



Positron Annihilation Lifetime Study of Pure and Doped Polyvinyl Chloride with Al₂O₃

E. E. Abdel-Hady, H. F. M. Mohamed, and H. B. Alaa

*Physics Department, Faculty of Science, El-Minia University, B. O. 61519 El-Minia, Egypt
e-mails: esamhady@link.net & hamdyfm@link.net*

Abstract

Positron annihilation lifetime of pure and doped polyvinyl chloride (PVC) with Al₂O₃ reflect the effect of concentration as well as temperature on free volume. Therefore, variations of the ortho-positronium (o-Ps) lifetime and its intensity have been correlated with changes in the dielectric properties of the pure and doped PVC. The o-Ps lifetime and its intensity show a linear dependence with a discontinuity at 30 % concentration of Al₂O₃. The size and the fractional of the o-Ps hole volume were estimated from the positron annihilation parameters. Therefore, the temperature dependence of the electrical conductivity and the positron annihilation parameters on pure and doped PVC with 30 % Al₂O₃ were studied in the range from 30 to 140 °C. The shift of the glass transition temperature to lower temperature for the 30 % Al₂O₃ doped PVC might explain the increase in the electrical conductivity with the concentration of the additive.

Keywords: Positron annihilation lifetime, polyvinyl chloride, free volume, electrical conductivity.

I. Introduction

The positron as the antiparticle of the electron was predicted by Dirac [1]. The annihilation of the positron with electrons in matter was first studied in the 1940s. It was discovered early that the energy and momentum conservation during the annihilation process could be utilized to study properties of solids. The bound state of a positron and an electron, as the lightest known atom to be formed, is analogous to a hydrogen atom, where the proton is replaced by the positron. This e⁺-e⁻ state is called positronium (Ps). In positronium, the positron and electron are bound together by 6.8 eV with a mean separation of 0.106 nm. Positronium formation occurs at the last stage of the positron thermalization process having two spin states: ortho (o-Ps) (triplet) and para (p-Ps) (singlet). Dirac predicted in vacuum that the spin allowed annihilation of p-Ps will occur with a lifetime of the order of 0.125 ns and decays with emission of two photons, whereas the spin-forbidden of the o-Ps will decay after approximately 100 ns. In condensed media 75 % of the Ps formed will be o-Ps and 25 % will be p-Ps and its existence depends on there being regions of low electron density. The o-Ps annihilation may be enhanced if it is able to interact with other electrons and a spin exchange or pick-off annihilation [2] occurs reducing the lifetime to around 0.5-5 ns.



8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

Positrons not forming Ps have a lifetime of ~ 0.4 ns through interaction with the outer electrons of molecules with which they collide.

The free volume is a central concept in considering both equilibrium thermodynamic properties and transport phenomena in polymers. The concept of free volume, proposed originally by Doolittle [3], has long been utilized to explain the physical properties of polymeric materials. The general definition of the free volume is the open space that is freely moving in a medium [4-6]. In a series of experiments [7-11], the free volume mean size, fraction, and anisotropic structure in polymers as a function of pressure, temperature, and time have been determined using the positron annihilation lifetime (PAL) technique. The sensitivity of (PAL) in probing free volume properties arises from the fact that the positronium atom (Ps) is preferentially trapped (localized) in atomic scale free volume holes. Evidence of (Ps) localization in free volumes has been found from temperature, pressure and crystallinity experiments [7,8,10,11]. It has been shown [7] that the ortho-positronium(o-Ps) lifetime undergoes a dramatic change at the glass transition temperature. Also, the o-Ps formation is found only in amorphous regions where free volumes exist. In contrast with other techniques [12-14], positron annihilation spectroscopy probes the free volume properties directly, without being significantly interfered with by the bulk properties.

Despite the high sensitivity of the PAL technique to the free volume fraction an attempt was made to correlate the positron annihilation parameters with the dielectric data (dielectric constant and a.c. conductivity). AL-Qaradawi and Abdel-Hady [15] applied the PAL technique to investigate the behavior of the free volume in pure and doped PVC as a function of Pb concentration and temperature. They explained that the shift of the glass transition temperature (T_g) to a lower temperature is due to the increase in electrical conductivity. Borek and Osoba [16] investigated the influence of the plasticization process on free volume in PVC using PAL measurements. They found that the mean radius (R) of free volume and the relative intensity of the long lived positron lifetime component, I_3 , increase linearly with the plasticizer concentration in PVC. Mostafa, et.al. [17] studied the microstructure of a FRPVC cable jacket of the electrical board room in the MPR using the PAL technique, as well as the electrical properties as a function of temperature. They found that FRPVC contains some flame retardants, fillers, and stabilizers from organic elemental analysis and X-ray fluorescence spectrum. The effect of Al_2O_3 concentration on PVC (10 %-50 %) by weight on the o-Ps lifetime, τ_3 , and its intensity, I_3 was studied by Mohamed et.al. [18] using the PAL technique. They found that, the o-Ps lifetime increases with increasing Al_2O_3 concentration up to 30 % and then it levels off. Also, the dielectric constant, ϵ decreases with increasing the



frequency verifying the fact that, for polar materials (PVC), the initial value of ϵ is high but as the frequency of the a.c. field is raised, the value of ϵ begins to drop.

In the present work, the positron lifetime has been used to study the free volume properties of pure and doped PVC with 30 % Al_2O_3 . The aim of this study is to establish a quantitative relationship between the electrical conductivity and the positron annihilation parameters through polymer structural properties and free volume hole parameters. To accomplish this aim, the variation of the positron annihilation lifetime (PAL) parameters are investigated and correlated with the electrical properties as a function of temperature in the range from 30 to 140 °C.

II. Theoretical background:

In recent years, positron annihilation lifetime (PAL) spectroscopy has emerged as a unique physical probe [12,14, 19-21], which is capable of directly probing the properties of free volume holes in polymeric materials. A simple expression [22, 23] of free volume (V_f) can be written as the total volume (V_t) minus the occupied volume (V_o); i.e.

$$V_f = V_t - V_o. \quad (1)$$

The utility of positrons in polymer studies is enhanced by the fact that positronium is preferentially localized in the free volume holes. Positronium can be formed in either a triplet state, ortho-positronium (o-Ps), or a singlet state, para-positronium (p-Ps), depending on the spin combination of the electron and the positron. While the lifetime of ortho-positronium, $\tau_{o\text{-Ps}}$ can be related to the free volume hole size, its intensity $I_{o\text{-Ps}}$ is often considered to be related to the number of free volume holes [14]. A correlation between the free volume hole size and the observed o-Ps lifetimes, $\tau_{o\text{-Ps}}$, has been formulated. In the approximation proposed by Tao [24] and Eldrup et al. [25] it is assumed that o-Ps resides in a simple spherical potential well of radius, R, having an infinite potential barrier. Then the following semiempirical expression is found:

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

where $R_o = R + \Delta R$ and $\Delta R = 1.656 \text{ \AA}$ is the thickness of the homogenous electron layer in which the positron annihilates [26]. From the above equation, one can determine the free volume hole radius R and the average of the o-Ps hole size: ($V_{o\text{-Ps}} = (4/3) \pi R^3$) can be calculated.



Wang et al. [10] proposed a semiempirical equation that may be used to evaluate the fractional of the o-Ps hole volume such that

$$f = A I_{o-Ps} V_{o-Ps}, \quad (3)$$

where A is the normalization constant. For convenience, the relative fractional of the o-Ps hole volume is defined as [27]

$$f_r = I_{o-Ps} V_{o-Ps}. \quad (4)$$

Since knowledge of the nature of electrical conduction in insulating materials is incomplete, it is sometimes not clear whether the charge transfer process involves the transportation of ions or electrons for a certain polymers. Much interest has been focused on theoretical and experimental studies concerning a basic understanding of ionic conduction in polymers [28]. It has been found that many physical properties of polymers are related to the free volume holes and depend on pressure [29], and degree of crystallinity [30].

The electrical conductivity σ and the dielectric constant ϵ' were estimated using the following relations [31, 32];

$$\sigma(\omega) = \frac{d}{AR}, \quad (5)$$

$$R = 1 / (2 \pi F C \tan \delta), \quad (6)$$

$$\epsilon' = \frac{dC}{A\epsilon_0}, \quad (7)$$

where ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m), A is the area of the sample, R is the resistance of the sample, d is the thickness of the sample, F is the frequency, c is the speed of light, $\tan \delta$ is the loss tangen, and C is the capacitance of the sample.

The amount of power lost in a dielectric under the action of the applied voltage is called dielectric loss, ϵ'' and is given by

$$\epsilon'' = \epsilon' \tan \delta. \quad (8)$$

The frequency dependence of the a.c. conductivity is given by, [33]

$$\sigma(\omega) = A\omega^s, \quad (9)$$

where A is a complex proportionality constant and s is the index which is \leq unity.



III. Experimental:

Samples of pure and doped PVC with 30 % concentration of Al₂O₃ have been used in this study. The PAL measurements were performed under vacuum at temperatures ranging from 30 to 140 °C in 10 degrees increments using a fast-fast coincidence system with a time resolution of 240 ps full width at half maximum (FWHM). A 20 μCi ²²Na positron source was deposited on kapton foil and then sandwiched between two similar pieces of the sample. At each measurement, the PAL spectrum took 10 h to accumulate more than one million counts. The PAL spectra have been analyzed to finite term lifetimes using the PATFIT [34] program without constraints and with no source correlation. Each spectrum consists of three different mean lifetimes (τ_1 , τ_2 , and τ_3), which have relative intensities (I_1 , I_2 , and I_3). These three lifetime components were found to give the best variance ratio and most reasonable standard deviations. The shortest lifetime component (τ_1 , I_1) is attributed to the annihilation of p-Ps, which is characterized by $\tau_1 = 0.125$ ns. The second lifetime component (τ_2 , I_2) is attributed to the positron annihilation with the free electrons at the polymer matrix-additive interface. The longest lifetime (τ_3 , I_3) is due to o-Ps annihilation in the free volume. The mean free volume hole size, V_{o-Ps} and its relative fractional of the o-Ps hole volume, f_r are calculated from Eq. (4).

The dielectric properties conductivity, the capacitance (C), the loss tangent ($\tan \delta$), and the resistivity of the investigated sample were measured using a Hioki 3532 LCR meter, at different frequencies ranging from 100 Hz to 1 MHz. The sample was in the form of area 1x1 cm² and thickness 0.1 cm. The a.c. conductivity (σ), the dielectric constant ϵ' , and the index s are calculated using Eqs. (5, 7, and 9), respectively. The accuracy for σ and ϵ' was ± 2 %. The measurements were carried out at temperature ranges from 30 to 140 °C.

IV. Results and discussion:

For the pure PVC, the temperature dependence of the o-Ps lifetime, τ_3 , its intensity, I_3 , and the relative fractional of the o-Ps hole volume, f_r are shown in Fig. (1). The scale at the right ordinate is the volume of the hole in which the o-Ps is trapped. As can be seen from this figure, the nature of the variation of the positronium parameters (τ_3 , I_3 , and f_r) with temperature is rather complicated. Taking o-Ps lifetime, τ_3 as a measure of the free volume hole size, change in τ_3



observed in the samples indicates an increase in the free volume hole growth rate. It is noticed for the τ_3 trend that there are three regions. In the first region (20- 85 °C) the o-Ps lifetime, τ_3 increases with increasing temperature. This is followed by a transition region and then it rises slightly (second region from 85 – 110 °C). A linear correlation between τ_3 and temperature is observed with a definite slope at 85 °C, reported as the glass transition temperature, T_g . This is in good agreement with the data of El-Qaradawi and Abdel-Hady [15]. In the third region from 110 – 140 °C, the o-Ps lifetime, τ_3 shows an onset at 110 °C after which τ_3 is almost flat. This transition temperature might be a decomposition temperature.

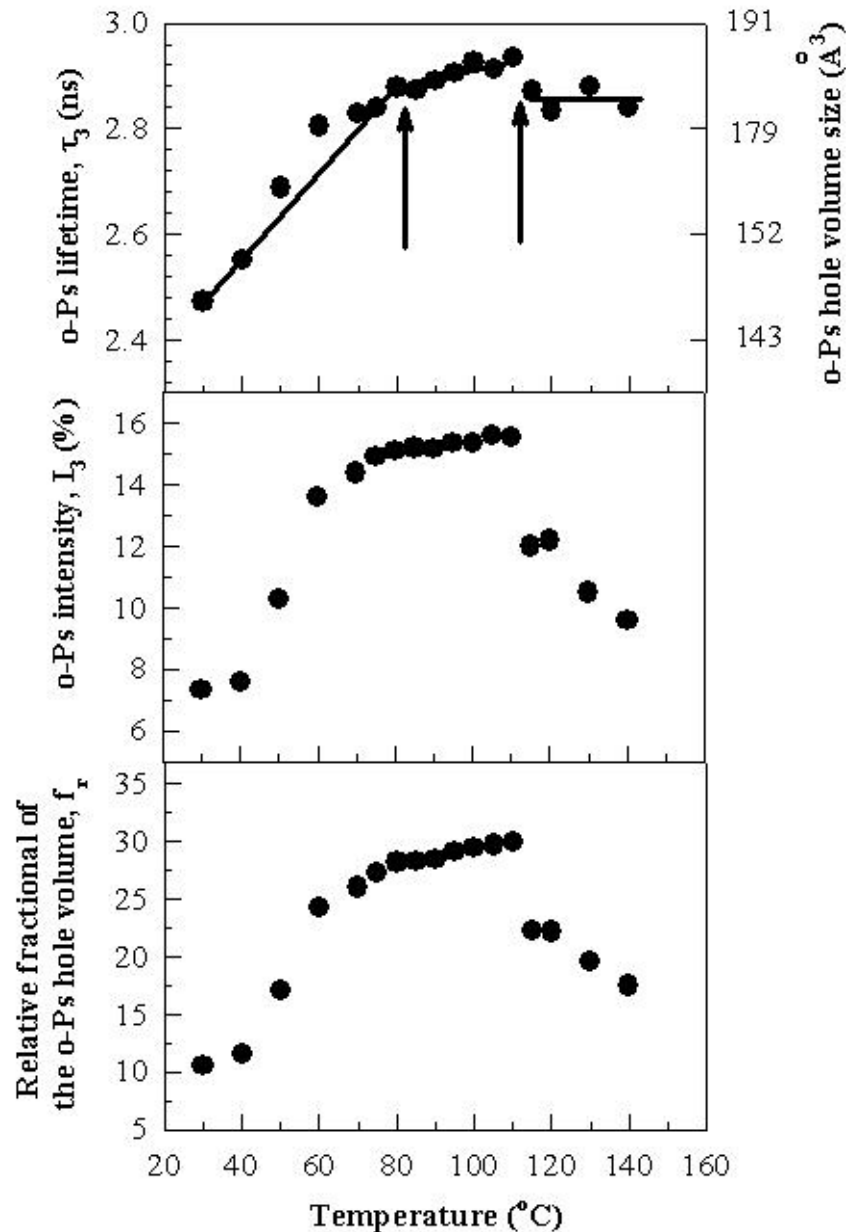




Fig. (1): The temperature dependence of the o-Ps lifetimes, τ_3 , its intensity, I_3 , and relative fractional of the o-Ps hole volume, f_r for the pure PVC. The scale at the right ordinate is the volume of the hole in which the o-Ps is trapped. The error bars are within the size of the symbol.

The behaviour of the o-Ps intensity, I_3 also appears to be composed of three regions as the o-Ps lifetime, τ_3 trend. However, the meeting point of the first and second regions is at about 75 °C, which is smaller than the T_g measured by the τ_3 values. This may be interpreted in terms of stimulated dissociation of the hydrogen bonds near strained sites. In the third region [110-140 °C], with increasing temperature, the o-Ps intensity, I_3 also shows an onset at 110 °C (decomposition temperature) after which I_3 decreases. Also, the relative fractional of the o-Ps hole volume versus temperature shows three regions. When $T < T_g$, the matrix is in the glassy state and f_r increases with increasing temperature due to segment motion of the polymer chain. Above T_g , the matrix become rubbery and the polymer segment are locally mobile like a liquid. After the decomposition temperature (> 110 °C), the polymer matrix structure may be changed and the free volume fraction decreases with increasing temperature.

For the PVC doped with 30 % Al_2O_3 , the temperature dependence of the o-Ps lifetime, τ_3 , its intensity, I_3 , and relative fractional of the o-Ps hole volume, f_r are shown in Fig.(2). The scale at the right ordinate is the volume of the hole in which the o-Ps is trapped. The o-Ps lifetime, τ_3 values also appear to be composed of three regions. In the first region (30 – 60 °C), with increasing temperature, τ_3 increases slightly up to 60 °C then it almost flat up to 105 °C (second region). The intersection between these two regions shows a transition temperature at $T = 60$ °C and is designated as the glass transition temperature, T_g . This is in agreement with the value obtained from the measurement of T_g using differential scanning calorimetry (DSC). In the third region (105 - 130 °C), the o-Ps lifetime, τ_3 shows an onset at 115 °C (decomposition temperature) after which τ_3 levels off. Since the glass transition temperature of polymers characterized the onset of a comparative motion of large segments of the molecule, the shift of T_g ($T_g = 85$ °C for pure PVC) to lower temperature ($T_g = 60$ °C for doped PVC) might explain the increase in the electrical conductivity. This is in a good agreement with the data obtained by Huang et al. [35] and EL-Sayed et al. [36], where they found that the glass transition temperature decreases with increasing doping concentration.

The I_3 values also appear to be composed of three regions: at lower temperatures, I_3 , increases with temperature to 60 °C (first region). Since I_3 is believed to be proportional to the

number of holes, the increase in I_3 suggests an increase in the number density of holes with increasing temperature. In the second region, I_3 slowly increases until 95 °C, after which, I_3 decreases. The variation of the relative fractional of the o-Ps hole volume with temperature also shows three regions, i.e, the behaviour of f_r is similar to the o-Ps intensity, I_3 .

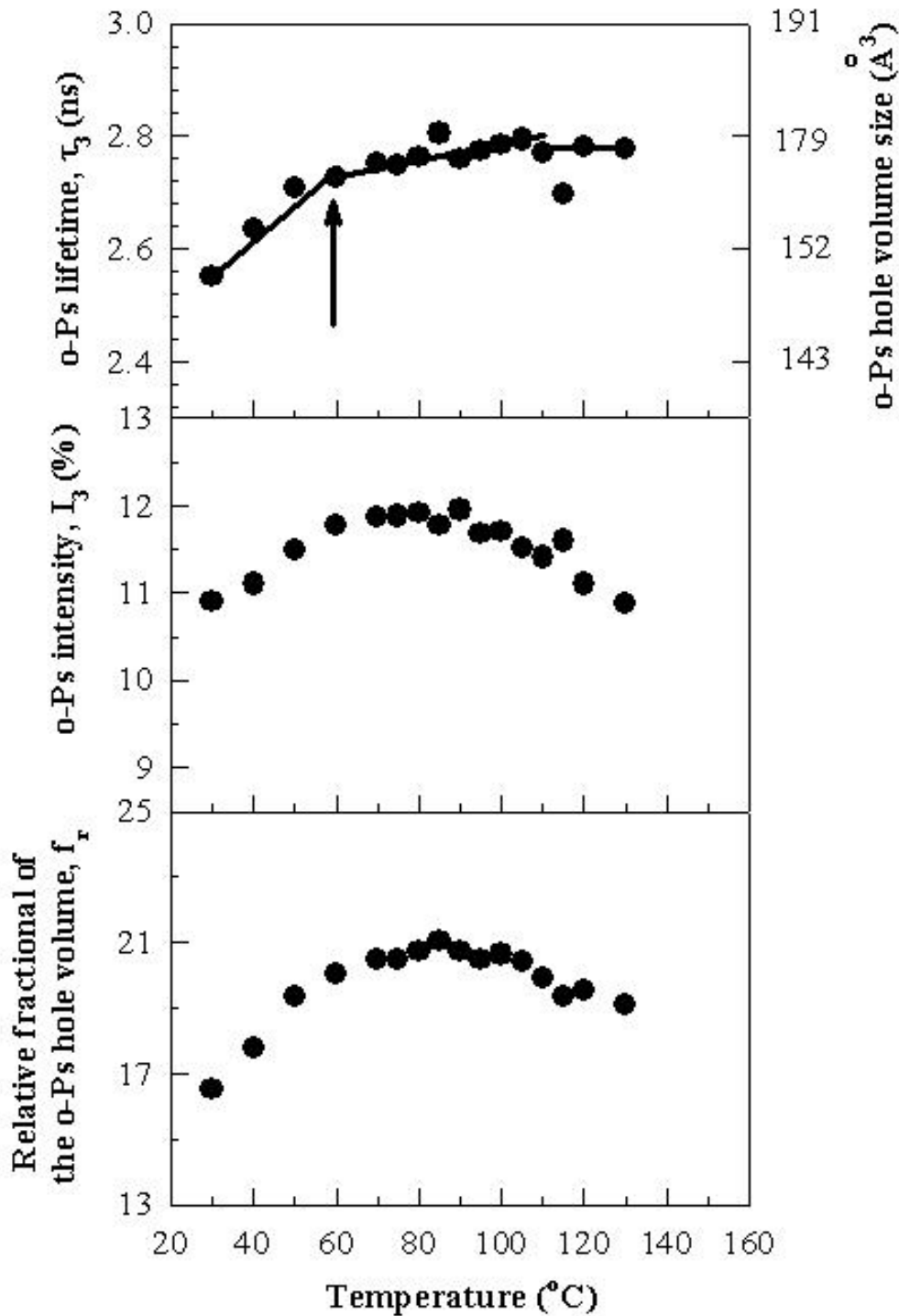


Fig. (2): The temperature dependence of the o-Ps lifetimes, τ_3 , its intensity, I_3 , and relative fractional of the o-Ps hole volume, f_r for the doped PVC with 30 % Al_2O_3 . The scale at the right ordinate is the volume of the hole in which the o-Ps is trapped. The error bars are within the size of the symbol.

Figure (3) shows the a.c. conductivity $\sigma(\omega)$ as a function of the frequency at different temperatures for pure and doped PVC with 30 % Al_2O_3 . The a.c conductivity $\sigma(\omega)$ shows strong frequency dependence at different temperatures for the samples under investigation. In order to investigate the relation between the temperatures and the dielectric data (ϵ' , σ), an interpolation of the straight lines in Fig. (3) to zero frequency has been made. Figure (4) shows the relation between log conductivity ($\log \sigma$), dielectric constant (ϵ'), and index s as a function of temperature for the pure and doped PVC with 30% Al_2O_3 . It is clear that, the logarithm of σ increases with increasing the temperature, indicating three regions as obtained before (Fig.1). The logarithm of σ gives an almost linear dependence with a discountuity at temperature of 85 and 110 °C for the pure PVC while at 80 and 110 for the doped PVC with 30 % Al_2O_3 . This might explain the increase in logarithm of σ on the basis of the motion of ions, which can be well regulated by the fraction of the free volume. A sudden increase in the electrical conductivity is observed at T_g and could be explained on the basis of semicrystalline to amorphous phase transition.

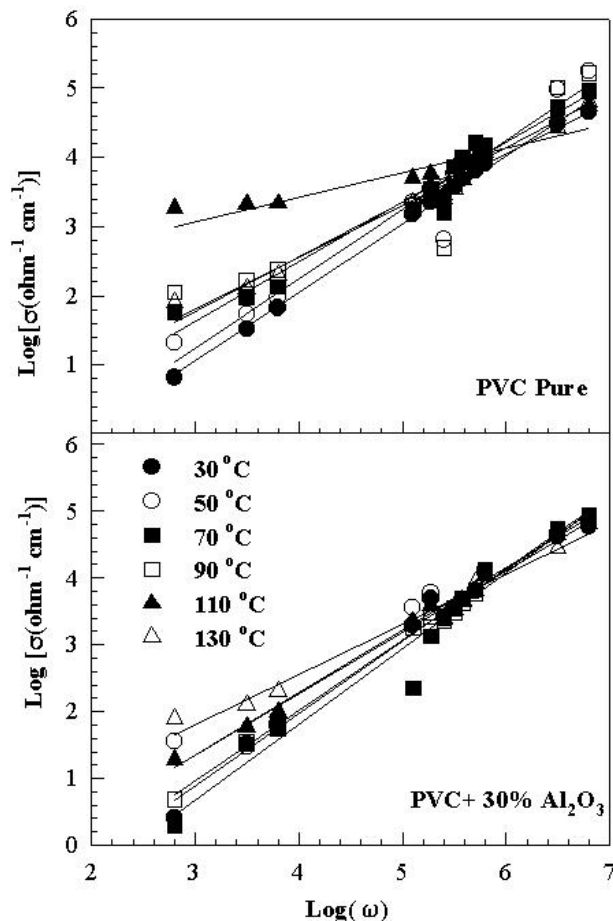


Fig. (3): The frequency dependence of $\log \sigma$ for the pure and doped PVC with 30 % Al_2O_3 at different temperatures.

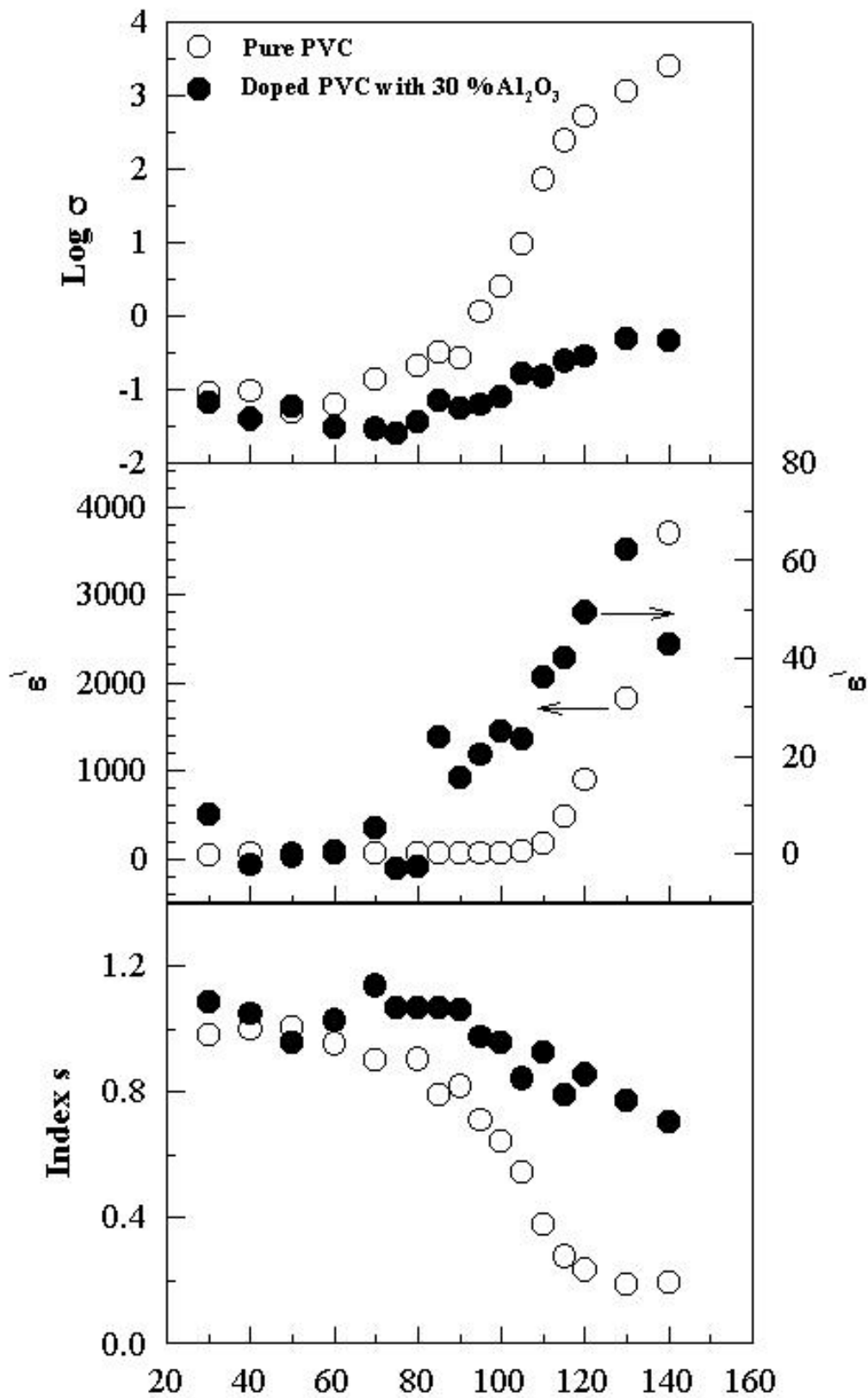




Fig. (4): The temperature dependence of the $\log \sigma$, ϵ' , and index s for the pure and doped PVC with 30 % Al_2O_3 . The error bars are within the size of the symbol.

The behavior of ϵ' seems to be similar to what has been obtained in the logarithm of σ behaviour with temperature. The increase of the dielectric constant, ϵ' with temperature is typical for the polar dielectric material, where the orientation of the dipoles is facilitated with increasing temperature. The increase in ϵ' is also due to the increase in the degree of the crystallinity [37, 38]. The occurrence of the shoulder of ϵ' at $T = 75^\circ\text{C}$ can be attributed to the decrease in the degree of ordering of the polymer molecules due to chaotic thermal vibrations [39]. The rapid increase in the dielectric constant ϵ' at higher temperatures is due to the fact that the sample is in a viscoelastic phase (above the glass transition temperature, T_g), which facilitates the rotation of the polar groups around the backbone. The value of index s is found to be more than unity in lower temperatures while it is less than unity in higher temperatures (from 50°C for the pure PVC and from 100°C for the doped PVC with 30 % Al_2O_3). The behaviour of s (less than unity) appears to indicate that hopping of charge carriers between localized states is the predominant conduction process over the frequency range studied. On the other hand, the increasing of s (larger than unity) is related to a progressive transition between hopping regimes, i.e. transition from an extended hopping regimes to one dominated by two-center hopping [40].

In order to establish a correlation between the electrical conductivity σ and the free volume V , the model suggested by Miyamoto and Shibayama [41] 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. The activation energies for the pure and doped PVC with 30 % Al_2O_3 are listed in the table (1). The critical hole γV_i^* is found to be 0.36 nm^3 for pure PVC and 0.80 nm^3 for 30 % treated samples. The larger value obtained for the latter might be the result of the existence of large ionic charge carriers.

Table (1): The activation energies for pure and doped PVC

	Pure PVC		Doped PVC	
	below T_g	above T_g	below T_g	above T_g
ΔE_b (eV)	0.21	2.43	0.17	0.50

The data in Fig. (5) represent an attempt to establish a correlation between the electrical properties of the pure PVC and the o-Ps parameters (τ_3 , I_3 , and f_r). Accordingly, the variation in the insulation properties is highly correlated with the o-Ps parameters (τ_3 , I_3 , and f_r). Three regions were also observed as obtained before [Figs. (1& 3)] with two transition temperatures for the pure PVC. In the first region, with increasing logarithm of the conductivity, the o-Ps parameters (τ_3 , I_3 , and f_r) are sharply increase while in the second region they are almost flat, and then decreasing with increasing logarithm of the conductivity (third region)

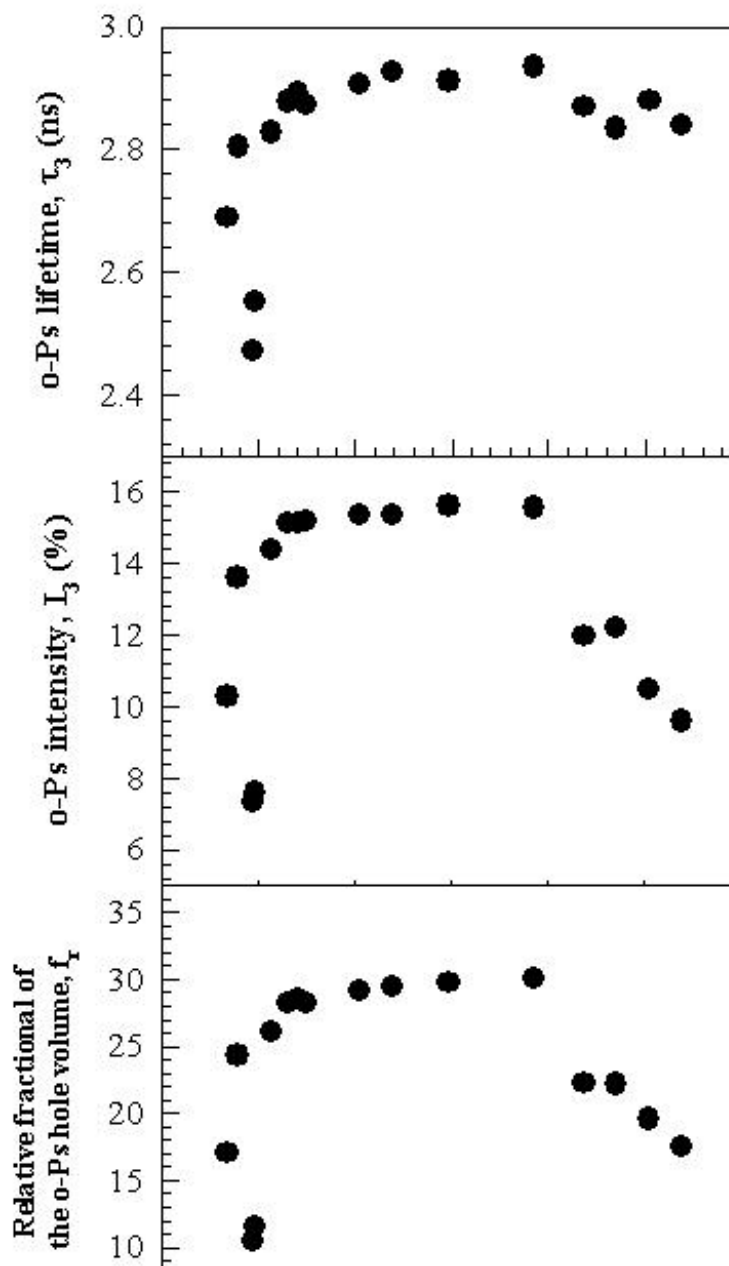




Fig. (5): The correlation between the logarithm of conductivity ($\text{Log } \sigma$) and the o-Ps parameters (τ_3 , I_3 , and f_r) for the pure PVC. The error bars are within the size of the symbol.

IV. Conclusion:

Positron annihilation spectroscopy has emerged as a powerful technique for investigation the structural changes and phase transitions in polymeric materials. The shift of the glass transition temperature for doped PVC might explain the increase in the electrical conductivity with the concentration of the additive. The electrical conductivity and dielectric results showed that ϵ has the same behavior as σ , while s has the reverse one as a function of temperature. A correlation between the o-Ps parameters (τ_3 , I_3 , and f_r) and electrical conductivity has been experimentally observed for the pure PVC. This linearity suggests that free volume (o-Ps lifetime) is important to mediating electrical conductivity.

References:

- [1] P. A. M. Dirac, "The principles of Quantum Mechanics", Oxford University Press, London (1958).
- [2] S. J. Wang, B. Wang, J. Zhu, Z. Wang, Y. Q. Dai, and C. Q. He, Mater. Sci. Forum 363-365, 219 (2001).
- [3] A. K. Doolittle, J. Appl. Phys. 22, 1471 (1951).
- [4] M. H. Cohen, and D. Turnbull, J. Chem. Phys. 31, 1164 (1959).
- [5] M. H. Cohen, and G. S. Grest, Phys. Rev. B 20, 1077(1979).
- [6] G. S. Grest, and M.H. Cohen, Adv.Chem. Phys. 48, 455 (1981).
- [7] Y. C. Jean, T. C. Sandreojki, and D. P. Ames, J. Polym. Sci. B 24, 1247 (1986).
- [8] H. Nakanishi, Y. C. Jean, E. G. Smith, and T. C. Sandreczki, J. Poly. Sci. B 27, 1419 (1989).
- [9] Y. C. Jean, H. Nakanishi, L. Y. Hao, and T. C. Sandreczki, Phys. Rev. B 42, 9705 (1990).
- [10] Y.Y. Wang, H. Nakanishi, Y. C. Jean, T. C. Sandreojki, J. Polym. Sci. B 28, 1431 (1990).
- [11] Q. Deng, C.S. Sunder, and Y. C. Jean, J. Phys. Chem. 96, 492 (1992).
- [12] W. C. Yu, C. S. P. Sung, and R. E. Roberstonn, Macromolecules 21, 355 (1988).
- [13] J. G. Victor, and J. M. Torkelson, Macromolecules 21, 3490 (1988).
- [14] Y. Tanake, N. Muller, and E. W. Fischer, J. Polym. 16, 445 (1984).
- [15] I. Y. Al-Qaradawi and E. E. Abdel-Hady, Mat. Sci. Forum 255-257, 366-368 (1997).



8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

- [16] J. Borek, and W. Osoba, *J. Polym Sci part B: Polym Phys.* 36, 1839 (1998).
- [17] N. Mostafa, M. Mohsen, S. Rashad, A. Aiob, and El. Salem, *J. of Appl. Polym. Sci.* 96, 638 (2005).
- [18] H. F. M. Mohamed, E. E. Abdel-Hady, and H.B. Alaa, *Materials Science Forum* 445-446, 328 (2004).
- [19] G. Consolati, *Mater Science Forume* 363-365, 244 (2001).
- [20] J. Bartos, J. Urban, P. Mach, and J. Kristiak, *Mater Sci Forume* 363-365, 294 (2001).
- [21] Y. C. Jean, *J. Macrochem.* 42, 72 (1990).
- [22] J. D. Ferry, “*Viscoelastic Properties of Polymers*” 3rd edn. John Wiley & Sons, New York, (1980).
- [23] R. N. Haward, *J. Macromol. Sci. Rev. Macromol. Chem.* C4, 191 (1970).
- [24] S. T. Toa, *J. Chem. Phys.* 56, 5499 (1972).
- [25] M. Eldrup, D. Lightbody, and J. N. Sherwood, *Chem. Phys.* 63, 51 (1981).
- [26] H. Nakanishi, S. J. Wang, and Y. C. Jean, in “*Positron annihilation studies of fluids*“, S.C. Sharam SC (Ed.), World Scientific, Singapore, p. 292 (1988).
- [27] Z. Peng, B. Wang, S. Li, and S. Wang, *J. Appl. Phys.* 77, 334 (1995).
- [28] M. A. Ranter, and D. F. Shriver, *Chem. Rev.* 88, 109 (1988).
- [29] S. Saito, H. Sasabe, T. Nakajima, and K. Yada, *JpPolym. Sci. A-2*, 1297 (1968).
- [30] B. I. Zazhin and N. G. Podesenova, *Sov Phys-Solid State* 6, 1755 (1965).
- [31] V. K. Bhatnagar and K. L. Bhatia, *J. of non-Crystalline Solids* 119, 214 (1990).
- [32] A. Elshafie, H. H. Afify, and A. Abdel-All, *Phys. Stat. (a)* 174, 301 (1999).
- [33] N. Balasundram, D. Magalaraj, S. K. Narayandass, and C. Balasubramanian, *Phys. Stat. Sol. A* 130, 141 (1992).
- [34] P. Kirkegaard, M. Eldrup, O. E. Mogensen and N. Pedersen, *Comput. Phys. Commu.* 23, 307 (1981), and PATFIT 88 (1988) VERSION.
- [35] C. M. Huang, T. C. Sandreczki, and Y. C. Jean, *Mater. Sci. Forum* 255-257, 302 (1997).
- [36] A. M. A. El-Sayed, E. E. Abdel-Hady, M. Mohsen, and A. Sawaby, *J. de Phys. IV, Colloque* C4, 3, 271 (1993).
- [37] R. Bahiri and H. P. Singh, *Thin Solid Films.* 62, 291 (1979).
- [38] B. C. Shekar, V. Veeravazhuthi, S. Sakthivel, D. Mangalaraj, and S. K. Narayandass, *Thin Solid Films* 348, 122 (1999).
- [39] S.L. Agrawal and P. K. Shukla, *Phys. Stat. Sol.(a)* 163, 247 (1997).
- [40] A. K. Jonscher, “*Dielectric relaxation in solids*”, Chelsea Dielectrics Press Ltd., London (1983).
- [41] T.Miyamoto and K. Shibayama, *Journal Applied Physics*, 44, 5372, (1973).