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Temperature dependence of free-volume holes in poly(vinyl alcohol) studied by positron annihilation technique

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The temperature dependence of free-volume holes in pure poly(vinyl alcohol) (PVA) and 30% $ZnCl_2$-treated PVA has been studied at different temperatures ranging from 25 to 150°C. The dependence of the electrical conductivity on the free-volume holes is probed by the positron annihilation lifetime (PAL) technique. The lifetime τ_3 of the *ortho*-positronium (*o*-Ps) and its intensity I_3 were measured for the two samples below and above the glass transition temperatures (T_g). The observed shift in the T_g to lower value might be attributed to the increase in the electrical conductivity σ. For treated PVA, the existence of large ionic charge carriers can be concluded from a large value of the critical hole size. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol); free-volume holes; electrical conductivity; positron annihilation lifetime)

Introduction

The study of the conductivity process in polymeric materials is difficult but important especially when different types of additives are used. The correlation between microscopic and macroscopic properties of polymers has long been of interest[1,2].

Positron annihilation spectroscopy (PAS) has been developed to probe the variation of average size and concentration of free-volume holes[3,4] on the basis that positronium (Ps) formation is found only in amorphous regions and the Ps atom is preferentially localized in the free-volume holes. Positron annihilation lifetime (PAL) spectra of polymers have a long-lived component that is ascribed to *ortho*-positronium (*o*-Ps) formed and finally annihilated with an electron from the surrounding medium through pick-off annihilation. The annihilation process is affected by many factors such as polymer structures[5], chemical structure[5], crystallinity[6] and temperature[7,8]. While the lifetime of *o*-Ps (τ_3) can be related to the size of the free-volume holes, its intensity (I_3) is considered to be a measure of the number of such holes as long as the chemical structures are similar.

Since the highest values of conductivity for treated poly(vinyl alcohol) (PVA) samples were obtained with a concentration of 30% of $ZnCl_2$, it seems therefore of interest to study both pure and 30% $ZnCl_2$-treated PVA samples. In this study, the effect of temperature on pure and treated PVA has been investigated using the PAL technique. Also, a correlation between the electrical conductivity σ and the free volume V has been established.

Experimental

A mixture of PVA and $ZnCl_2$ in water was stirred overnight at room temperature. The viscous solution was then treated with KOH ($KOH/ZnCl_2 = 1.1$), and stirred overnight at room temperature again. The resultant mixture was cast on a polyethylene moulding plate and left to dry in air for 3 days. The peeled film was then cut into samples suitable for measurements.

For electrical measurements[9], the film sample was sandwiched between two copper electrodes using a specially designed holder. A conventional d.c. electrical circuit was used. On the other hand, a conventional fast–fast coincidence system having a time resolution of 200 Ps (full width at half-maximum) with energy windows set for ^{60}Co was used for the measurement of the positron annihilation lifetime. Details of the experimental set-up can be found elsewhere[10]. The positron annihilation lifetimes were measured over the temperature range from 25 to 150°C.

Results and discussion

The positron lifetimes in PVA were measured for temperatures up to 150°C. Each spectrum was resolved into three components using the PATFIT[11] program. The variances of fit (χ^2) are smaller than 1.15. The shortest component (τ_1) is due to *para*-positronium annihilation and positron annihilation in the bulk of crystalline regions. The second component (τ_2) is assigned to positron annihilation in the crystalline regions. The longest component (τ_3) is attributed to *o*-Ps pick-off annihilation in the free-volume holes of amorphous regions and its intensity (I_3) is directly proportional to the concentration of free-volume holes.

The temperature dependence of τ_3 and I_3 for pure PVA is shown in *Figure 1*. It can be seen from this figure that τ_3 remains constant up to 50°C, then increases with temperature (T). Furthermore, it is clear that the relationship between τ and T reveals two onsets at the two known glass temperatures, $T_{g1} = 80°C$ and

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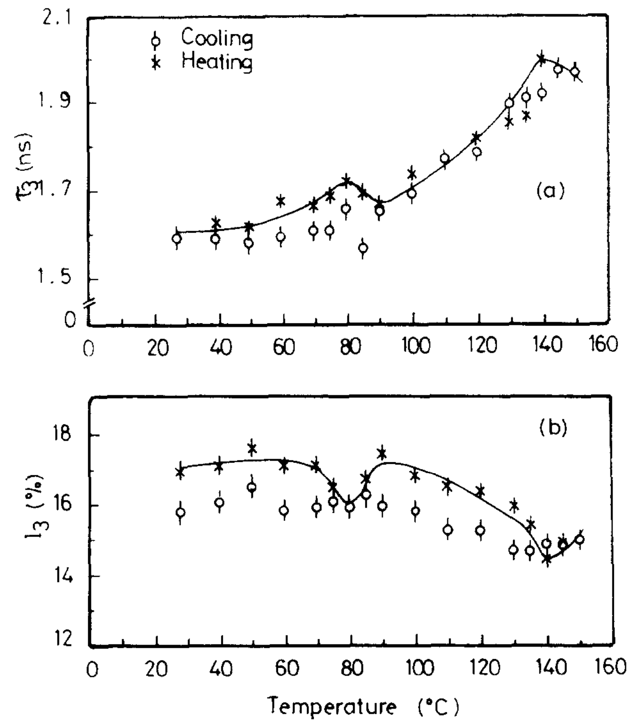

Figure 1 Temperature dependence of (a) τ and (b) I_3 for pure PVA

$T_{g2} = 140°C$. On the other hand, I_3 exhibits similar temperature trends, being constant up to 70°C then decreasing sharply giving rise to two inflection points at T_{g1} and T_{g2}. In the cooling process, the two onsets are still occurring at $T_{g1} = 80°C$ and $T_{g2} = 140°C$ for both τ and I_3. However, the changes in I_3 and τ_3 were significantly different from those in the heating process.

The variations of τ_3 and I_3 with temperature over the range from 25 to 150°C for 30% $ZnCl_2$-treated PVA are shown in *Figure 2*. It is clear that τ_3 is almost constant with temperatures up to 40°C, showing an onset at 60°C, and then increases monotonically up to 120°C. A second onset is also observed at 140°C. On the other hand, I_3 exhibits a strong temperature dependence showing two inflection points at temperatures of 60 and 140°C. During the cooling process, I_3 and τ_3 were found to behave differently from the heating process similar to the case of pure PVA (*Figure 2*). The relatively significant increases of free volume may be attributed to some chemical reaction between PVA and $ZnCl_2$ leading to the formation of polymer–metal complexes. Therefore the increase in the electrical conductivity σ for 30% $ZnCl_2$-treated PVA, compared with pure PVA, may be explained in terms of the motion of ions regulated mainly by the amount and distribution of free volume[12].

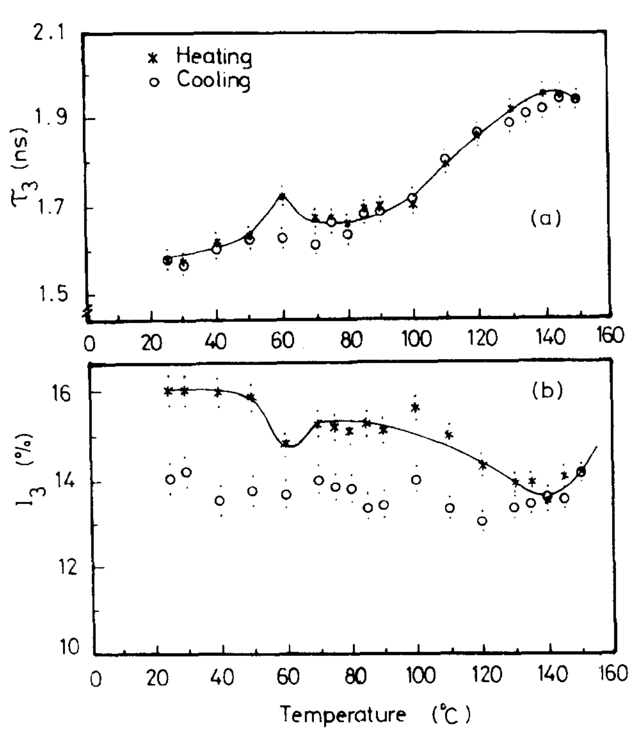

Figure 2 Temperature dependence of (a) τ and (b) I_3 for 30% $ZnCl_2$-treated PVA

In order to determine the thermal expansion coefficients of free volume α, the radius of the free-volume hole R has to be determined. Assuming a spherical shape for the free-volume holes, the thermal expansion coefficients α for pure and 30% $ZnCl_2$ PVA were found to be 3.4×10^{-3} and 3.9×10^{-3} °C^{-1}, respectively. Also, the activation energies were deduced from the experimental electrical conductivity measurements for pure and 30% $ZnCl_2$ PVA. The large values of the activation energies suggest[13–15] an ion transport conduction. Moreover, the effect of the free volume on the electrical conductivity σ can be predicted. It can be expected that σ would increase with the increase of the thermal expansion coefficient of free volume. This conclusion applies for pure as well as for 30% $ZnCl_2$ PVA and agrees quite well with the model suggested by Miyamoto and Shibayama[12]. This model is based on the assumption that the movement of ions is regulated by the amount and distribution of free volume, such that σ can be expressed as

$$\sigma = \sigma_0 \exp\left\{-\left[\frac{\gamma V_i^*}{V_f} + \frac{E_b}{kT}\right]\right\} \quad (1)$$

where σ_0 is a constant, γ is a numerical factor used to correct the overlap of free-volume and polymer segments, V_i^* is the critical volume required for transport of an ion, E_b is the apparent activation energy at temperature below T_g and k is Boltzman's constant. *Figure 3* shows a least-squares fit of our data with equation (1). The deduced critical hole size γV_i^* was found to be 15.57 and 20.23 Å^3 for pure and 30% $ZnCl_2$ PVA, respectively.

Conclusion

The following conclusions may be drawn from the above results.

1) The difference in the I_3, τ_3 *versus* temperature curves for pure and treated PVA samples on heating and cooling cycles suggests a change in the structure during the heating process, which seems to be irreversible.
2) Since the glass transition temperatures of polymers characterize the onset of a cooperative motion of large segments of the molecule, the shift of T_g to lower temperature in the 30% ZnCl-treated PVA might explain the increase in the electrical conductivity σ with the concentration of the additive.

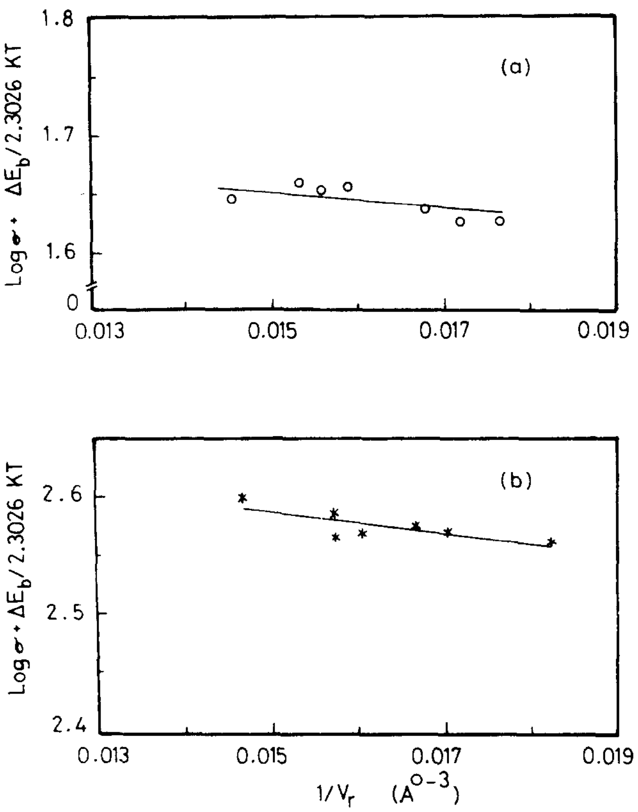

Figure 3 Log $\sigma + E/2.3026kT$ *versus* reciprocal free volume for (a) pure PVA and (b) 30% $ZnCl_2$-treated PVA

3) The large value of the critical hole size γV_i^* obtained for treated PVA might be the result of large ionic charge carriers.
4) PAL may be considered as a powerful technique for studying microscopic structure changes and transitions of polymers.

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