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Study of sorption in poly(vinyl alcohol) using the positron annihilation technique

Hamdy F M Mohamed, A M A El-Sayed and E E Abdel-Hady

Physics Department, Faculty of Science, El-Minia University, BO 61519, El-Minia, Egypt

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Abstract. The vacancy states of fresh and annealed poly(vinyl alcohol) polymers sorbing CO₂ gas at various pressures have been investigated by the positron annihilation lifetime (PAL) technique. The change of the bulk volume and the amount of sorbed CO₂ gas were measured simultaneously to compare the free volume fraction with the size of the *ortho*-positronium holes. The PAL data indicate that the size of the *ortho*-positronium hole increases with the progress of the sorption while the sorption and the bulk volume data show that the free volume fraction becomes constant. Also, it supports the existence of local plasticization and the improvement of the dual mechanism model of sorption of gas.

1. Introduction

Rubbery polymers are similar to simple liquids and respond quickly to imposed changes so that thermodynamic equilibrium is maintained. Thus, properties such as gas solubility and transport behaviour in membranes made of these materials effectively do not depend on previous thermal or sorption history. On the other hand, glassy polymers are quite different since thermodynamic equilibrium is virtually never achieved; hence, many properties may be expected to depend on the prior history of the membrane [1].

When a polymer film is exposed to high pressure CO₂ atmosphere, the polymer chains are elasticized by CO₂ molecules sorbed at high concentration. Sorption behaviour in polymer is classified into two types: Henry type and Langmuir type [2]. In the Henry type the sorbed molecules are dissolved into the polymer in which plasticization is induced, but in the Langmuir type the sorbed molecules are filled in pre-existing vacancies. Gas sorption and transport are important characteristics of polymers for many applications. It is well known that CO₂ conditioning, which is exposing a polymer film to high pressure CO₂ and degassing it *in vacuo*, increases gas permeability of glassy polymers [3–5]. The gas permeation property in a polymer film is closely related to the size and volume fractions of the free volume in the film.

A positron injected into matter can pick up an electron from the substance and form a natural particle called positronium (Ps). Positronium with spins of the electron and positron anti-parallel, called *para*-positronium (*p*-Ps), annihilates very fast but that with parallel spins (*ortho*-positronium, *o*-Ps) annihilates much more slowly. The lifetime of the *o*-Ps is strongly affected by the external conditions which provide the electron that can be picked off by the positron in positronium. Due to its sensitivity toward vacancies, positron annihilation has attracted the attention of polymer scientists. Although much is left to be clarified regarding the details of the relation between the *o*-Ps parameters (lifetime and intensity) and the free volume characteristics, vacancy spectroscopy using Ps is considered promising. Various studies [6–11]

are being carried out in that field, among which is the idea of using positronium as a probe of gas sorption in polymers. When the sorbed molecules are filled in pre-existing vacancies (Langmuir-type sorption) both the intensity and the lifetime of *o*-Ps are reduced. On the other hand when the sorbed molecules are dissolved into polymer chains (Henry-type sorption) the *o*-Ps parameters become larger.

The aim of this work is to: (a) investigate the effect of CO₂ conditioning on the free space holes of poly(vinyl alcohol) polymer and (b) study the state after-effect of the CO₂ conditioning. To accomplish these aims, the positron annihilation lifetime, the bulk volume and the gas permeation are measured.

2. Experiment

The poly(vinyl alcohol), PVA, powder was supplied by Hayashi Pure Chemical Industries Ltd, with an average degree of polymerization of 1700. The fresh sample was prepared as described in detail before [12]. The annealed sample was obtained by annealing the fresh one at 110 °C for 12 h. The densities of the fresh and annealed samples ($\rho_f = 1.286$ and $\rho_a = 1.298 \text{ g cm}^{-3}$) were measured at room temperature by the floating method using *n*-hexane and carbon tetrachloride. The glass transition temperatures (T_g) were measured for the fresh and annealed samples following the previous work [13]. The temperature dependence of the *o*-Ps lifetime measurements indicated that there are two regions for each sample. The two regions correspond to $T_g = 88 \text{ °C}$ for the fresh sample while they correspond to $T_g = 80 \text{ °C}$ for the annealed one.

The positron annihilation lifetime (PAL) measurements were performed using a conventional fast-fast coincidence system with time resolution 230 ps (FWHM). The sample/positron source/sample sandwich was put in a high pressure tube of 12 mm internal diameter. The measurements of PAL were performed at room temperature, first in vacuum, then 1–50 atm of CO₂ and finally in vacuum again.

The amount of the sorbed CO₂ and the dilation of the bulk volume were measured using polymer samples taken from the same batch as used for the PAL measurements. The amount of sorbed CO₂ was measured using an electric micro-balance. For the determination of the volume dilation, a strip of the polymer sheet was vertically hung in a high pressure vessel made of thick glass and the elongation of the strip was measured from outside using a cathetometer [14].

3. Results and discussion

The lifetime spectra have been analysed to finite term lifetimes using the PATFIT program [15] without source correction. We found that the three-lifetime-component results give the best variance ratio and most reasonable standard deviations. The shortest-lived component ($\tau_1 = 0.11\text{--}0.18 \text{ ns}$, $I_1 = 24\text{--}43\%$) and the intermediate component ($\tau_2 = 0.32\text{--}0.49 \text{ ns}$, $I_2 = 39\text{--}54\%$) are attributed mainly to *p*-Ps and direct annihilation of positrons, but detailed analysis is difficult because of possible formation of positron and positronium compounds contributing to both components. The long-lived component ($\tau_3 = 1.2\text{--}1.5 \text{ ns}$, $I_3 = 16\text{--}21\%$) is due to the pick-off annihilation of the *o*-Ps in free volume holes. For the fresh and annealed PVA, the free volume fractions have been calculated using Bondi's method [16]. These two fractions were found to be 0.089 and 0.08, respectively, after correcting for the crystallinity (corresponding to 100% amorphous).

3.1. CO₂ pressure dependence of the *o*-Ps parameters

The *o*-Ps lifetime, τ_3 , and its intensity, I_3 , are shown in figure 1 as a function of CO₂ pressure. For the fresh PVA τ_3 slowly increases and then levels off at 10 atm, while for the annealed PVA τ_3 decreases at low pressures and then increases at higher pressures with the minimum appearing around 1 atm. On the other hand, I_3 decreases up to 10 atm and is almost constant from 10 to 50 atm for the fresh sample while it has an oscillating behaviour for the annealed sample.

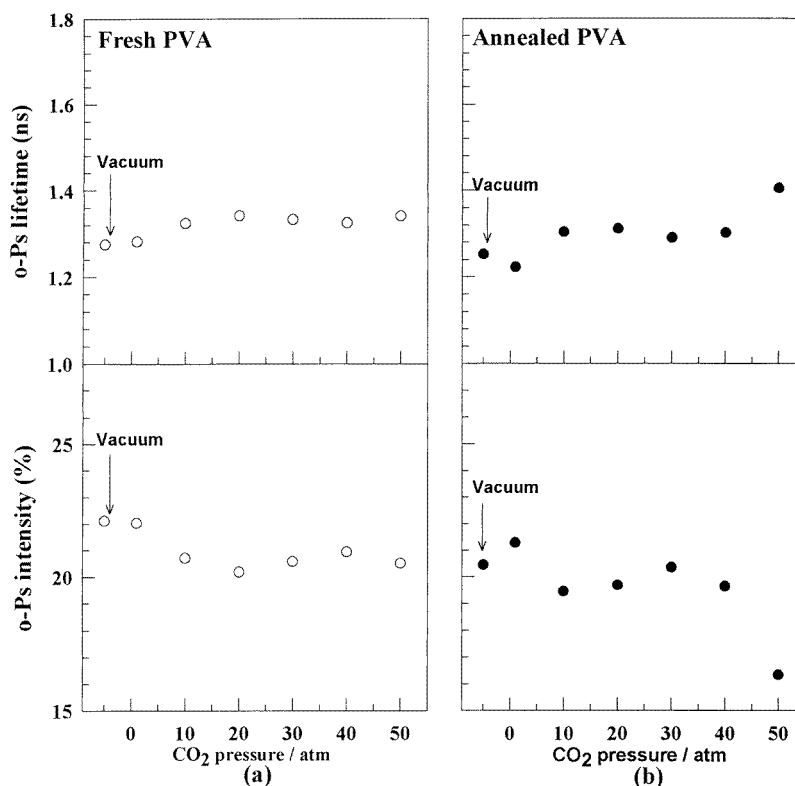


Figure 1. The *o*-Ps lifetime and its intensity as a function of CO₂ pressure for the fresh and annealed PVA. The error bars are within the size of the symbols.

The initial decrease of the *o*-Ps parameters could be attributed to the absorption of CO₂ into pre-existing vacancies (Langmuir-type sorption) leading to a reduction in the number and size of vacancies in the amorphous part of polymers. Dissolution of CO₂ (Henry-type sorption) would take place simultaneously, but not to an extent to affect the *o*-Ps hole structure. At higher pressures the dissolution is promoted up to a certain point where its effect starts to be reflected in the *o*-Ps parameters. This effect could be explained as follows: when CO₂ molecules are dissolved in the amorphous part (Henry-type sorption), the micro-Browning motions of the chains are simulated; i.e. the polymer becomes plasticized. As a result of the plasticization, the equilibrium distribution of the free volume is shifted to a larger size. Hence, the *o*-Ps yield is enhanced and can find larger vacancies to be accommodated.

3.2. After-effect of the CO₂ conditioning

In order to see the after-effect of the CO₂ conditioning, the gas was evacuated and the PAL measurement was continued in vacuum as shown in figure 2. On evacuation of CO₂ gas, the τ_3 and I_3 of both samples have regained their initial values. This is quite similar to the results for low density polyethylene (LDPE) polymer [17] but the results for PVA samples are puzzling because PVA is believed to be glassy even in 50 atm CO₂. A clue to this puzzle would be to consider that the glassy state normally refers to the bulk of the polymer while positronium may be looking selectively at local sites containing larger vacancies. If the sorbed CO₂ molecules are concentrated in such sites, the polymer is plasticized only around those local sites. Such a state, being still glassy as the bulk of the polymer but containing locally rubbery sites, can provide enough space for Ps to be stabilized by expanding the size of the pre-existing vacancies. Such a sorption state will no longer be described properly by the existing models as Henry-type or Langmuir-type sorption.

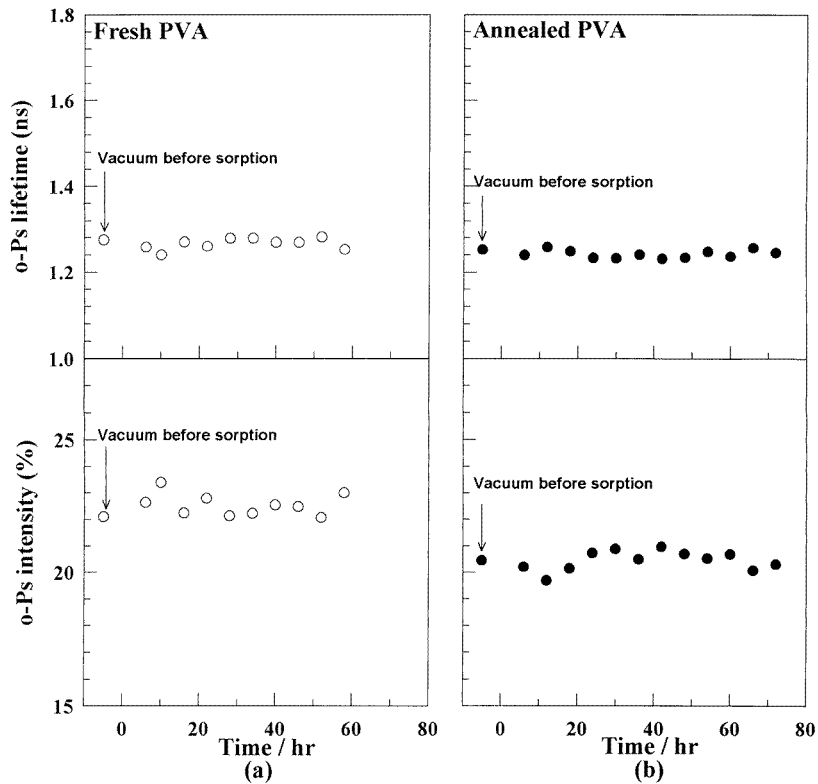


Figure 2. The *o*-Ps lifetime and its intensity as a function of time for the fresh and annealed PVA after evacuating the CO₂ to see the after-effect of the gas conditioning. The error bars are within the size of the symbols.

3.3. Comparison between the *o*-Ps data and the sorption data

It is important to compare the *o*-Ps parameters with other sorption-related quantities. The amount of sorbed CO₂ C (cm³ (STP)/cm³ polymer), the expansion of bulk volume $\Delta V_b/V_b^0$ and the expansion of the volume of positronium holes $\Delta V_h/V_h^0$ are shown in figure 3 for the fresh

and the annealed samples. The superscript zero indicates the value before the CO₂ conditioning. The elongation measurement was used to calculate the bulk volume $V_b = V_b^0 + \Delta V_b$ while the *o*-Ps hole size $V_h (=V_h^0 + \Delta V_h)$ was calculated from the value of τ_3 using the well known equation [18] for the pick-off annihilation in spherical shaped holes. The sorption data were corrected for the crystallinity (22.4% for fresh and 37.5% for annealed PVA) so that the indicated values of the amount of CO₂ sorption and the volume expansion correspond to those for 100% amorphous PVA.

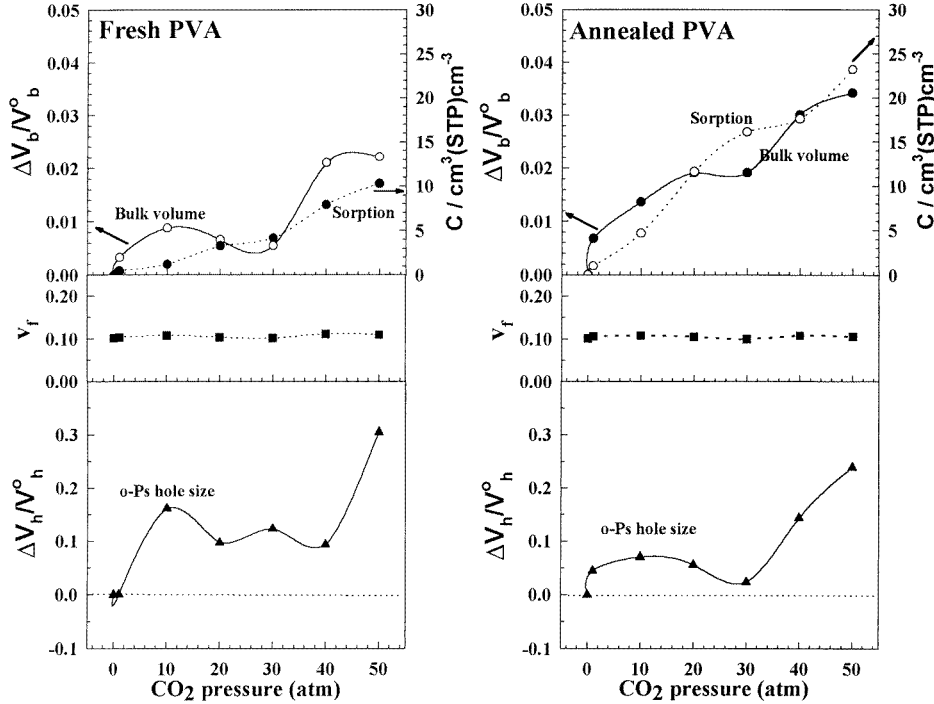


Figure 3. Comparison of sorption of CO₂ gas (●), dilation of bulk volume (○) and *o*-Ps hole size (▲) for fresh and annealed PVA. The free volume fractions (■) estimated from the sorption data are also shown. The error bars are within the size of the symbols.

Figure 3 demonstrates that the amount of sorbed CO₂ and the bulk volume increase with the gas pressure. The size of the *o*-Ps hole slightly increases at low pressure and levels off until 40 (30) atm for fresh (annealed) samples due to the Langmuir-type sorption and then increases at higher pressure where the Henry-type sorption takes over. For polymers before sorption, the occupied volume V_p and the free volume V_f^0 (both defined in the unit of cm³/cm³ of raw polymers, hence $V_b^0 = V_p + V_f^0 = 1$) can be estimated from specific density using the Bondi group contribution method [16]. For the sorbed states, the free volume V_f can be calculated by subtracting the occupied volume V_p and the volume V_{CO_2} of sorbed CO₂ from the total volume as

$$V_f = V_b - V_p - V_{CO_2}.$$

The volume V_{CO_2} is calculated from the amount of sorbed CO₂ as

$$V_{CO_2} = \frac{C}{22414} \times 19.7 \times 1.3$$

where $19.7 \text{ cm}^3 \text{ mol}^{-1}$ is the effective molar volume of CO_2 according to Bondi [19] and the factor 1.3 describes the packing efficiency of molecular groups. The free volume fraction, v_f , is given as

$$v_f = \frac{V_f}{V_b} = 1 - \frac{V_p + C/22414 \times 19.7 \times 1.3}{(V_b^0 + \Delta V_b)} \quad (V_b^0 = 1).$$

Also, figure 3 illustrates that v_f is almost constant for both samples. On the other hand, the o -Ps hole size (V_h) increases monotonically at high pressures. If τ_3 and I_3 measure the average size and number of the free volume holes, respectively, then the increase in these values should be an indication of the increase of the free volume fractional which is in contradiction with the present result. However, the product $V_h I_3$ is expanding more than the fraction of the free volume. Thus it becomes a common question why the o -Ps hole size expands while the free volume fraction does not expand correspondingly. A solution to this contradiction could be reached by assuming the formation of a bubble-like state. Formation of a 'Ps bubble' [20] does not seem strange for LDPE since it is considered to be nearly liquefied under 50 atm CO_2 . The PVA, however, was neither liquefied nor in a rubbery state at 50 atm CO_2 . It is not conceivable that Ps makes bubbles in glassy polymers, but it is probable that, at local free volume holes, where the molecules are dissolved, some segmental motions are allowed and Ps accommodated in it can expand its size creating a 'bubble-like' state there. Another possible explanation is that the o -Ps prefers larger free volume holes.

The o -Ps is a light particle, so the zero-point energy is large [17] and could be determined, according to the spherical potential well model with infinite length, by

$$E_0(\text{eV}) = 0.188/R(\text{nm})^2.$$

Since the mass of Ps is small, the zero-point energy is substantially large and a small difference in the vacancy size R can easily cause an energy difference corresponding to thermal energy. Owing to this particular quantum mechanical nature Ps can be preferentially transported to larger holes. Thus it is quite probable that Ps is transported to larger holes generated as a result of the plasticization.

4. Conclusion

The measurement of the intensity and the lifetime of the o -Ps provides a unique tool for direct observation of the free spaces in polymers containing sorbed CO_2 gas. It has been shown that the Langmuir-type sorption occurs at low CO_2 pressure while at high CO_2 pressures the Henry-type mechanism takes place. The samples are believed to be glassy under 50 atm of CO_2 but the PAL data suggest a local plasticization. This local plasticization is a suggestive way for improving the 'dual mechanism model' of sorption with the PAL technique. It is found that the size of the o -Ps hole increases with the progress of the sorption while the free volume fraction becomes constant. This is probably because, from the Ps viewpoint, Ps is digging a hole or seeking larger vacancies in polymers. Since this view can cast serious fundamental doubt on the usefulness of the PAL technique in measuring free volume holes of polymers, it must be carefully examined.

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