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A. El-Sayed, E. Abdel-Hady, M. Mohsen, A. Sawaby. Positron annihilation lifetime study of pure and Na(acac) treated polyvinylalcohol. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-271-C4-273. 10.1051/jp4:1993442 . jpa-00251485

HAL Id: jpa-00251485

<https://hal.science/jpa-00251485>

Submitted on 1 Jan 1993

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Positron annihilation lifetime study of pure and Na(acac) treated polyvinylalcohol

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ABSTRACT

Positron annihilation lifetime studies of pure and treated polyvinyl alcohol (PVA) reflect the effect of concentration as well as temperature on free volume. Therefore, variations of the lifetime of the o-Ps longlived component τ_3 and the probability of its formation I_3 have been studied and correlated with changes in the electrical conductivity σ as well as with X-ray diffraction data. For the 10% treated sample the existence of large ionic charge carriers could be concluded from a large value of the critical free volume.

INTRODUCTION

The study of the electrical properties of polymers is of great technical interest. In the present work, the effect of concentration and temperature on PVA treated with sodium acetyl acetate Na(acac) has been investigated using positron annihilation lifetime technique (PAL). Despite the high sensitivity of this method to the size and number of free volume, which can highly regulate (1) the electrical conduction process, it is of considerable value in determining any variation in the degree of crystallinity (2).

EXPERIMENTAL

Polyvinyl alcohol is added to distilled water at room temperature. In order to prevent a thermal decomposition of the polymer, a water bath was used for heating the solution. The hot solution was stirred until the polymer is completely dissolved and forms a clear viscous solution. The solution was treated by adding sodium acetyl acetate Na(acac) in different weights to prepare different ratio of Na(acac)/PVA ranging from 5% to 50% per weight. To prepare the polymeric films of the above treated polymer, the viscous solution was casted onto polyethylene plates and left to dry in air for three days, thin films of 1 to 2 mm thicknesses were then obtained.

The positron lifetime measurements were carried out using a fast-fast lifetime spectrometer having a resolution of 200 ps for the Co-60 prompt peak. A 20 μ Ci Na-22 positron source on kapton foil was sandwiched between two same PVA films of 1 mm thickness and placed together in a temperature adjustable sample chamber. The obtained lifetime spectra were fitted and resolved into three components by using PATFIT program (3) with 5% source correction.

RESULTS

1- EFFECT OF ADDITIVE CONCENTRATION :

The effect of concentration of Na(acac) in PVA varying from 5% to 50% by weight on τ_3 and I_3 at room temperature is shown in Fig.(1). Whereas τ_3 is almost constant, it turned out that, at low concentrations and up to 10% Na(acac) the number of free volume increases significantly, so that I_3 increases from ~ 22% for pure PVA to 32% for 10% Na(acac). At high concentrations, a decrease in I_3 to ~ 24% is observed for 20% Na(acac). This value of I_3 remains almost constant up to 40% Na(acac). For the 50% concentration a remarkable decrease in I_3 is observed from 24% to 21%. These results are in agreement with those deduced from X-ray investigations, which suggest an increase in the degree of crystallinity for samples with concentration above 40 %. The structure changes and the

relatively significant increase of free volume at low concentration, may be attributed to some chemical reaction between PVA and Na(acac) leading to the formation of polymer metal complexes. These changes might explain the increase in the electrical conductivity (4) σ for 5% concentration by almost two orders of magnitude compared to pure PVA, on the basis of the motion of ions, which can well be regulated(1) by the number of free volume.

2. EFFECT OF TEMPERATURE ON PURE AND 10% Na(acac) TREATED PVA:

Figure [2(a,b)] shows that, for pure PVA, with increasing temperature, τ_3 is almost constant up to 40 °C then increases sharply showing two onsets at the known glass transition temperatures T_{g1} = 80 °C and T_{g2} = 140 °C. In these temperature regions, I_3 exhibited similar temperature trends being constant up to 40 °C then decreasing sharply giving rise to two inflection points at T_{g1} and T_{g2} . For 10% Na(acac) treated PVA, Fig.[2(c,d)] shows that τ_3 is not appreciably changing up to 60 °C showing an onset at 70 °C then it increases monotonically up to 120 °C. A second inflection point can be observed at ~ 135 °C after which τ_3 increases sharply up to 170 °C. In these temperature regions, I_3 shows also a complicated behaviour. On the other hand, the difference in the I_3 , τ_3 versus temperature curves for pure and treated PVA samples on heating and cooling suggests a change in the structure (annealing) during the heating process, which seems to be irreversible.

DISCUSSION

In order to determine the thermal expansion coefficients of free volume α , the radius R of the free volume hole has been determined (3). The free volume V for pure and 10% Na(acac) treated PVA as a function of temperature is shown in Fig.(3). The thermal expansion coefficients α below T_{g1} and above T_{g2} together with the activation energies ΔE_b (4), are shown in table (1). The large values of activation energies suggest (5-7) an ion transport conduction. In order to establish a correlation between the electrical conductivity σ and the free volume V , the model suggested by Miyamoto and Shibayama (1) has been applied:

$$\sigma = \sigma_0 \exp \left\{ - \left[\frac{\gamma V_i^*}{V} + \frac{\Delta E_b}{KT} \right] \right\}$$

where σ_0 is a constant, γ is a numerical factor to correct the overlap of free volume and polymer segments, V_i^* is the critical volume required for transport of an ion, ΔE_b is the apparent activation energy at temperature below T and K is Boltzman's constant. Fig.(4) shows this relationship for pure and treated PVA.

Table(1)

	pure PVA		10% Na(acac)	
	below T_{g1}	above T_{g1}	below T_{g1}	above T_{g1}
α (/°C)	0.00484	0.0248	0.00224	0.0074
ΔE_b (eV)	0.68	0.30	0.67	0.26

CONCLUSION

From the above mentioned results one can deduce the following:

- 1- Thermal expansion coefficients of free volume (α) are larger for pure PVA than for 10% Na(acac) treated PVA. In both cases, α -values below T_{g1} are smaller than above it. These values are significantly larger than the thermal expansion coefficient of pure PVA of 5×10^{-5} /°C.
- 2- The shift of the glass transition temperatures, which characterizes the onset of cooperative motion of large segments of the molecule, to lower temperatures for the 10% Na(acac) treated PVA might explain the increase in σ with the concentration of the additive.
- 3- The critical hole γV_i^* is found to be $7.75 \text{ \AA}^3$ for pure PVA and $12.5 \text{ \AA}^3$ for 10% treated samples. The larger value obtained for the latter might be the result of the existence of large ionic charge carriers.

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Figures

Fig.(1) Variation of (a) τ_3 and (b) I_3 with Na(acac) concentrations. Fig.(2) Temperature dependence on τ_3 and I_3 :
(a,b) For pure PVA (c,d) For 10% treated PVA (○ heating, △ cooling). Fig.(3) Free volume size V versus temperature for a) pure PVA and b) 10% Na(acac). Fig.(4) $\log \sigma + E_b / 2.303 kT$ versus reciprocal free volume:
a) pure PVA and b) 10% Na(acac).