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Structural characteristics and gas permeation properties of polydimethylsiloxane/poly(propylene oxide) urethane/urea bi-soft segment membranes

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Abstract

Segmented polyurethane/urea membranes, containing two soft segments, poly(propylene oxide) and polydimethylsiloxane, were prepared by extending a polypropylene oxide-based tri-isocyanated prepolymer (PU) with polydimethylsiloxane bis(hydroxyalkyl) terminated (PDMS). PU/PDMS membranes were characterized by infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and by the gel content. It was concluded that the two soft segments are phase separated and the urethane/urea groups form small aggregates somewhere in these two phases. Gas permeation experiments led to the conclusions that the permeabilities of CO_2, O_2 and N_2 increased with the increase of PDMS membrane content, while the permeability ratios, $P(CO_2)/P(N_2)$ and $P(O_2)/P(N_2)$ did not significantly changed. The membrane with highest PDMS content and highest permeabilities is characterized by a lower degree of cross-linking and by a lower contribution of hydrogen bonding between hard segments.

Keywords: Urethane/area polymer; Membrane structure; Gas permeation

1. Introduction

The polyurethanes are multi-block copolymers usually consisting of hard and soft segments. The hard segments are based on diisocyanate and/or a chain extender, while the soft segments are typically polyester or polyether. These alternating hard and soft segments structures are responsible for the very interesting physical and mechanical properties displayed by these materials. Their applications are varied, such as medical implants, membranes, adhesives and coatings.

Polydimethylsiloxane polymers have many applications due to their unique properties, which arise mainly from the nature of the siloxane bond [1–3]. These properties include the low glass-transition temperature, low surface energy, high permeability to gases and very good thermal stability. However, they exhibit very poor mechanical properties.

The possibility of combining the advantages of polyurethanes and polysiloxanes has attracted particularly attention of many researchers in the last decades [4–10]. These combinations would have better heat resistance and lower temperature flexibility than polyurethanes themselves and better mechanical strength and abrasion characteristics than polysiloxanes.

The study of gas transport properties through polyurethane membranes is especially interesting because the molecular structure of the polymer chain can be easily changed. Various researchers [11–17] have shown that the gas permeability of polyurethane membranes increases with the decrease of the hard segment content and the increase of the soft segment molecular weight. In addition, a correlation has been established between the gas permeability and the chemical nature of the polyols and chain extenders. It affects the transport properties of polyurethane membranes through the modification of the phase separation domain, polyfunctional cross-linking, crystallinity, density and glass transition of the membranes. Despite the many studies on the gas permeation properties of polyurethanes based in

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polyether or polyester, there are a few studies on the gas permeation of polyurethanes based in polysiloxane [18,19].

The versatility of the structure design of bi-soft segment polyurethanes is used in the present work to obtain membranes with different structures and gas permeation properties. Novel urethane/urea polymer membranes with two soft segments, where one of the soft segments is a polyether and the other one is a polysiloxane, were prepared. The relationships between structure and gas permeation properties of the obtained materials were studied.

2. Experimental part

2.1. Materials

Poly(dimethylsiloxane), bis(hydroxyalkyl) terminated (PDMS) with a number average molecular weight of 5600 was obtained from Aldrich. Polypropylene oxide-based prepolymers with three isocyanate terminal groups (PU) and molecular weight of approximately 3500, was supplied by Portuguese Hoechst. The structures of these oligomers are given in Fig. 1. 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 synthesis

Polyurethane/urea membranes were prepared through the co-dissolution of PU and PDMS in toluene and 1–2 drops of DBTDL were added. The polymer solutions were prepared by changing the weight ratio of PU/PDMS to yield membranes with a wide range of siloxane content. The total solid content of the solutions was about 20 wt%. The solutions were stirred for 2 h at 60 °C, under dry N_2 atmosphere. Subsequently, the solutions were cast onto glass plates and heated at 70–80 °C for 3 h. The film was exposed to air and continued curing for at least 24 h by atmospheric moisture.

2.3. Membrane characterization

The gel content of the membranes was determined by Soxhlet extraction using toluene for 24 h. The insoluble materials were dried under vacuum for about 2 days and weighed. The gel content of the membranes was determined from the difference in weight before and after the extraction operation.

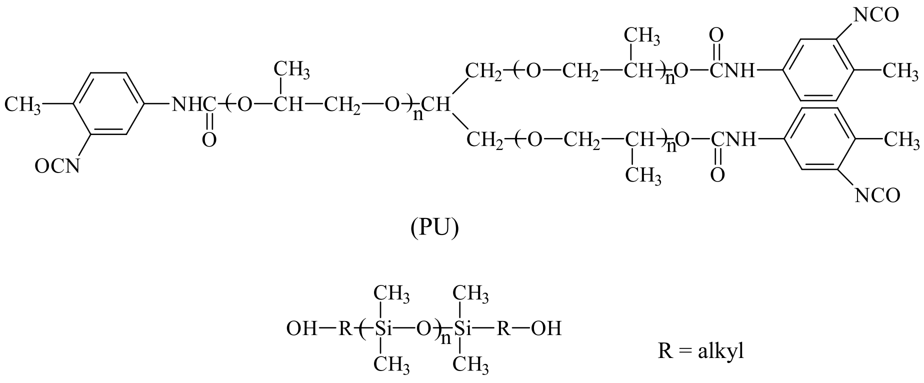
The analysis of glass transition temperature of the membranes was performed on a modulated differential scanning calorimeter, MDSC TA-I 2920. Temperature scan was run from −150 to 50 °C at a heating rate of 5 °C/min.

The bulk morphology of the membranes was analyzed by transmission electron microscopy (TEM). The membranes were ultra-microtomed into 60 nm thick sections. The electron microscopy was taken with a Carl Zeiss CEM 902 instrument using an accelerating voltage of 80 kV.

The molecular structure of the membranes was analyzed by ATR-FTIR spectroscopy, which 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°. Samples were taken randomly from flat sheet membranes, cut to ATR crystal size (20 × 50 mm) and mounted on both sides of the trapezoid crystal.

2.4. Gas permeability measurements

Gas permeation experiments were carried out for carbon dioxide, oxygen and nitrogen. The method used to measure the gas permeability was the constant pressure or variable volume method. For the measurements we built a system where a gas inlet and vent are connected to the bottom plate of the permeability cell while a flow meter is connected to



(PU)

(PDMS)

Fig. 1. Chemical structures of polydimethylsiloxane and poly(propylene oxide) based oligomers used in the reactions.

the top plate. The feed pressure used ranged from 1 to 5 bar and the effective membrane surface area was 27.3 cm^2.

The gas permeability was determined by the following equation:

$$P = (qL)/(P_1 - P_2)At$$

where P is the gas permeability (cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}), q/t is the volumetric flow rate of the gas permeation, L is the membrane thickness, P_1 and P_2 are the pressures and A is the effective membrane area.

3. Results and discussion

3.1. Polymer synthesis

The urethane/urea bi-soft segment membranes were synthesized by the reaction of the hydroxyl PDMS endgroups with the isocyanate PU endgroups, leading to the formation of urethane linkages. Urea linkages are also formed during film curing through reaction with atmospheric moisture of the non-reacted isocyanate endgroups. An ideal structure of the PU/PDMS membranes is given in Fig. 2.

A series of cross-linked urethane/urea membranes was obtained by varying the ratio of PU and PDMS. The gel content for the various membranes is shown in Table 1. It can be seen that the membranes with PDMS content equal to or lower than 50 wt% are highly cross-linked. An accentuated decrease of the degree of cross-linking is verified when the PDMS content is increased to 75 wt%. This result is in accordance with the functionality of the PU and PDMS that were three and two, respectively. Thus, when the PU/PDMS ratio is lower than 2:3, the amount of hydroxyl groups was lower than the one of the isocyanate groups, and the resulting films were still highly cross-linked. With the increase of PDMS content, a few hydroxyl groups were left unreacted, leading to a decrease of the degree of cross-linking.

3.2. Structure analysis

The molecular structure of the PU/PDMS membranes was characterized by ATR-FTIR spectroscopy. The spectra of the membranes synthesized with different proportions of the two soft segments are shown in Fig. 3. An absence of one NCO peak at 2270 cm^{-1} indicates that the isocyanate reaction was complete. The signals of the urethane linkages appear at 3300 cm^{-1} (N–H stretching) and 1700–1730 cm^{-1} (C=O stretching). The formation of urea linkage is also

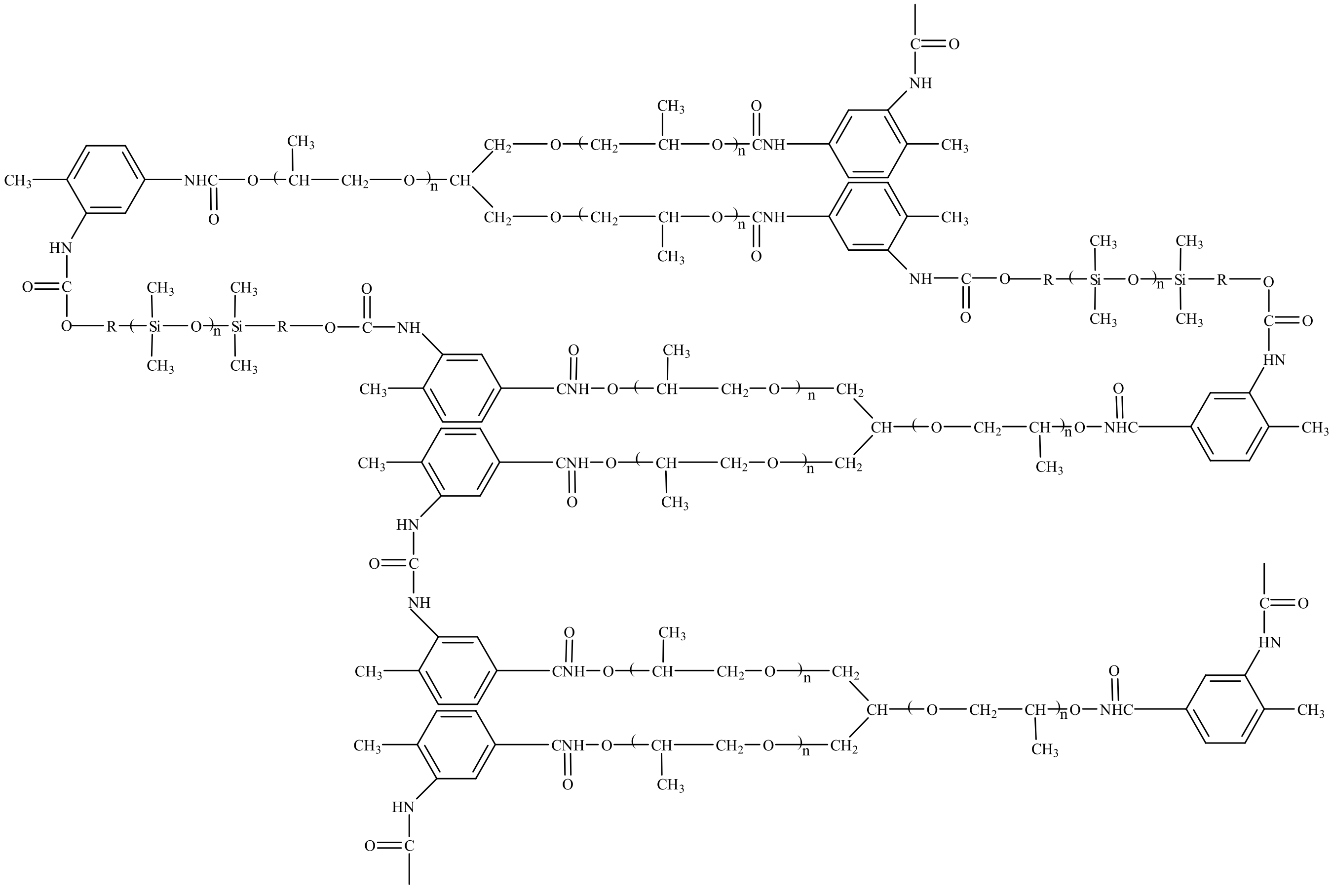


Fig. 2. Chemical structure of PU/PDMS urethane/urea bi-soft segments membranes.

Table 1
Gel content and glass-transition temperature (T_g) of PU/PDMS urethane/urea membranes

PDMS content (%)	Gel content (%)	T_g (°C)
25	90	−130, −52
40	89	−127, −52
50	87	−126, −52
75	65	−124, −60

confirmed by the bands around 3320 cm^{-1} (urea N–H stretching) and 1645–1690 cm^{-1} (urea C=O stretching). The peak at 1000–1100 cm^{-1} (Si–O–Si stretching) is associated to the PDMS, whereas the peaks at 1260 cm^{-1} (symmetric CH_3 bending), 800 cm^{-1} (CH_3 rocking) and 2960 cm^{-1} are related to the methyl group, that is present in both soft segments but is especially present in the main chain of the PDMS soft segment. Thus, the intensity of the peaks related to CH_3 and to the Si–O–Si stretching vibration increases with the increase of the PDMS content in the membranes.

The ATR-FTIR spectra may also yield information about the interactions of hydrogen bonding that occur in the PU/PDMS urethane/urea membranes. 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 ether linkage of the polyether soft segment.

In the infrared spectra, two regions can be used to characterize hydrogen bonding of urethane or/and urea groups: the region at approximately 3500–3000 cm^{-1} related to the N–H stretching vibration and the region at approximately 1750–1600 cm^{-1} related to the carbonyl C=O stretching vibration. These vibrations are strongly perturbed by the formation of the hydrogen bonds. Both frequency shifts and intensities are characteristics of the specificity or magnitude of the hydrogen bonds formed. The quantification of the hydrogen bonding of urethane/urea groups in the N–H stretching region has shown some limitations [20]. On the other hand, the carbonyl region has been widely used to characterize, at least semiquantitatively, the hydrogen bonding of polyurethanes [21–24], and this is object of investigation in the present work.

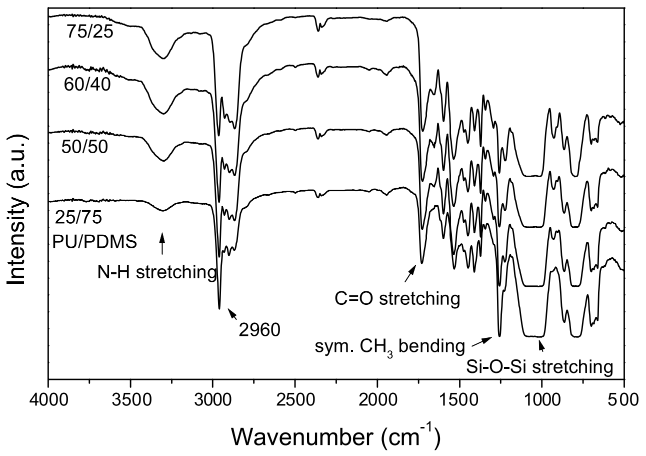


Fig. 3. ATR-FTIR spectra of PU/PDMS urethane/urea bi-soft segment membranes.

Fig. 4 shows the infrared spectra of the carbonyl stretching vibration region for the membranes with different PU/PDMS compositions. A broad peak formed by several band contributions characterizes all spectra. A major band is centered at about 1730 cm^{1}, attributed to free C=O urethane groups, and a shoulder at 1710 cm^{-1}, is ascribed to hydrogen-bonded urethane. For some compositions there is also two weak shoulders at around 1690 cm^{-1} and 1660 cm^{-1} attributed to free and disordered hydrogen-bonded urea carbonyl. The band centered at 1645 cm^{-1} corresponds to the ordered hydrogen-bonded urea carbonyl. This band is not present in the membrane contaning 75 wt% of PDMS.

In previous works of polyurethanes, the C=O absorption region was fitted to two components, one related to the free urethane and the other to the hydrogen-bonded urethane groups [25,26]. The first infrared studies of polyurethane/urea split the carbonyl absorption of the urea groups into two components, in the same way that for polyurethanes [27]. The peak in the vicinity of 1700 cm^{-1} was related to non-associated C=O and the peak around 1640 cm^{-1} to hydrogen-bonded C=O. Latter, an additional peak was found between these two at approximately 1660 cm^{-1}, and a disordered hydrogen-bonded urea group was invoked, leaving the peak at 1640 cm^{-1} as belonging to ordered hydrogen-bonded urea groups [28]. The work of Born and Hespe [29] on model ureas demonstrated that the urea groups could form bifurcated hydrogen bonds with each carbonyl oxygen bonded to both N–H dipoles of the opposite urea group. This originated the term ordered hydrogen-bonded urea groups, and the peak at lower frequency was then attributed to the bifurcated hydrogen bonds.

It was performed a curve fitting of the C=O stretching vibration region. Five gaussion bands corresponding to free and hydrogen-bonded urethane carbonyl groups, free carbonyl urea groups, disordered and ordered hydrogen-bonded carbonyl urea groups were employed in the fitting procedure. The frequencies of the bands used to find the five gaussion curves were stablished from the second-derivative spectra of the membranes. In the spetra of the membranes with PDMS content lower than 75 wt%, the peaks at 1730, 1710, 1690, 1660 and 1645 cm^{-1} could be resolved. In the membrane with 75 wt% PDMS content, only four peaks were observed at 1730, 1710, 1690 and 1660 cm^{-1}. For this composition, there is no contribution of the ordered hydrogen-bonded urea carbonyl groups. This band can be originated by the ordering of microdomains in systems presenting microphase separaration structures.

Curve-fitting results for the spectra are listed in Table 2. The results obtained by curve-fitting procedures represent a quantitative but relative measure of the amount of different

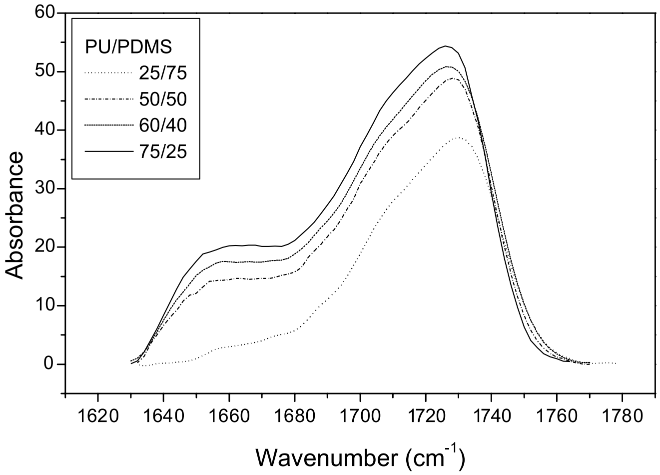


Fig. 4. ATR-FTIR spectra in the carbonyl stretching region of PU/PDMS bi-soft segment membranes.

species. In these simulations, the values of the absorptivity coefficients of the different bands were not considered. In the Table 2 is also presented the total area of urethane groups ($\sum$Area UT), the total area of urea groups ($\sum$Area UA), the degree of hydrogen bonding of urethane groups ($X_{b,UT}$) and the degree of hydrogen bonding of urea groups ($X_{b,UA}$). These last ones were defined as follows [24]:

$$X_{b,UT} = \frac{1}{1 + \text{Area}(1730\ \text{cm}^{-1})/\text{Area}(1710\ \text{cm}^{-1})}$$

$$X_{b,UA} = \frac{\sum \text{Area(bonded)}}{\text{Area}(1690\ \text{cm}^{-1}) + \sum \text{Area(bonded)}}$$

From the Table 2 we can notice that the increase of PDMS is followed by the increase of the urethane groups ($\sum$Area UT), it means free and hydrogen-bonded urethane, and the decrease of the urea groups, free and hydrogen-bonded urea ($\sum$Area UA). This was expected since the increase of PDMS in the membrane preparation, leads to the formation of more urethane linkages, due to the presence of higher amount of hydroxyl groups that react with isocyanate. This was indirectly observed through the values of gel content that decreased with the increase of PDMS content, as reported earlier.

Relatively to the hydrogen bonding, the degree of urethane hydrogen bonding decreases with the increase of PDMS content. For urea groups, the degree of hydrogen bonding does not vary for membranes with PDMS content up to 50 wt%, but it decreases when the PDMS content increases to 75 wt%.

Estimation of segregation effects 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$\cdots$O=C hydrogen bonding, since both groups involved are associated with the hard segments, then phase separation occurs [30,31]. This work presents clear evidence of hydrogen bonding between NH and C=O groups, that suggest 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 PDMS content in the membranes. An analogous behavior has been verified in bi-soft segments polymers based in polypropylene oxide and polybutadiene [32].

3.3. Thermal analysis

Thermal transitions of the PU/PDMS urethane/urea membranes were investigated by DSC. The DSC diagrams are showed in Fig. 5 and the glass-transition temperatures (T_g) of the membranes are displayed in Table 1. The membranes show two glass-transition temperatures, the first around −130 °C and the second around −60 °C, representing the T_g for polydimethylsiloxane and for poly(propylene oxide), respectively. The T_g of the siloxane soft segment shifted from −130 to −124 °C when the PDMS content in the membranes increased from 25 to 75 wt%, while the T_g of the poly(propylene oxide) soft segment moved from −52 to −60 °C. The presence of two T_gs indicated that the two soft segments in the membranes are phase-separated.

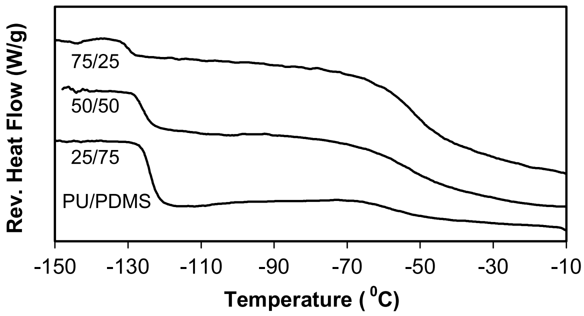


Fig. 5. DSC heating curves of PU/PDMS urethane/urea bi-soft segments membranes.

Table 2
Curve-fitting results for C=O region of ATR-FTIR spectra of PU/PDMS membranes

PDMS content (%)	Peak areas (%)					$\sum$Area UT (%)	$\sum$Area UA (%)	$X_{b,UT}$	$X_{b,UA}$
	$1730\ cm^{-1}$	$1710\ cm^{-1}$	$1690\ cm^{-1}$	$1660\ cm^{-1}$	$1645\ cm^{-1}$				
25	29	31	24	12	5	60	41	0.52	0.41
40	39	24	22	11	4	63	37	0.38	0.41
50	39	25	21	12	3	64	36	0.39	0.42
75	56	29	11	4	–	85	15	0.34	0.27

3.4. Morphological analysis

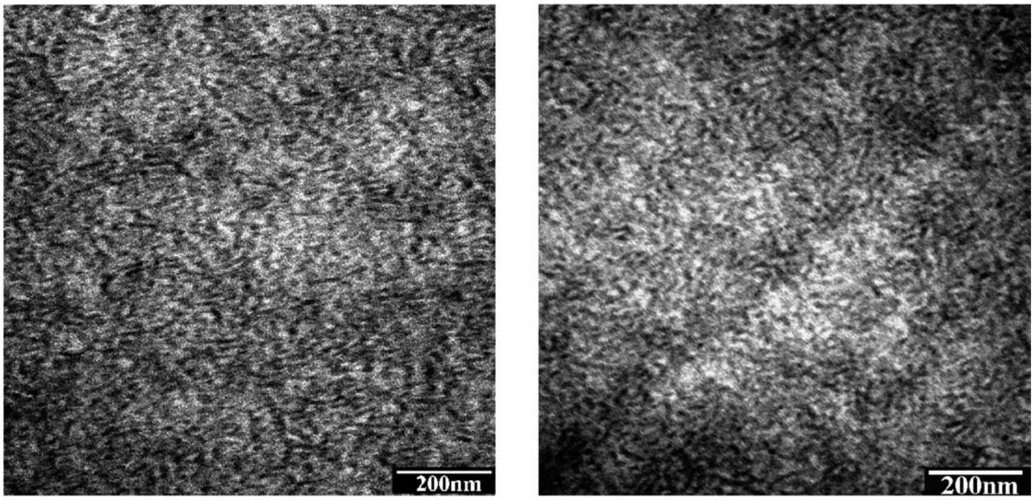
The microphase-separated structures of the membranes were confirmed by transmission electron microscopy observations. Fig. 6 shows the micrographs of the bulk morphology of the membranes with 25 wt% and 75 wt% PDMS content. In this TEM analysis, it was not necessary to submit the sample to staining, due to the significant difference in electron density between inorganic polydimethylsiloxane segments and the hydrocarbon based poly(propylene oxide) segments. The siloxane regions, characterized by higher electron densities were more resistant to the transmittance of electrons and, therefore, appear darker in the TEM images. The membranes show a fine co-continuous phase-separation structure. The same type of morphology was reported by Wang et al. [10], for segmented siloxane-urethane/urea copolymers. All the PU/PDMS membranes with PDMS contents ranging from 25 to 75 wt% presented the same type of morphology. The TEM micrographs did not give evidence of significant morphological changes.

The most important driving factor to phase-separation between the two soft segments, observed in the PU/PMDS membranes, is the difference of the solubility parameters, δ. For PDMS, δ is 14.9–15.3 $J^{1/2}/cm^{3/2}$ [19] and for the polyether segment, polypropylene oxide, δ is 17.3 $J^{1/2}/cm^{3/2}$ [33]. Such a difference between solubility parameters gives rise to phase separation between the segments in the solid state.

3.5. Gas permeation properties

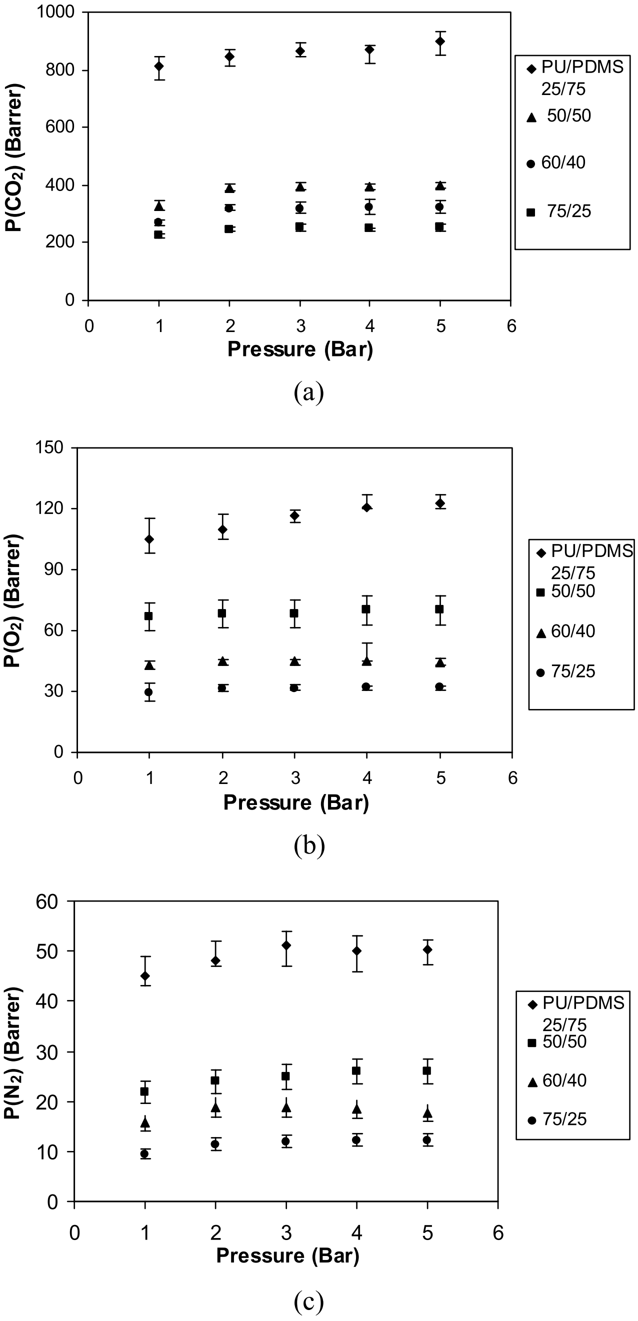
The permeability to carbon dioxide, oxygen and nitrogen for the urethane/urea membranes with different ratios of PU/PDMS is showed in Fig. 7 as function of feed pressure. For all the membranes, the permeabilities decrease in the order $P(CO_2) > P(O_2) > P(N_2)$. The higher CO_2 permeability is probably due to the relative high solubility of CO_2 in the membranes when compared with O_2 and N_2.

The permeability of CO_2, O_2 and N_2 for all membranes is practically independent of the upstream pressure. The permeabilities of the membranes to the three gases increase with the increase of the PDMS content. The higher permeability of the membrane containing 75 wt% of PDMS may be attributed to the higher fraction of siloxane segments that form a elastomeric phase which has a high backbone flexibility. As the PDMS soft segments have much lower T_g than the PU soft segments, the gas permeation should occur preferentially through the PDMS microdomains.



(a) (b)

Fig. 6. Transmission electron micrographs of PU/PDMS urethane/urea membrane containing (a) 25 wt% and (b) 75 wt% PDMS content.



(a)

(b)

(c)

Fig. 7. Gas permeability of the PU/PDMS bi-soft urethane/urea membranes with different compositions versus feed pressure. (a) CO_2, (b) O_2 and (c) N_2.

Other factor that may contribute to the higher permeability of the membrane with 75 wt% PDMS content is its lower degree of cross-linking. The decrease of the cross-linking degree usually results in an increase of membrane permeability, since the existence of a cross-linking network restricts the mobility of the molecular chains.

The aggregation of urethane/urea groups would also have some effect on the gas permeabilities of the membranes. The literature relative to polyurethanes [34–37] reports that the increase of phase separation between hard and soft segments, leads to the increase of membrane gas permeability. In the present work we have a very distinct situation as we are dealing with polyurethanes containing two soft segments, that are phase-separated and the short urethane/urea groups are located somewhere in these phases. The aggregation of urethane/urea groups containing aromatic rings will form points with higher rigidity that would reduce the mobility of the polymer chains. The decrease of the aggregates will decrease these rigid points, increasing the membrane gas permeability.

Fig. 8 shows the effect of PDMS segment content on the permeability ratio of $P(O_2)/P(N_2)$ and $P(CO_2)/P(N_2)$ of PU/PDMS urethane/urea membranes at 5 bar. The permeability ratio of O_2 over N_2 practically does not change with the membrane composition and is approximately equal to 2.4. For the $P(CO_2)/P(N_2)$ selectivity we can verify that the membrane with 25 wt% of PDMS content has an higher value of this permeability ratio, 21, when compared to the other membranes where this ratio is 18. The values of $P(O_2)/P(N_2)$ and $P(CO_2)/P(N_2)$ reported in the literature for pure PDMS are 1.9 and 7.4–8.6, respectively [18,38]. In comparison with the results for pure PDMS from the literature, an improvement of the $P(CO_2)/P(N_2)$ permeability ratio also accompanied by a permeability reduction, is verified in the PU/PDMS membranes. The lower permeability of the PU/PDMS membranes should be related to the phase-separation morphology of the films. As we demonstrated the membranes present a co-continuous phase-separation structure, producing a tortuous pathway for the diffusion of the molecules.

4. Conclusions

Urethane/urea bi-soft segments membranes were prepared from polydimethylsiloxane bis(hydroxyalkyl) terminated and polypropylene oxide tri-isocyanate terminated. In

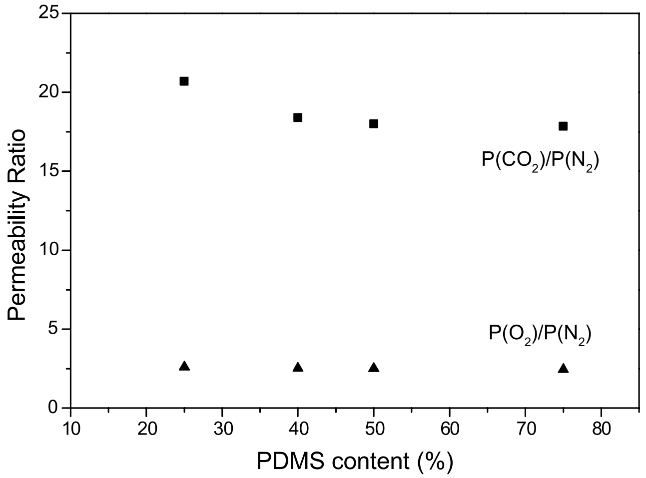


Fig. 8. Effect of PDMS content on the selectivity of O_2/N_2 and CO_2/N_2 of PU/PDMS bi-soft segment urethane/urea membranes at 5 bar.

the membranes with PDMS contents ranging from 25 to 75 wt%, DSC and TEM analysis gave evidence of soft/soft segment phase-separation where the short hard segments should be located somewhere in these two phases. The ATR-FTIR has shown that the urethane urea groups interact by hydrogen bonds and can form small aggregates. This aggregation decreased with the increase of PDMS content. The permeability of the membranes to CO_2, O_2 and N_2 increased with the increase of PDMS. The higher permeability of the membrane containing 75 wt% of PDMS was attributed to the higher fraction of siloxane segments, lower degree of cross-linking and lower aggregation of urethane/urea groups. The $P(CO_2)/P(N_2)$ permeability ratio was higher for the bi-soft segment membranes described in this work than in case of PDMS pure.

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