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ATR−FTIR Studies of Poly(propylene oxide)/Polybutadiene Bi-Soft Segment Urethane/Urea Membranes

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ABSTRACT: ATR−FTIR is used to investigate the hydrogen-bonding properties of urethane/urea polymers with two soft segments, poly(propylene oxide) and polybutadiene. The polymers are prepared by extending a poly(propylene oxide)-based triisocyanate-terminated prepolymer (PU) with poly(butadienediol) (PBDO). The C═O and N−H stretching bands in the spectra of the polymers are deconvoluted into five components, which are ascribed to different free and hydrogen-bonded groups. Results gave evidence of hydrogen bonding between hard/hard segments, leading to the formation of aggregates of urethane/urea groups. This aggregation changed upon variation of the proportion of the two soft segments in the membranes. The increase of PBDO content in the membranes leads to an improvement of the mixing of the two soft segments and also the decrease of the urethane/urea aggregation.

1. Introduction

Segmented polyurethanes are generally composed of a polyether or polyester soft segment and a polyurethane/urea hard segment. The composition on the latter varies, but it frequently involves the reaction product of an aromatic diisocyanate and an aliphatic diol. In the segmented polyurethanes, phase separation of the urethane/urea hard segments into microdomains has been observed even when the segment length is relatively short. The microphase separation is caused by the thermodynamic immiscibility between hard and soft segments. Factors that control the degree of microphase separation include copolymer composition, block length, crystallization of either segment, and the method of sample fabrication.

Polyurethanes are capable of forming several kinds of hydrogen bonds. In all cases, the hydrogen atom of the N−H group in the urea and urethane linkage is the donated proton, while the acceptor groups may include urethane C═O and urea C═O as well as the oxygen atom of the ester or ether linkage when a polyester or a polyether soft segment is present. Hydrogen bonding in polyurethanes has been the subject of numerous investigations using infrared spectroscopy.[1−9] Some of the localized vibrations such as the N−H stretching vibrations or C═O stretching vibrations are strongly perturbed by the formation of hydrogen bonds. Both the frequency shifts and intensities changes are characteristics of the specificity or magnitude of the hydrogen bonds formed. The intensity of each type of hydrogen-bonded vibration, if properly assigned, can potentially yield the degree of phase separation in the polyurethanes.

Up until the present time, studies of hydrogen bonding of polyurethanes by using infrared spectroscopy were mostly limited to polyurethanes formed by one hard segment and one soft segment. In the present work, we use infrared spectroscopy to analyze the hydrogen bonding of urethane/urea membranes with two soft segments, poly(propylene oxide) and polybutadiene. The urethane/urea bi-soft segments polymers were developed previously in our laboratory,[10] and it opened wide horizons on the tailoring of polymer films. In fact, the two soft segments were mixed or phase-separated to different degrees according to the proportions of the soft segments in the polymers, and associated with that, very different optical and mechanical properties were displayed.[11] In the present work, we use the ATR−FTIR to elucidate the phase behaviors of urethane/urea groups in these bi-soft polymers. As one of the two soft segments is a polyether, hydrogen bonding may occur between urethane/urea groups (hard/hard segments) and between the poly(propylene oxide) and urethane/urea groups (soft/hard segments). Estimation of segregation effects or mixing of hard and soft segments can therefore be obtained through the assessment of these two types of hydrogen bonding.

2. Experimental Section

2.1. Materials. The poly(propylene oxide)-based prepolymers with three isocyanate terminal groups were designated as PU. They were supplied by Portuguese Hoechst, S.A. Figure 1 shows its chemical structure. The molecular weight was approximately 3500. The polybutadienediol (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. Cross-linked membranes were prepared through the reaction of the isocyanate groups of PU with the hydroxyl groups of PBDO catalyzed by DBTDL at 70−80 °C (Figure 1). The ratio of PU and PBDO was varied to yield cross-linked polymers with different compositions.

2.3. ATR−FTIR Spectroscopy. ATR−FTIR spectroscopy was performed by means of a Perkin-Elmer 1600 spectrometer. Data were collected over 64 scans with a resolution of 2 cm^{-1}. The ATR measurements were made, at room temperature, on a KRS-5 crystal using a variable-angle ATR unit (Groseby Specou Ltd.) at a nominal incident angle of 45°. Optical alignment of the unit was set to achieve maximum throughput of the infrared beam to the detector.

Samples were taken at random from flat sheet membranes, cut to ATR crystal size (20 mm × 50 mm), and mounted on both sides of the trapezoid crystal.

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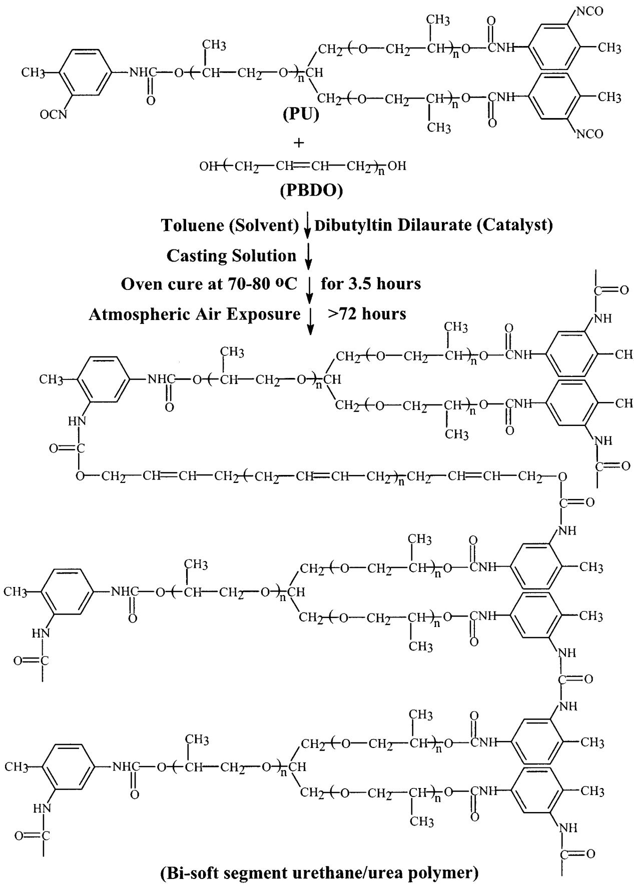

Figure 1. Preparation of poly(propylene oxide)/polybutadiene bi-soft segment urethane/urea membranes.

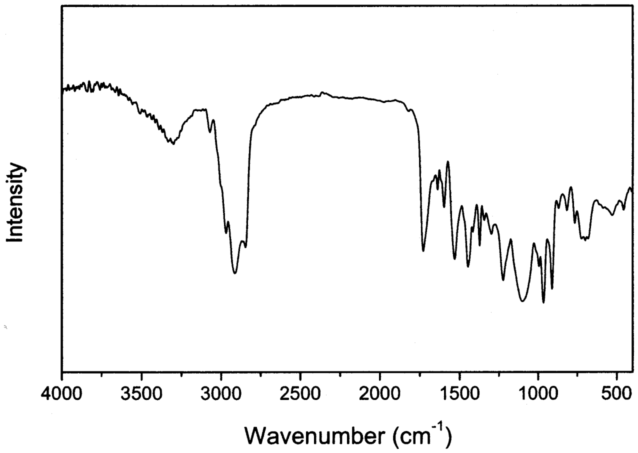

Figure 2. ATR−FTIR spectrum of the bi-soft segment urethane/urea membrane with 60 wt % PBDO.

2.4. Curve-Fitting Simulations. The curve-fitting simulations were performed using a standard Origin 5.1 software program. The ν(N−H) band and ν(C=O) band were deconvoluted considering peaks as Gaussian. Caution was taken in not overestimating the number of peaks since the additional degree of freedom afforded by too many peaks would always provide a better fit. The ν(C=O) bands were centered at 1730, 1710, 1690, 1665, and 1640 cm^{-1}, and the ν(N−H) bands were centered at 3180, 3275, 3315, 3430, and 3550 cm^{-1}.

3. Results and Discussion

Figure 2 shows a typical infrared spectrum (4000−500 cm^{-1}) of the urethane/urea bi-soft segments membranes (PU/PBDO). This spectrum is mainly characterized by bands at 3150−3500 cm^{-1} (NH stretching vibrations), at 2800−3000 cm^{-1} (CH stretching vibrations), at 1600−1800 cm^{-1} (C=O stretching vibrations), at 1530 cm^{-1} (NH in plane bending), and at 1080 cm^{-1} (C−O−C stretching vibration). As the major concern of this work focus on hydrogen bonding and their relation to the segregation of hard and soft segments, two especial regions are of main interest: the C=O stretching vibration from 1600 to 1800 cm^{-1} and the NH stretching vibration from 3150 to 3500 cm^{-1}.

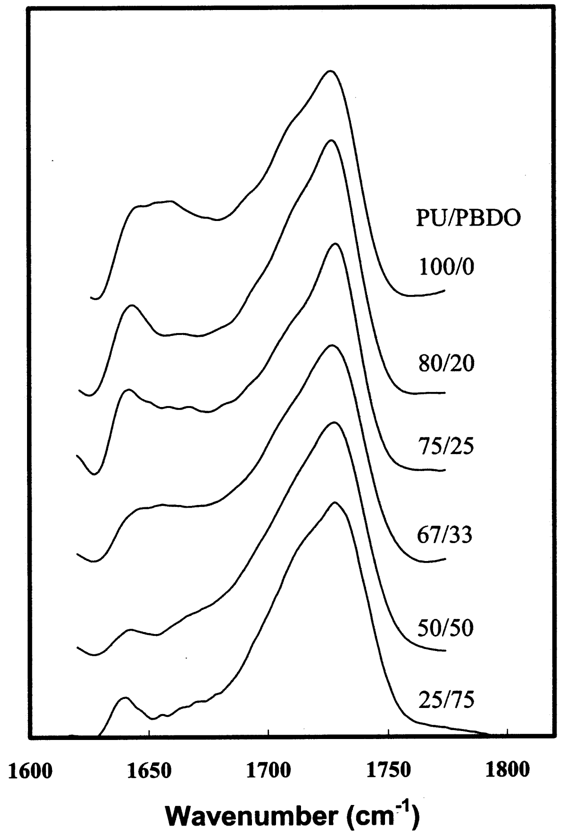

Figure 3. ATR−FTIR spectra in the carbonyl stretching region of PU/PBDO bi-soft membranes.

The C=O Stretching Region. Figure 3 shows the infrared spectra of the carbonyl stretching region for the PU/PBDO bi-soft segments membranes with different compositions. Multiple absorption bands are observed, which would reflect the complex properties of hydrogen bonding in the PU/PBDO membranes. All spectra are characterized by a major band centered at approximately 1730 cm^{-1}, attributed to free C=O urethane groups, and a shoulder at about 1710 cm^{-1}, which is ascribed to hydrogen-bonded urethane. We can also see for some compositions two weak shoulders at 1690−1700 and 1660−1675 cm^{-1}, attributed to free and disordered hydrogen-bonded urea carbonyl, respectively. The band centered at 1640 cm^{-1} corresponds to the hydrogen-bonded ordered urea carbonyl.

The main difference in the hydrogen bonding of the carbonyl urea groups and the carbonyl urethane groups is the capacity of the carbonyl moiety of the urea to interact simultaneously with two NH, forming hydrogen bonds in different directions. As a consequence, a three-dimensional structure of hydrogen-bonded urea groups can be formed. This give meaning to the term ordered hydrogen-bonded urea groups, and it has been reported by several authors in the literature.[9,12−14]

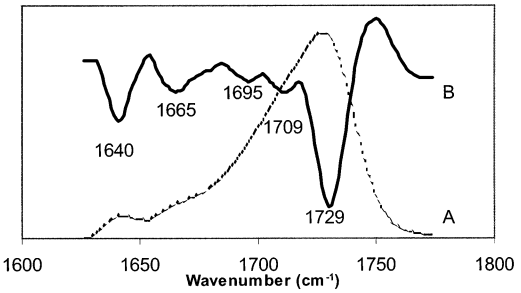

Figure 4. ATR−FTIR spectra of the bi-soft segment urethane/urea polymer with 50 wt % PBDO in the range 1600−1850 cm^{-1}: (A) absorbance spectrum; (B) second-derivative spectrum.

The PU/PBDO membranes do not crystallize, but they present a two-phase morphology originated by the immiscibility of the two soft segments, poly(propylene oxide) and polybutadiene, described in a previous work.[10] It is known from the literature[15,16] that in systems with microphase separation the microdomains of the different phases may form an ordered structure where the morphology depends on the fractions of each component. So, in the membranes studied in the present work, it is possible that the microdomains rich in poly(propylene oxide) and the microdomains rich in polybutadiene form a structure with certain degree of order. This could justify the presence of the ordered urea H-bonds.

Curve fitting of the carbonyl stretching region was performed. A linear baseline was drawn between 2000 and 850 cm^{-1}. The limits of the curve-fitting procedure were set between 1620 and 1780 cm^{-1}. Five Gaussian bands corresponding to free and hydrogen-bonded urethane carbonyl groups and free and hydrogen-bonded disordered and ordered carbonyl urea groups were employed in the fitting procedure. The frequencies of the bands used to find the five Gaussian curves were established from the second-derivative spectra of the bi-soft polymers. Second-derivative spectroscopy indicates the presence of five spectral components in the carbonyl stretching region of the bi-soft segment membranes. An example of a second derivative is shown in Figure 4 for the PU/PBDO membrane containing 50% of PBDO.

Figure 5 shows the simulation and deconvolution of the bands for the PU/PBDO membranes with different compositions. The frequency (ν), the width at half-height ($W_{1/2}$), and relative areas of the deconvoluted bands are shown in Table 1. The results obtained by curve-fitting procedures represent a quantitative but relative measure of the amount of different species. In these simulations, the values of the absorptivity coefficients of the different bands were not considered.

The frequency of the free and hydrogen-bonded urethane carbonyl stretching vibrations remained essentially constant for all PU/PBDO membranes, with values between 1727 $\pm$ 1 cm^{-1} ($W_{1/2} = 23 \pm 3$ cm^{-1}) and 1708 $\pm$ 2 cm^{-1} ($W_{1/2} = 15 \pm 4$ cm^{-1}), respectively.

For all compositions we also verify that the area of the free urethane carbonyl groups is higher than that one of the bonded urethane carbonyl. As reported in the literature,[7] the absorptivity coefficient of the hydrogen-bonded carbonyl is larger than the non-hydrogen-bonded carbonyl; therefore, we can surely state that most urethane carbonyls were not hydrogen bonded. Furthermore, it can be observed that, with the increase of PBDO content in the PU/PBDO bi-soft segments membranes, there is an increase of the area of the peak corresponding to free urethane carbonyl groups and a decrease of the peak area corresponding to the hydrogen-bonded urethane carbonyl. It means that the fraction of hydrogen bonding decreases with the increase of PBDO content.

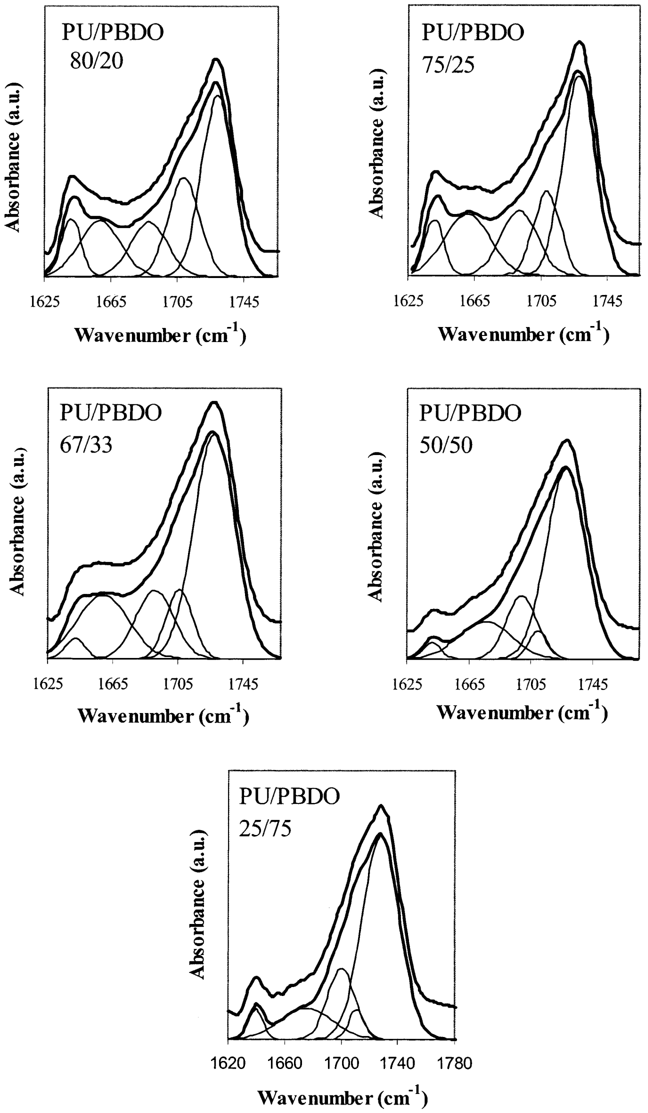

Figure 5. Experimental (upper curve) and simulated (lower curve) ATR−FTIR spectra in the C=O stretching region of PU/PBDO urethane/urea membranes.

For all membrane compositions, the contribution of the disordered hydrogen-bonded urea is higher than the ordered one. The increase of PBDO content leads to a decrease of the area of both disordered and ordered hydrogen-bonded urea peaks. This effect is more pronounced for the ordered hydrogen-bonded urea.

Related to the peak positions we verify that the frequency of free and disordered hydrogen-bonded urea carbonyl bands shift to higher values with the increasing of PBDO content in PU/PBDO membranes. This indicates that the local environment around these urea carbonyls groups change with sample composition. The shift to higher frequency implies that the strength of the hydrogen bond is becoming weaker.

The NH Stretching Region. The NH stretching vibration yields complementary structural information to the C=O stretching vibration. NH groups can form hydrogen bonding with C=O groups of the hard segments as well as with ether groups of the soft segment.

Table 1. Frequency (ν), Width at Half-Height ($W_{1/2}$), and Relative Area (*A*) of the Five Components of the C=O Stretching Band

	urethane						urea								
	free			hydrogen bonded			free			hydrogen bonded: disordered			hydrogen bonded: ordered		
polybutadiene content in PU/PBDO membranes (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	*A* (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	*A* (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	*A* (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	*A* (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	*A* (%)
20	1729	19	40	1709	19	21	1688	22	14	1658	25	16	1641	12	8
25	1728	20	43	1709	16	15	1692	22	16	1661	27	19	1641	12	7
33	1727	25	53	1706	16	11	1691	23	15	1659	31	19	1642	12	2
50	1727	26	61	1710	12	4	1699	20	16	1675	34	16	1641	12	2
75	1728	26	62	1711	11	4	1700	20	18	1674	35	13	1640	10	4

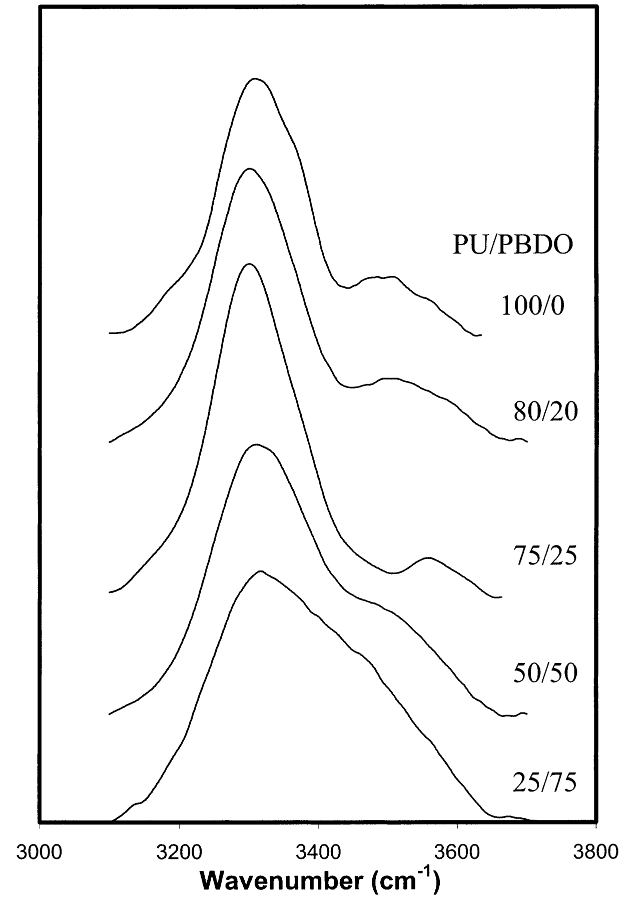

Figure 6. ATR−FTIR spectra in the NH stretching region of PU/PBDO bi-soft membranes.

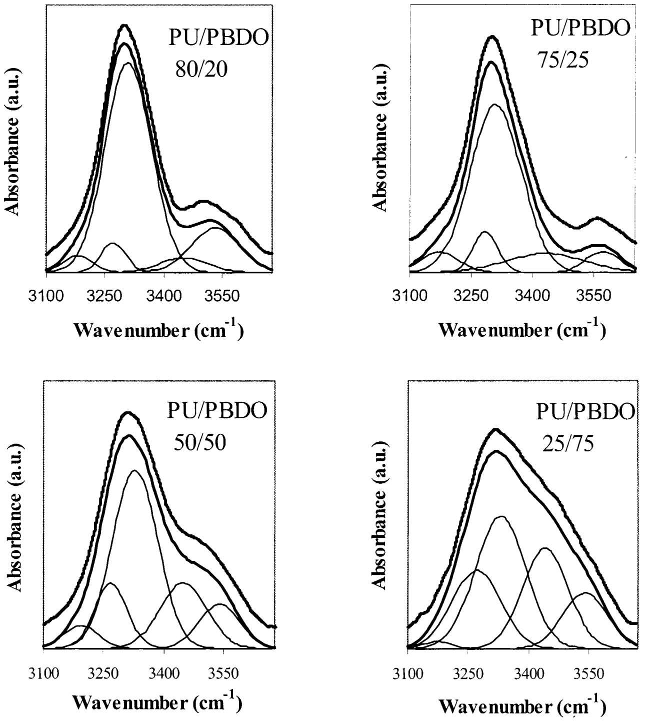

Figure 7. Experimental (upper curve) and simulated (lower curve) ATR−FTIR spectra in the NH stretching region of PU/PBDO urethane/urea membranes.

Figure 6 shows the ATR−FTIR spectra of NH stretching region for the PU/PBDO membranes with different relative amounts of the two soft segments. For all of them, the NH stretching vibration exhibits a strong absorption peak centered at around 3310 cm^{-1}, arising from the NH hydrogen bonded. The free NH stretching vibration appears as a shoulder at about 3440 cm^{-1}. The intensity of this shoulder increases with the increase of PBDO content in the membranes.

In Figure 6 are also observed small contributions from a two-photon band at approximately 3180 cm^{-1} and from a band at around 3550 cm^{-1}.

Deconvolution of NH stretching region is performed and Gaussian functions are used. A flat baseline was chosen from 3800 to 2500 cm^{-1}. The limits of the curve-fitting procedure were set between 3100 and 3700 cm^{-1}. Considering the polyurethane literature, the band region was resolved into five components. The peak centered at 3440 cm^{-1} corresponds to the free NH stretching mode. Other two bands have been assigned to NH bonded to carbonyl groups at 3315 cm^{-1} and NH bonded to the ether oxygen. With respect to this last one, some authors[5,6,8] have reported that the stretching vibration of NH- - -O− hydrogen bond occurs at 3295 cm^{-1} while other authors[6,17] verified this same absorption at lower frequency. Christenson et al.,[17] for example, observed this band at 3258−3265 cm^{-1}. Latter, Teo et al.[6] reported that the NH- - -O− hydrogen bond appears at around 3264−3280 cm^{-1}. In this work the band of NH bonded to the ether oxygen were centered at around 3275 cm^{-1}. The last two bands of the curve fitting were centered at 3180 and 3550 cm^{-1}.

Figure 7 shows the simulation and deconvolution of the bands for the PU/PBDO membranes with different compositions. Table 2 shows the relative areas and the widths at half-height of the three of spectra components relative to free and hydrogen-bonded NH groups. The bandwidths of the deconvoluted components change significantly. The width at half-height of the band corresponding to NH hydrogen bonded to carbonyl groups increase from 61 to 121 cm^{-1} as the PBDO content is increased. This can be interpreted as a broadening of the distribution of the hydrogen-bonded distances and geometries as the PBDO content increases.

Table 2. Relative Area (*A*) and Width at Half-Height ($W_{1/2}$) of the Three Components of the NH Stretching Band

			hydrogen bonded			
	free		NH- - -O═C		NH- - -O-	
polybutadiene in membranes (%)	*A*, %	$W_{1/2}$, cm^{-1}	*A*, %	$W_{1/2}$, cm^{-1}	*A*, %	$W_{1/2}$, cm^{-1}
20	5	122	70	64	5	118
25	12	185	69	61	8	125
50	19	118	50	82	14	113
75	26	115	38	121	21	127

The peak areas corresponding to the free NH groups increase with the increase of PBDO content in the membranes. This is in accordance with the results of the free carbonyl groups. It is clear from the curve-fitting results that most NH stretching vibrations are hydrogen bonded. This is opposite to carbonyl stretching results that showed that most carbonyl vibrations are free of hydrogen bonds. This is partially attributed to the different absorptivity coefficient ratios of the two spectral regions (C═O and N−H). The absorptivity coefficients of hydrogen-bonded carbonyl and non-hydrogen-bonded carbonyl differ but there are not widely disparate.[7] As the absorptivity coefficient of the hydrogen-bonded carbonyl is larger than the non-hydrogen-bonded carbonyl, we can surely state that most urethane carbonyls were not hydrogen bonded. In the case of the NH stretching vibrations, the absorptivity coefficients of the free and hydrogen-bonded stretching vibrations are very different. The absorptivity coefficient of free NH stretching vibrations is much smaller than the absorptivity coefficient of the hydrogen-bonded NH,[18,19] which makes detection of free N−H groups difficult. Moreover, another fact that can contribute to the difference in the areas of C═O and N−H is the fact that NH groups make hydrogen bonds with both carbonyl and ether oxygen groups.

It can also be verified from the results of curve fitting that the area of the peaks corresponding to NH hydrogen bonded to carbonyl groups decreases with the increase of PBDO content in the membranes, while the peak areas corresponding to NH hydrogen bonded to ether oxygen groups increase with the increasing PBDO contents. This implies that a fraction of NH groups are hydrogen bonded to the ether of the poly(propylene oxide) soft segments, and this fraction increases with the increase of PBDO content.

Estimation of segregation effects or mixing of the hard and soft segments in polyurethanes can be obtained through the assessment of the type and extension of hydrogen bonding. If there is significant N−H- - -O═C hydrogen bonding, since both groups involved are associated with the hard segments, then phase separation occurs. On the other hand, the observation of N−H- - -O− hydrogen bonding suggests the mixing of hard and soft segments.

In this work it was detected the hydrogen bonding between NH and C═O groups, which suggests the formation of aggregates of urethane/urea groups. This aggregation varies upon variation of the ratio of the two soft segments. In fact, the urethane/urea aggregation decreases with the increase of the PBDO content in the membranes; this was verified by the decreasing of the fraction and strength of NH- - -O═C hydrogen bonding. The decrease of the degree of hydrogen bonding can be explained on the basis of the size of the hard segments. In this bi-soft membrane, two different hard segments can be formed (Figure 1): (1) the hard segments originated by the reaction of two segments of poly(propylene oxide), which consist of two urethane groups linked by two toluene and one urea group; (2) the hard segment originated by the reaction of one segment of poly(propylene oxide) and one segment of polybutadiene, which consist of two urethane groups linked by one toluene group. This last hard segment is shorter than the first one. So, with the increase of PBDO content in the membranes, the number of urea linkage decreases and more hard segments composed by two urethane groups and one toluene are formed. As this hard segment is shorter than the other one, it will be more difficult for them to segregate.

Furthermore, it was also verified, by the results of NH stretching region, that the mixing of the hard segments with poly(propylene oxide) increase with the increasing of PBDO content. So, we can say that with the increase of PBDO content the freedom of the hard segments is improved, and some mixing with the soft segments is allowed.

As related in a previous work,[10] the two soft segments of the PU/PBDO membranes, poly(propylene oxide) and polybutadiene, were in principle thermodynamically immiscible below room temperature. So, the two soft segments favored the formation of separate microphases. However, with increasing polybutadiene content, the mixing of the two soft segments increases until that they become molecularly mixed.

From the present work we can say that the variation of the ratio of poly(propylene oxide)/polybutadiene leads to polymers with different degree of aggregation of urethane/urea groups. The increase of PBDO content in the membranes leads not only to improve of mixing between of the two soft segments but also to the mixing of hard and soft segments.

4. Conclusion

Changes in the frequency, intensity, and relative area of the C═O and NH absorption bands have been studied in poly(propylene oxide)/polybutadiene bi-soft segments urethane/urea polymers, and these results were correlated to structural changes.

The results obtained gave evidence that in PU/PBDO membranes aggregates of hard segments (urethane/urea groups) are formed. This aggregation decreased with the increasing PBDO content in the polymers, and the urethane/urea groups increased their mixing with the soft segments.

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