

Free Volume and Electrical Conductivity in Pure and Doped Polyvinyl Chloride with Al₂O₃

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THE mechanism of ionic conductivity (σ) in pure and doped polyvinyl chloride (PVC) with 30 % Al₂O₃ has been investigated from the viewpoint of free volume. Free volume was quantified using the positron annihilation lifetime (PAL) technique and ionic conductivity was measured as a function of temperature in the range from 30 to 140 °C. Positron annihilation lifetime of pure and doped PVC with Al₂O₃ reflect the effect of concentration as well as temperature on hole volume. Good linear correlations between $\text{Log}(\sigma) + \Delta E_a / 2.303KT$ [ΔE_a is the activation energy, K is the Boltzmann constant and T is the absolute temperature] and the reciprocal of the *o*-Ps hole volume size ($1/V_{o\text{-Ps}}$) at different temperature indicate that the ionic motion in pure and doped PVC with 30 % Al₂O₃ is controlled by free volume.

Keywords: Positron annihilation lifetime, Polyvinyl chloride, Free volume, Electrical conductivity.

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 positron-electron state is called positronium (Ps) atom. 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-positronium (*o*-Ps) (triplet state) and para (*p*-Ps) (singlet state). The intrinsic lifetime of the *o*-Ps is 142 ns in vacuum while lifetime of the *p*-Ps is 0.125 ps [2]. The *o*-Ps and *p*-Ps will annihilate into three and two annihilation gamma, respectively, with total energy 1.022 MeV. 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 [3]. The *o*-Ps annihilation may be enhanced if it is able to interact with other electrons and a spin exchange or pick-off annihilation [4] occurs reducing the lifetime to around 0.5-5 ns. 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 [5], 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 [6-8]. In a series of experiments [9-16], the free volume mean size, fraction, and anisotropic structure in polymers as a function of sorption gas, permeability, doped concentration, time, electric field and temperature have been determined using the positron annihilation lifetime (PAL) technique. The sensitivity of PAL in probing free volume properties arises from the fact that Ps is preferentially trapped (localized) in atomic scale hole volume. Evidence of Ps localization in hole volumes has been found from temperature, pressure and crystallinity experiments [17-19]. It has been shown [20] that the *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 [21-23], positron annihilation spectroscopy probes the free volume properties directly, without being significantly interfered with by the bulk properties.

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DOI : 10.21608/ejphysics.2017.17396

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 [24] 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 [25] 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. [26] studied the microstructure of a flame retardant poly(vinylchloride), (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.* [27] 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 alternated current (a.c.) field is raised, the value of ϵ begins to drop. Mohamed [28] used the coincidence Doppler broadening technique to investigate the correlation between the Doppler broadening parameters (S and W) and Vickers hardness (macroscopic data) for the PVC doped with Al_2O_3 . He found that the hardness of the samples enhanced with increasing the Al_2O_3 concentration and a linear correlation between Vickers hardness and W -parameter was achieved.

It is pointed out the largest hole volume was at 30% concentration of Al_2O_3 on PVC [27, 29], so that the aim of this work is to study the free volume properties at different temperature of pure and doped PVC with 30 % Al_2O_3 . In addition, a quantitative relationship between the electrical conductivity and the positron annihilation parameters through polymer structural properties and free volume hole parameters is established.

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.

Theoretical background

In recent years, positron annihilation lifetime (PAL) spectroscopy has emerged as a unique physical probe [30-32], which is capable of directly probing the properties of free volume holes in polymeric materials. A simple expression [33, 34] 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. The lifetime of ortho-positronium, τ_3 , can be related to the free volume hole size, its intensity I_{o-Ps} is often considered to be related to the number of free volume holes [24]. A correlation between the free volume hole size and the observed *o*-Ps lifetimes, τ_{o-Ps} , has been formulated. In the approximation proposed by Tao [35] and Eldrup *et al.* [36] 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:

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

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 [37]. From Eq. (2), one can determine the free volume hole radius R and the average of the *o*-Ps hole size is:

$$V_{o-Ps} = (4/3) \pi R^3 \quad (3)$$

Wang *et al.* [19] proposed a semiempirical equation that may be used to evaluate the fractional of the *o*-Ps hole volume such that

$$f = A I_{o-Ps} V_{o-Ps}, \quad (4)$$

where A is the normalization constant. For convenience, the relative fractional of the *o*-Ps hole volume is defined as [38]

$$f_r = I_{o-Ps} V_{o-Ps}. \quad (5)$$

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 [39]. It has been found that many physical properties of polymers are related to the free volume holes and depend on pressure [40], and degree of crystallinity [41].

The a.c. electrical conductivity σ and the dielectric constant ϵ' were estimated using the following relations [42- 44];

$$\sigma(a.c.) = \frac{G}{A} \quad (6)$$

where G is the measured conductance as a function of frequency, d is the thickness of the sample, and A is the cross sectional area of the electrode.

Experimental

Samples of pure and doped PVC with 30 % concentration of Al_2O_3 ($1 \times 1 \times 0.1 \text{ cm}^3$) were used in this study. The PAL measurements were performed under vacuum at temperatures from 30 to 140 °C as a heating runs and from 135 to 25 °C as a cooling runs with a step of 10 degrees, using a fast-fast coincidence system with a time resolution of 240 ps full width at half maximum (FWHM). A 20 μCi ^{22}Na 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 PALSfit [45] program without constraints and with no source correction. 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 $\tau_1 = 0.125 \text{ ns}$. The second lifetime component (τ_2 , I_2) is attributed to the positron annihilation with the free electrons at the polymer matrix and 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. (5).

At constant temperature, the conductance (G) for pure and doped PVC with 30% Al_2O_3

was measured using a Hioki 3532 LCR meter as a function of frequency (100Hz - 1MHz). All the measurements were carried out at temperature range from 30 to 140 °C. The a.c. conductivity ($\sigma_{a.c.}$) was calculated using Eq. (6) with accuracy $\pm 2\%$.

Wide angle x-ray diffraction (WAXD) was measured in the $\theta - 2\theta$ mode for the present samples by Ultima IV (Rigaku Corporation) with a 285 mm goniometer. A parallel monochromatic x-ray beam acquired by reflection of $Cu K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) from a fine focus x-ray tube worked at 40 kV and 40 mA by a parabolic multi-layer membrane mirror was utilized. Scattering profiles were recorded with a scintillation one-dimension position-sensitive detector over a range of $5^\circ < 2\theta < 70^\circ$ with a step of 0.01° .

IV. Results and discussion:

Figure 1 presents the temperature dependence of the *o*-Ps lifetime, τ_3 for the pure and doped PVC with 30% Al_2O_3 in the heating and cooling runs. The scale at the right ordinate in the figure is the volume of the hole in which the *o*-Ps is trapped calculated using Eqs. (2 and 3). As can be seen from this figure, the nature of the variation of the *o*-Ps lifetime τ_3 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. For pure PVC, the behaviour of τ_3 in the heating and cooling runs are almost the same except in the region of low temperature from 60 to 25 °C. This indicates that the effect of temperature in the pure PVC is irreversible process. For doped PVC with 30% Al_2O_3 , the trends of the τ_3 values for the heating runs are almost the same compared with the cooling runs. For both samples, the τ_3 trend could be divided into three regions.

For pure PVC, the *o*-Ps lifetime, τ_3 increases with increasing temperature sharply in the first region (30 - 60 °C) for heating runs while it increases smoothly for the cooling runs (25 - 80 °C). This is followed by a transition region and then it rises slightly (second region up to 110 °C). A linear variation between τ_3 and temperature was observed with a definite slope at the end of the first region (60 or 80 °C), reported as the glass transition temperature, T_g . This is in a good agreement with the data of El-Qaradawi and Abdel-Hady [24]. The difference in T_g between the heating and cooling runs may be interpreted in terms of stimulated dissociation of the hydrogen

bonds near strained sites. In the third region, from 110 to 140 °C, the *o*-Ps lifetime τ_3 shows an onset at 110 °C after which τ_3 was decreased with temperature. This transition temperature might be a decomposition temperature. 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 from 60 °C for heating runs to 80 °C for the cooling runs might explain the increase in the free volume size after the sample passing to the decomposition temperature.

For doped PVC with 30% Al_2O_3 , in the first region (30 – 50 °C), with increasing temperature, τ_3 increases slightly up to 50 °C then it almost flat up to 105 °C (second region). The intersection between these two regions shows a transition temperature at $T = 50$ °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) [46]. In the third region (105 - 130 °C), the *o*-Ps lifetime, τ_3 shows an onset at 105 °C (decomposition temperature) after which τ_3 levels off. It is clear that, there is no change in the glass transition temperature between the heating and the cooling runs. 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 ($T_g = 60$ °C for pure PVC) to lower temperature ($T_g = 50$ °C for doped PVC with 30% Al_2O_3) might explain the increase in the electrical conductivity. This is in a good agreement with the data obtained by Huang et al. [47] and EL-Sayed et al. [48], where they found that the glass transition temperature decreases with increasing doping concentration.

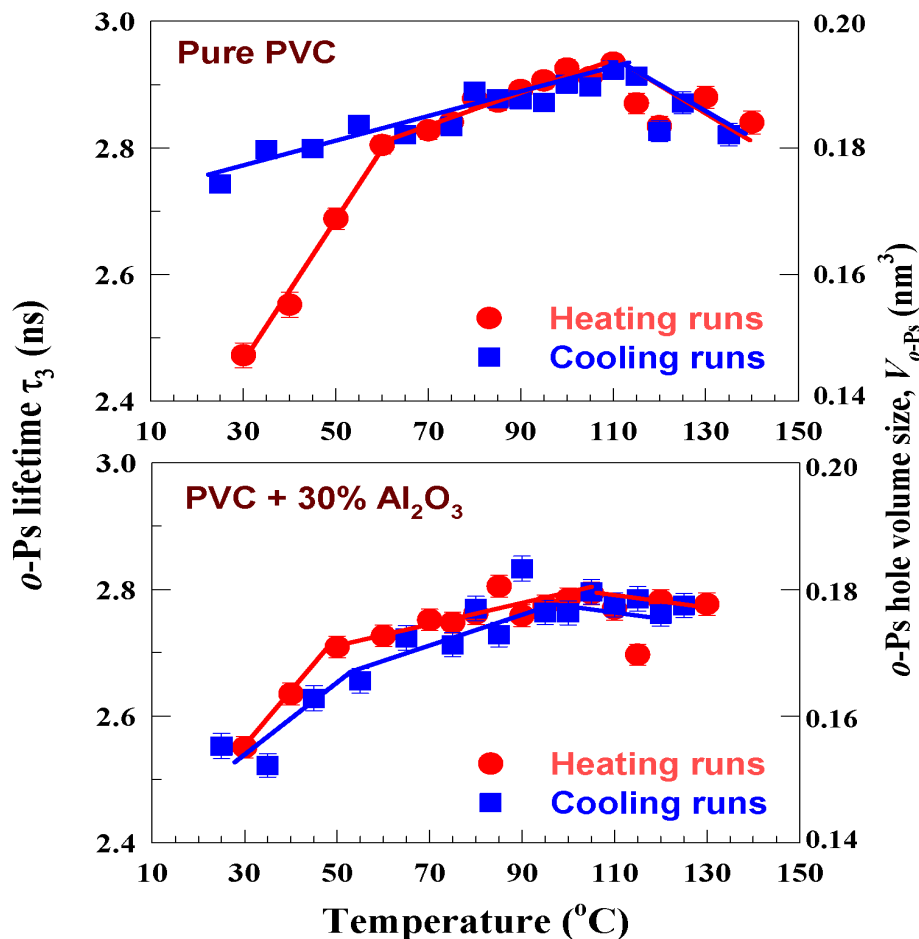


Fig. 1. The temperature dependence of the *o*-Ps lifetimes, τ_3 for the pure and doped PVC with 30 % Al_2O_3 in the heating and cooling runs. The scale at the right ordinate is the volume of the hole in which the *o*-Ps is trapped calculated using Eqs. (2 and 3). The error bars are within the size of the symbol.

The temperature dependence in the heating and cooling runs of the *o*-Ps intensity, I_3 for the pure and doped PVC with 30% Al_2O_3 is shown in Fig. 2. The behaviour of the *o*-Ps intensities for pure PVC is similar to that in the *o*-Ps lifetime. It also appears to be composed of three regions; 1) from 30 to 60 °C, 2) from 60 to 110 °C, and 3) from 110 to 140 °C. The interpretation of the behaviour of the temperature dependence of I_3 for the three regions are almost the same as explained for the τ_3 trends. The meeting point of the first and second regions is at about 60 °C, which is similar to that seen by τ_3 and was indicated as T_g . 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. For doped PVC with 30 % Al_2O_3 , at lower temperatures, I_3 increases

with temperature up 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 110 °C, after which, I_3 decreases. Again for both the samples the temperature dependences are irreversible process because the trends for the heating runs are not similar to those in the cooling runs. The *o*-Ps intensity I_3 at room temperature for both the samples are higher than those in the heating runs indicating that the samples became highly crystalline after passing to the decomposition temperature. This is conformed by comparing the wide angle x-ray spectra for the samples before and after PAL measurements as will be discussed below.

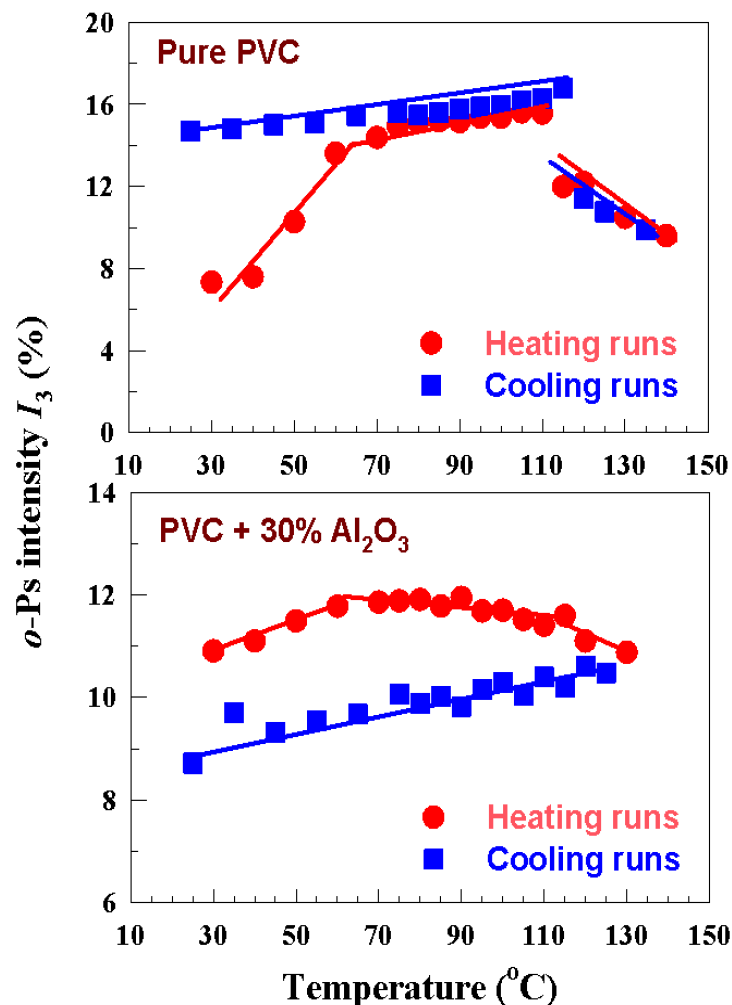


Fig. 2. The temperature dependence of the *o*-Ps intensity, I_3 for pure and doped PVC with 30 % Al_2O_3 in the heating and cooling runs. The error bars are within the size of the symbol.

Figures 3 & 4 shows the wide angle x-ray diffraction (WAXD) for the pure and doped PVC with 30% Al_2O_3 before and after PAL measurements. The pure PVC generally exhibits an amorphous phase [49, 50], but some of the crystalline peaks are observed at 12.5° and 25.4° of 2θ for the unheated sample used in the present study (Fig. 3). After heating the sample, the intensities of the crystalline peaks increase indicating increasing of the degree of crystallinity. The same behaviour was occurred in the doped PVC with Al_2O_3 sample (Fig. 4) and also the Al_2O_3 peaks at $2\theta \sim 67^\circ$ became narrow. For good comparison between the results obtained from WAXD and the positron annihilation parameters, the relative fractional of *o*-Ps hole volume f_r was calculated for the heating and cooling runs using Eq. (5) and presented in Fig. 5 for pure and doped PVC with 30 % Al_2O_3 . For pure PVC, the relative fractional of the *o*-Ps hole volume, f_r versus temperature shows three regions similar to both τ_3 or I_3 . 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 ($> 110^\circ\text{C}$), the polymer matrix structure may be changed and the free volume fraction decreases with increasing temperature. For doped PVC with 30 % Al_2O_3 ,

the variation of the relative fractional of the *o*-Ps hole volume f_r with temperature also shows three regions, *i.e.*, the behaviour of f_r is similar to the *o*-Ps intensity, I_3 .

Figure 6 shows the a.c. conductivity σ as a function of temperatures for pure and doped PVC with 30% Al_2O_3 . It is clear that the ionic conductivity increases as the temperature increases with different slopes. The meeting temperature of these slopes are at 83 and 110°C for pure and doped PVC with 30 % Al_2O_3 , respectively. These transition temperature could be connected with those obtained previously from the positron annihilation data. A discrepancy between the transition temperature estimated from positron annihilation and ionic conductivity data can be resolved assuming that the ionic conductivity responds mainly on the free segmental motion but positron annihilation spectroscopy on the segmental motion of coordinated polymer chains. The temperature dependence of the ionic conductivity might explain the increase in the ionic conductivity σ on the basis of the motion of ions, which can be well regulated by the fraction of the free volume. The quickly increase in the electrical conductivity was observed above the transition temperature and could be explained on the basis of glassy to amorphous phase transition.

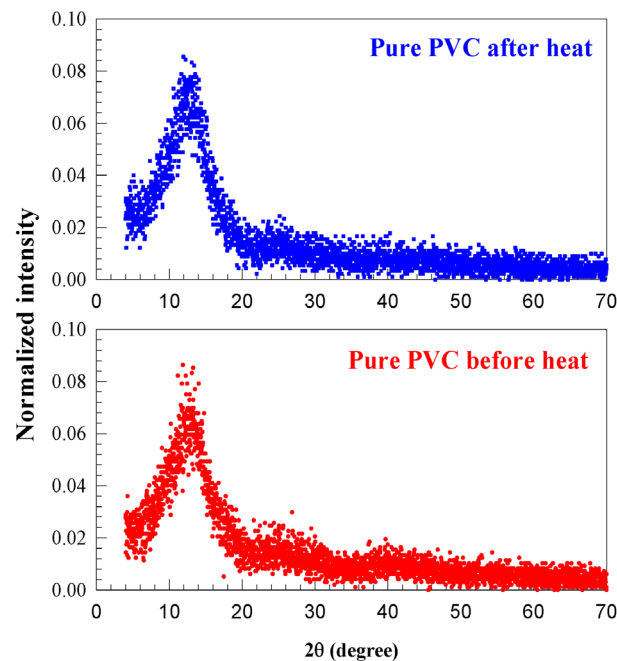


Fig.3. The wide angle x-ray pattern for pure PVC before and after heating (PAL measurements) at room temperature (25°C).

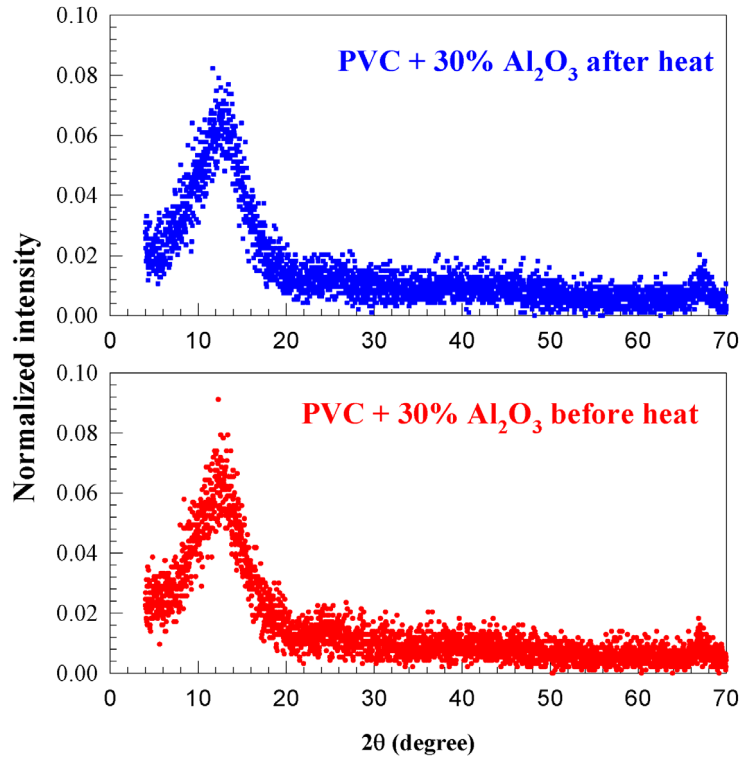


Fig. 4. The wide angle x-ray pattern for doped PVC with 30 % Al₂O₃ before and after heating (PAL measurements) at room temperature (25 oC).

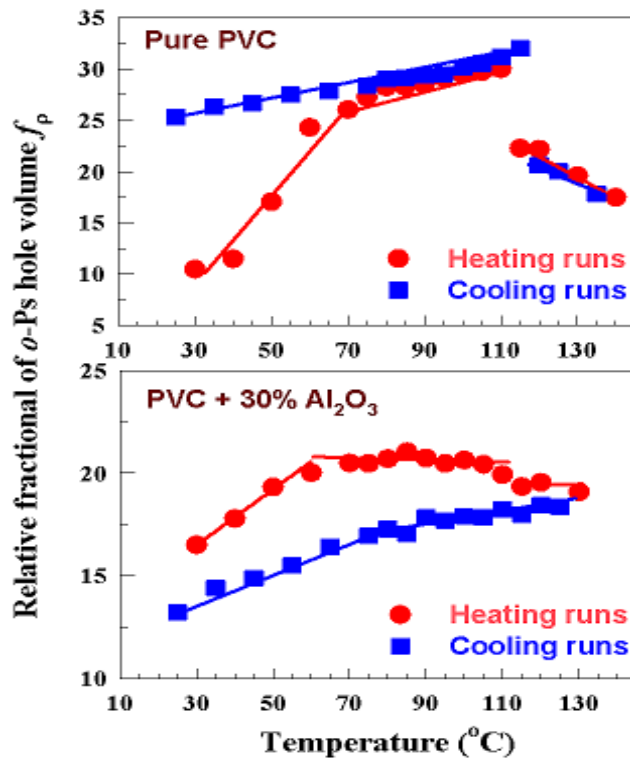


Fig. 5. The temperature dependence of the relative fractional of the o-Ps hole volume, f_r for pure and doped PVC with 30 % Al₂O₃. In the heating and cooling runs. The error bars are within the size of the symbol.

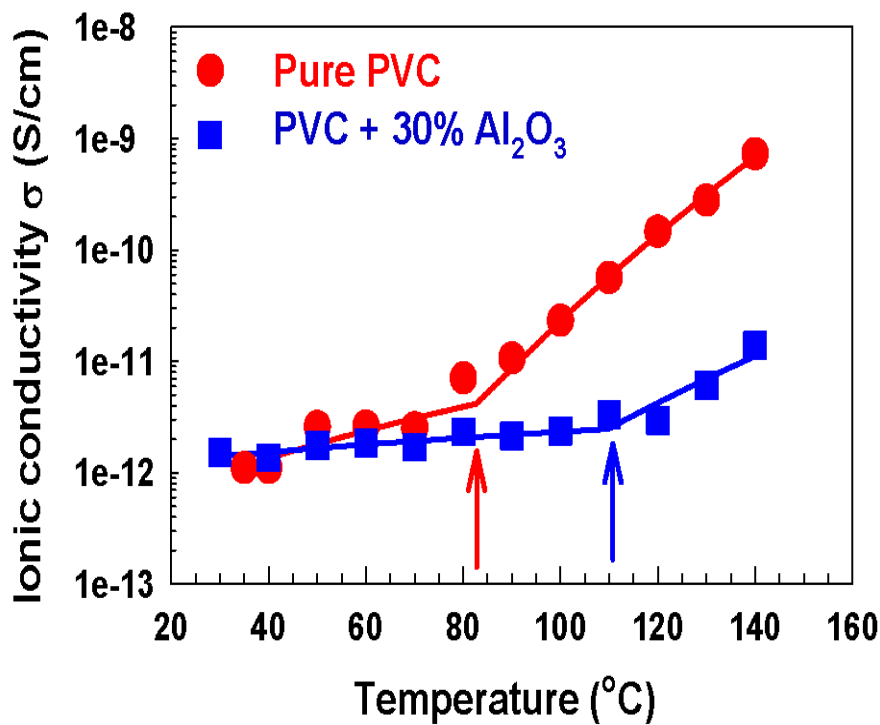


Fig. 6. The temperature dependence of the ionic conductivity σ for pure and doped PVC with 30 % AL₂O₃.

As can be seen from Fig. 6, the values of the ionic conductivity for pure PVC is higher than that for doped PVC with 30% Al₂O₃. This can be interpreted as; when the salt dissolves in polymer and dissociates into ions, it generates carrier ions and at the same time increases the viscosity. These two results have opposite effects on conductivity in which the former increases the conductivity, while the latter decreases the conductivity [51]. This phenomenon is due to salt ions acting as transient cross-linking agents that decreases the ionic mobility. The trend of the ionic conductivity for doped PVC with Al₂O₃ can be discussed as following; the polymeric chains and the filler particles (Al₂O₃) behaves as a trap centers for the charge carriers which transited by hopping [52]. As the temperature increases segmental motion start to occur leads to releasing the trapped charge carriers. The release of trapped charges is intimately associated with molecular motion. The increase of the conductivity depending on charge carriers concentration and their mobility. The concentration of charge carriers increases

exponentially with the increase of temperature but the mobility depends on the structure and the temperature [53]. It was reported that, the electron mobility value of the electron in PVC sample is 10⁻² cm² V⁻¹s⁻¹ reveals that the conduction mechanism is hopping [54].

The temperature dependence of the ionic conductivity σ for pure and doped PVC with 30 % Al₂O₃ is shown in Fig. (7). The activation energy E_a can be calculated using the Arrhenius plot using equation [55]:

$$\sigma = \sigma_o \exp (\Delta E_a / KT), \quad (7)$$

where σ_o is the preexponential factor, ΔE_a is the activation energy, K is the Boltzmann constant and T is the absolute temperature. The activation energy values for pure and doped PVC with 30% Al₂O₃ were listed in Table (1) before and after the transition temperatures. The high activation energy values for the samples after the transition can be attributed to the thermal movement of ions and molecules.

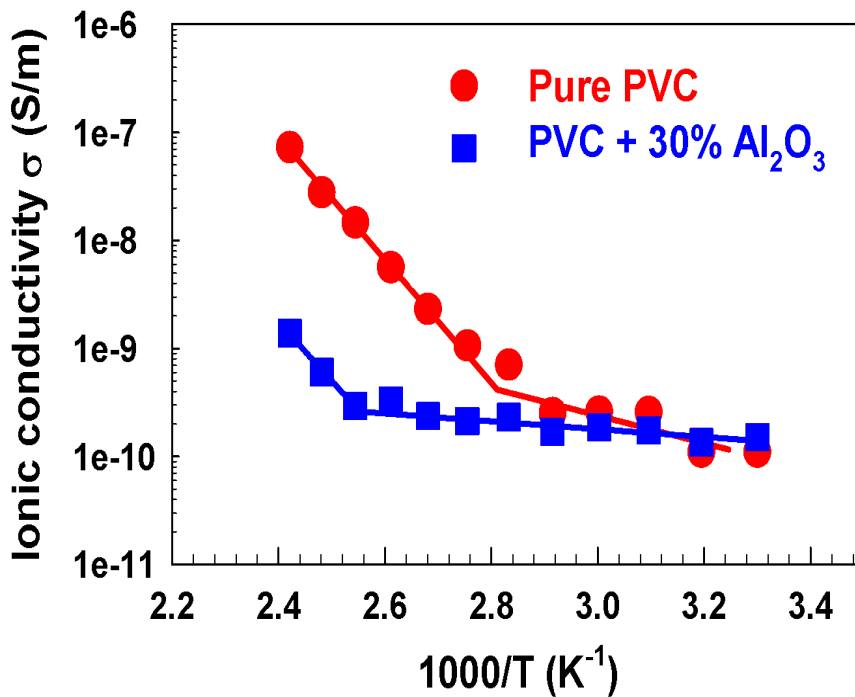


Fig. 7. The ionic conductivity σ as a function of $1000/T$ for pure and doped PVC with 30% Al_2O_3 .

TABLE 1. The activation energies for pure and doped PVC with 30 % Al_2O_3 .

	Pure PVC		Doped PVC with 30% Al_2O_3	
Region	below T_g	above T_g	below T_g	above T_g
ΔE_a (eV)	0.11	0.49	0.031	0.30

In order to establish a correlation between the ionic conductivity σ and the free volume V , the model suggested by Miyamoto and Shibayama [56] has been applied:

$$\sigma = \sigma_0 \exp \left\{ - \left[\frac{\gamma V_i^*}{V} + \frac{\Delta E_a}{K} \right] \right\} \quad (8)$$

Where σ_0 is the preexponential factor (constant), γ is a numerical factor between 0.5 and 1.0 to correct the overlap of free volume and polymer segments [56], V_i^* is the critical volume required for transport of an ion, ΔE_a is the apparent activation energy at temperature below T and K is Boltzmann constant. The *o*-Ps hole volume size (V_{o-Ps}) will be used in state of the free volume (V) in Eq. (8). Figure 8 shows the

correlation between $\text{Log}(\sigma) + \Delta E_a / 2.303KT$ and the reciprocal of the *o*-Ps hole volume size ($1/V_{o-Ps}$) for pure and doped PVC with 30 % Al_2O_3 . A linear correlation was obtained indicating that the ionic conductivity is controlling by the free volume in the polymers under study. This behaviour is similar to the data of Pas el al. [57] who found the same behaviour for polymer electrolyte. From the slopes of the straight lines shown in Fig. 8, the critical hole size γV_i^* was calculated and found to be 1.169 nm^3 for pure and 0.243 nm^3 for PVC doped with 30 % Al_2O_3 . The smaller value obtained for the latter might be the result of the existence of smaller ionic charge carriers.

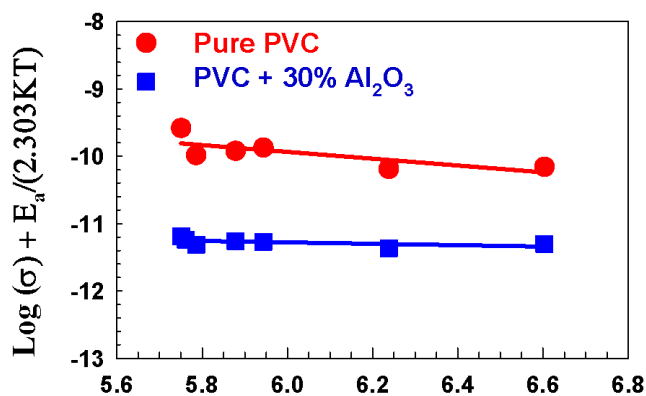


Fig. 8. The correlation between $\text{Log}(\sigma) + E_a/2.303KT$ and reciprocal o-Ps hole volume size ($1/V_{o-Ps}$) for pure and doped PVC with 30 % AL₂O₃.

Conclusion

Positron annihilation spectroscopy has emerged as a powerful technique for investigation the structural changes (free volume) and phase transitions in polymeric materials. For both the sample, the temperature dependence of the electrical conductivity reflected the transition temperatures and also the conductivity mechanism (hopping mechanism). A correlation between the o-Ps parameters (τ_3 , I_3 , and f_T) and the electrical conductivity has been experimentally observed for the pure and doped PVC with Al₂O₃. The linear relationships between $\text{Log}(\sigma) + \Delta E_a/2.303KT$ and the reciprocal of the o-Ps hole volume size ($1/V_{o-Ps}$) at different temperatures suggest that ionic motion in pure and doped PVC with 30 % AL₂O₃ is mediated by free volume.

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(Received: 30/5/2017 ;

Accepted:26/ 7/ 2017)

الحجم الحر والتوصيل الكهربى فى البولى فنيل كلورايد النقى والمطعم باكسيد الالومنيوم

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في هذا البحث تم فحص آلية التوصيل الايوني في البولى فنيل كلوريد النقى والمطعم باكسيد الالومنيوم بنسبة ٣٠٪ من وجهة نظر الحجم الحر وقد تم تعيين الحجم الحر باستخدام تقنية الفناء البوزيتروني وقياس الموصلية الأيونية كدالة في درجة الحرارة في المدى من ٣٠ إلى ١٤٠ درجة مئوية. وقد أظهرت النتائج التي تم التوصل إليها أن قيم زمن الفناء البوزيتروني للمادة النقية والمطعمة باكسيد الالومنيوم تعكس تأثير كل من التركيز ودرجة الحرارة علي حجم الفجوة وقد وجد أيضا ترابط خطي بين $\text{Log}(\sigma) + \Delta E_g / 2.303KT$ ومقلوب حجم الفراغ الحر للبوليزيترونيوم ($1/V_{o-ps}$) عند درجات الحرارة المختلفة وهذا يدل علي ان حركة الايونات داخل المادة النقية والمطعمة باكسيد الالومنيوم مرتبطه بالفراغات الحرة في المادة.