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Positron studies of the temperature-dependence of free volumes in Polydimethylsiloxane/poly(propylene oxide) urethane/urea membranes

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Abstract

Free-volume parameters in polyurethane/urea membranes have been studied by positron annihilation lifetime and Doppler broadening measurements. The bi-soft segment membranes were obtained by varying the ratio of the structural constituents, polypropylene oxide and polydimethylsiloxane (PU/PDMS), with PDMS content from 25 to 75 wt%. The free-volume holes determined by PALS are correlated with gas permeation features. The phase separation of the various soft and hard segments in the membranes is mirrored in both lifetime and Doppler results.
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1. Introduction

Polyurethanes, extensively used in different applications (medical implants, membranes, adhesives, coatings, etc.) usually exhibit a two-phase microstructure which arises from the chemical incompatibility between the soft and the hard segments. The alternating hard and soft segment structures are responsible for some valuable physical and mechanical properties.

The possibility of combining the advantages of polyurethanes and polysiloxanes due to their high permeability to gases, excellent heat stability, low glass-transition temperature, etc. (Ioan et al., 2002; Vlad et al., 2000), has attracted particular attention in the last decades.

Positron annihilation techniques, both lifetime (PALS) and Doppler spectroscopy, became powerful tools for the characterization of free-volume fractions and free-volume size distributions (Jean, 1993) in various crystalline and amorphous solids. In polymers, the long lifetime component, connected with the ortho-positronium, o-Ps, is expected to give information on characteristics of holes appearing due to the structural (static or dynamic) disorder in amorphous polymers (e.g., Dlubek et al., 2000, 2002; Jean et al., 2003).

Positrons emitted from a radioactive source enter the polymer matrix, thermalize and may either annihilate with electrons or form positronium (Ps). The long-lived

o-Ps may get localized in the free-volume holes within the polymer, and subsequently, undergo so-called "pick-off" annihilation.

The Doppler shape parameter S depends on the momentum of annihilating valence electrons, giving structural information (defects, free volumes), whereas W is mainly related to annihilations with core electrons (electrons with higher momenta), giving chemical information. The S and W parameters were defined at the central part and the tails of the energy annihilation peak, respectively.

In the present work, which is an extension of our previous studies (Ferreira Marques et al., 2003, 2004) polyurethane/urea membranes obtained through the introduction of two soft segments, poly(propylene oxide) and polydimethylsiloxane, were studied by PALS and Doppler broadening with the aim of establishing how the free-volume holes are influenced by phase separation and how the free volume is correlated with permeability.

2. Experimental

The polymer membranes were produced as described previously (Queiroz and Pinho, 2005). The two basic components, polypropylene-oxide-based prepolymer with three isocyanate terminal groups (PU) and poly(dimethylsiloxane) bis(hydroxyalkyl) terminated (PDMS), were supplied by Portuguese Hoechst and by Aldrich, respectively.

PALS measurements were carried out on PU/PDMS samples with various compositions up to 75% PDMS. The LT spectra were recorded using a fast–fast time spectrometer (with BaF_2 and Pilot-U scintillators) with a time resolution of 240 ps FWHM for ^{60}Co. The positron source, ca. 7×10^5 Bq of ^{22}Na, was sandwiched between two identical specimens cut from 2 mm thick polymer sheets. The DB spectrometer featured a HPGE detector with 1.2 keV resolution and 13% efficiency at 497 keV. All measurements were carried out in the temperature range 298–324 K, chosen as to lie above the glass transition temperatures (T_g) of the present membranes. Each sample was counted three times at each temperature. Lifetime spectra had a total number of ca. 2.3×10^6 integral counts and were evaluated through the LT (version 9) program (Kansy, 1996). The DB spectra were analysed in terms of the conventional S and W shape parameters.

Gas permeation measurements were carried out with CO_2 for all membranes as described in (Queiroz and Pinho, 2005).

3. Results and discussion

The high statistics of PALS spectra enabled a significant evaluation into four components, assigned to distinct positron and Ps states, i.e. the short-lived states of positronium (para-positronium, *p*-Ps), free positrons, and two long-lived triplet states of positronium (ortho-positronium, *o*-Ps). The two longest components (lifetimes τ_3 for the shorter and τ_4 for the longer one, with intensities I_3 and I_4, respectively) are associated with pick-off annihilation of *o*-Ps in two different hole types.

Since the *o*-Ps lifetime is assumed to be inversely proportional to the square of the overlap of the positron component of the Ps wave function with the cavity wall electron wave function (Tao, 1972; Eldrup et al., 1981), it is a measure of the size of the low electron density free-volume. Assuming spherical free-volume sites of radius R, this can be modelled by a spherical potential of radius R_0 with an electron layer of thickness R. For *o*-Ps confined in an infinitely deep well, the above model gives a correlation between the free-volume hole radius R (in Å), and the *o*-Ps pick-off lifetime in ns,

$$\tau_{o\text{-}Ps} = 0.5\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1},$$

where $R_0 = R + \Delta R$ and $\Delta R = 1.656$ Å (Nakanishi et al., 1987). This expression, extensively employed with success (e.g., Maurer and Schmid, 2000), has been extended further to non-spherical shapes (Gidley et al., 1999; Goworek et al., 2000).

The two long components (lifetimes τ_3 and τ_4) were ascribed to two Ps states decaying in different regions, indicating the coexistence of two phases corresponding to separate domains of the two soft segments in the membranes (polydimethylsiloxane and polypropylene oxide). This phase-separation was also detected by TEM observations that showed morphologies corresponding to two distinct phases. These data are in agreement with previous thermal analysis studies (Queiroz and Pinho, 2005), which showed two glass transition temperatures (T_g) for membranes in this range of PDMS content.

In Fig. 1, lifetime τ_4 and intensity I_4 increase continuously with increasing PDMS concentration and temperature. R_4 also increases with increasing PDMS concentration and shows a similar dependence on temperature. No clear trend is observed for τ_3 (present only with low intensity), which remains more or less constant for the whole range of PDMS concentrations and temperatures.

Although real voids are probably not spherical, the two free-volume radii R_3 and R_4 may be interpreted as a rough estimate of the actual hole sizes, the shorter one should correspond to holes in the PU phase and the (temperature dependent) longer one to the PDMS phase, respectively.

The increase of τ_4 with increasing PDMS content might be ascribed to a decrease of cross-linking resulting in increased hole sizes. In turn, the increase of I_4 means
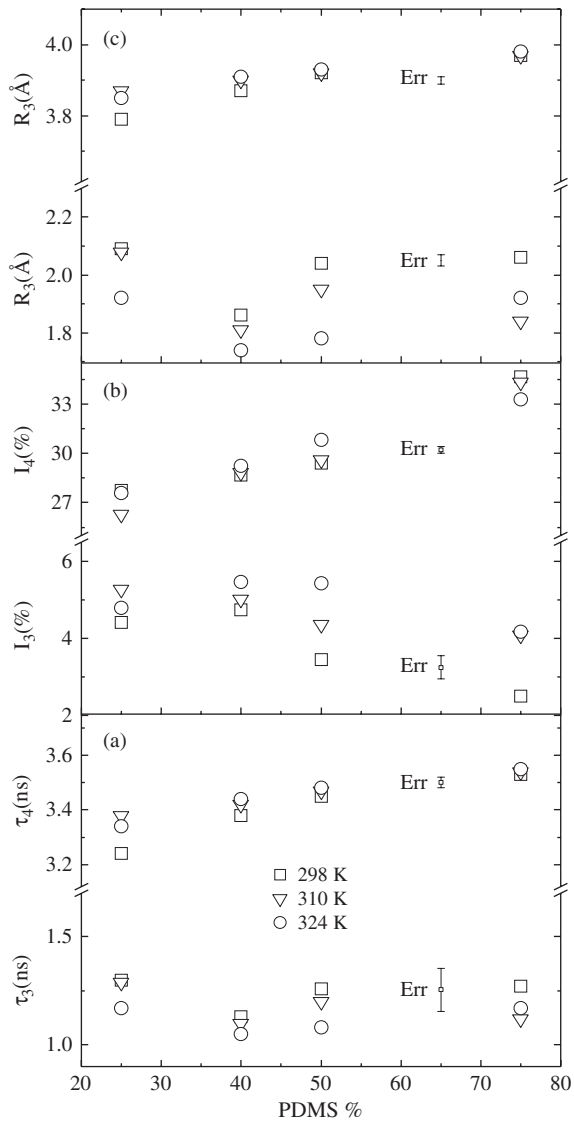
Fig. 1. PALS parameters and calculated radii as a function of PDMS content for three different temperatures.

left unreacted, leading to a decrease of the degree of cross-linking. These results of LS strongly indicate that the increase of PDMS content leads to a decrease of cross-linking and an increase of the free-volume density. The results of LS are thus in agreement with the degree of cross-linking obtained (see Queiroz and Pinho, 2005).

The LS parameters also show that I_{total} is almost constant until 50 wt% of PDMS, increasing only at 75 wt%. At this highest concentration, the largest τ_4 and I_4 are observed, meaning higher free-volume holes and higher density of holes, bringing along the highest permeability for the CO_2.

Fig. 2 represents the dependence of both the CO_2 permeability and the intensities I_3 and I_4 on PDMS content. The permeability increases with the PDMS content and the highest permeability corresponds to membranes containing 75 wt% of PDMS (Queiroz and Pinho, 2005). The higher permeability of such membranes may be attributed to the higher fraction of siloxane segments that form an elastomeric phase. The intensity I_4 follows the same trend as the permeability, whereas I_3 has its minimum for 75 wt% PDMS. This can be understood as the permeability being determined by the largest size holes.

The S and W parameters from Doppler measurements are shown in Fig. 3. The value of S increases continuously with increasing PDMS concentration, and the same behaviour is observed with increasing
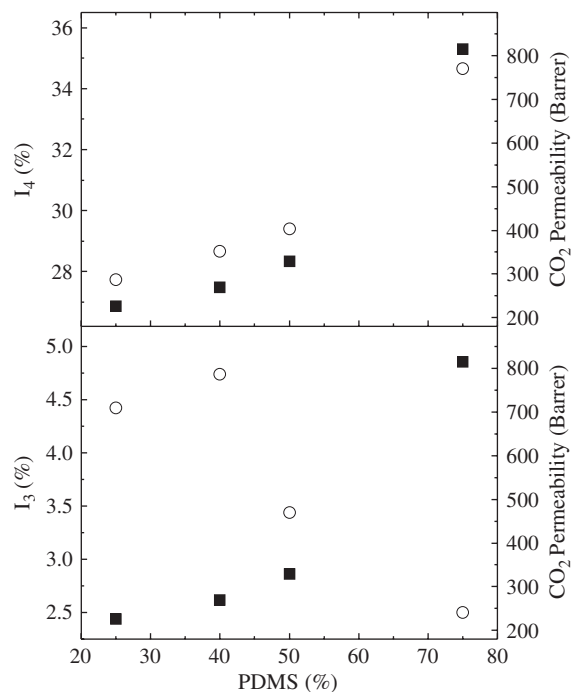
increased hole density with growing PDMS content. As R_3 is almost constant for all concentration regions, and the same behaviour is observed with increasing temperature, only the larger holes (R_4) could be associated to the decrease of cross-linking. The increase of PDMS in the PU samples is observed to increase the dimensions of the cavities present and also to increase free-volume hole sizes in the membranes. The peak observed for 75 wt% of PDMS indicates small cross-linkage and the largest free spaces. In the membrane preparation, the increase of PDMS leads to the formation of more urethane linkages, due to the presence of higher amount of hydroxyl groups that react with isocyanate. With the increase of PDMS content, a few hydroxyl groups are

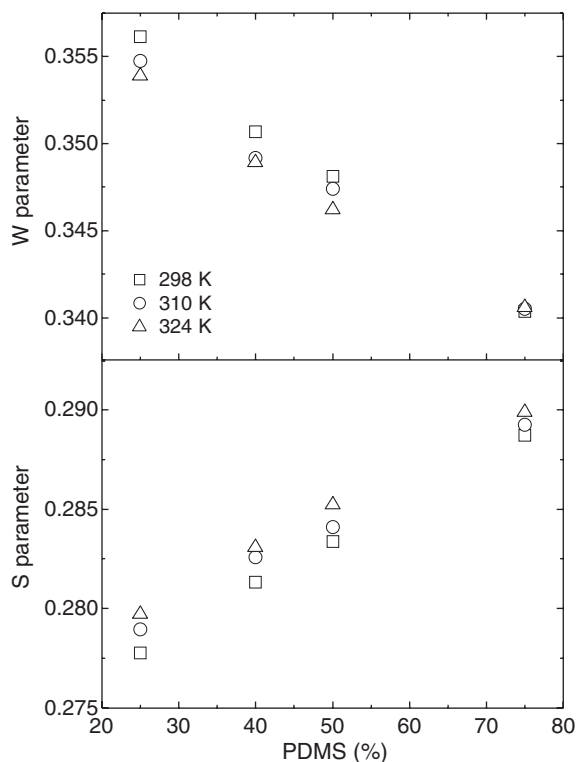Fig. 2. Intensities (○) and CO_2 permeability (■) observed at 298 K as a function of PDMS content.

Fig. 3. S and W parameters from DB measurements as a function of PDMS content for three different temperatures.

Fig. 4. S–W plot from DB measurements at $T = 298$ K, for various PDMS content.

temperature. For Ps localized in large size holes, a larger S parameter is observed due to the smaller average momentum of the annihilating electrons. The S parameter is, thus, a qualitative measurement of the defect size and concentration.

On the other hand, the W parameter decreases both with increasing PDMS content and with increasing temperature, as it is seen in Fig 3. Given its sensitivity to annihilations with core electrons, i.e., to the chemical environment, parameter W shows that the annihilations at 75% and at 25% PDMS take place in chemically different regions.

The behaviour of the Doppler parameters is in agreement with the FTIR analysis (Queiroz and Pinho, 2005), showing that the urethane urea groups interact by hydrogen bonds and can form small aggregates and such aggregations decrease with the increase of PDMS content.

The correlation of Doppler parameters seen in the S–W plot (Liszkay et al., 1994), which is presented in Fig. 4, shows a linear decrease and a clear separation of the samples with different composition, revealing a high specific sensitivity of the Doppler effect measurements for these membranes materials. Indeed the interest to apply the Doppler broadening method to polymer studies (Dlubek et al., 2002) has gained momentum, as
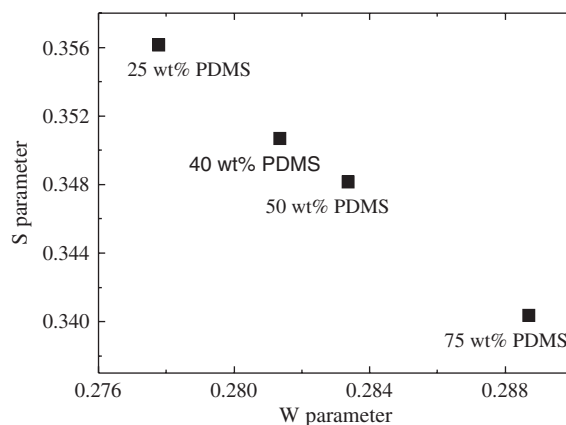
it has been shown by several contribution at PPC-8 Workshop, in Coimbra.

4. Conclusions

As expected, all free-volume sizes have a direct correlation with CO_2 gas permeability, i.e., the larger the free-volume hole size, the greater the gas permeation.

In addition to the absolute amount of free-volume probed by the o-Ps, other factors are definitely also involved in the permeation. The interconnectivity and transmissibility between holes may play an important role, and it seems that the CO_2 gas permeability is essentially determined by I_4.

The extension of the study of temperature dependence to a broader temperature range seems to be necessary and is in progress.

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