4] Brunette CM, MacKnight WJ. Rubber Chem Technol 1982;55:1413.
[5] Schneider NS, Matton RW. Polym Engng Sci 1979;19:1122.
[6] Boddeker KW, Bengtson G, Pingel H. J Membrane Sci 1980;54:1.
[7] Cipriano MM, Diogo A, de Pinho MN. J Membrane Sci 1991;61:65.
[8] Sterrazza RA, Escobosa R, Gooding CH. J Membrane Sci 1988;35:125.
[9] di Landro L, Pegoraro M, Bordogna L. J Membrane Sci 1991;64:229.
[10] Yoshikawa M, Wano T, Kitao T. J Membrane Sci 1993;76:255.
[11] Yoshikawa M, Wano T, Kitao T. J Membrane Sci 1994;89:23.
[12] Sung CSP, Schneider NS. Macromolecules 1977;10:452.
[13] Brunette CM, Hsu SL, MacKnight WJ. Macromolecules 1982;15:71.
[14] Lee HS, Wang YK, Hsu SL. Macromolecules 1987;20:2089.
[15] Lee HS, Hsu SL. Macromolecules 1989;22:1100.
[16] Coleman MM, Skrovanek D, Hu J-B, Painter PC. Macromolecules 1988;21:59.
[17] Coleman MM, Lee KH, Skrovanek D, Painter PC. Macromolecules 1986;19:2149.
[18] Strikovsky AG, Zharkov VV. Polymer 1993;34:3397.
[19] Luo N, Wang D-N, Ying S-K. Macromolecules 1997;30:4405.
[20] Tsubomura H. J Chem Phys 1956;24:927.
[21] Krimm S, Abe Y. Proc Natl Acad Sci USA 1972;69:2788.
[22] Beamont RH, Clegg B, Gae G, Herbet JBM, Sims D. Polymer 1966;7:401.
[23] Dianton FS, Evans DM, Hoave FE, Melia TP. Polymer 1962;3:297.
[24] Nishi T. CRC Crit Rev Solid State Mater Sci 1985;12(4):331.
[25] Mulder MHV, Smolders CA. J Membrane Sci 1984;17:289.
[26] Mulder MHV, Franken T, Smolders CA. J Membrane Sci 1985;22:155.