

Effect of Temperature on Some Nano free Volume Parameters in Natural Rubber

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Positron annihilation lifetime (PAL) technique is applied on natural rubber to determine the parameters of nano free volumes such as size, concentration and distribution as a function of temperature. In agreement with the Differential Scanning Calorimeter (DSC) measurements and X-ray diffraction (XRD) measurements, the results showed that the (PAL) technique is sensitive to probe the glass transition temperature (T_g) and its ability to determine the melting transition temperature (T_m). Above T_g , the isothermal measurements showed an intermediate transition point before the melting point. Moreover, the ortho-positronium (o-Ps) was able to probe the variation of free volumes in the amorphous domains with the change of temperature. The calculated expansion coefficient of free volume indicates that o-Ps is selectively probing free volume sites in amorphous domains.

1. Introduction

Polymers have become an increasingly important group of engineering materials. Some important industries such as those for fibers, rubbers and plastics are based on polymers. Utilization of polymers in industrial applications requires a basic understanding of their physical properties. One of the important properties of polymeric materials is their mechanical flexibility in engineering processing; where the existence of free volumes in polymers plays an important role. Therefore, applying positron annihilation lifetime spectroscopy (PALS) is essential for studying polymeric material such as natural rubber.

A correlation between ortho-positronium (o-Ps) lifetime components and the Young's modulus in butyl rubber filled with carbon black was reported [1]. The effect of temperature on the lifetime component τ_3 and its concentration I_3 in polyisoprene samples for the temperature range from 150 to 300 K was

measured; a minimum in I_3 just above the glass transition temperature (T_g) was also observed [2]. The positron annihilation lifetime (PAL) as a probe for free volumes in three natural polyisoprene samples with different percentages of dicumyl peroxide additives and one synthetic isoprene sample as a function of temperature (-196°C to 42°C) was used [3]. PAL was applied to investigate microstructure properties of carbon black- silica- styrene butadiene rubber (SBR) composites [4]. Nuclear magnetic resonance (NMR) was carried out to examine crystallinity, chain mobility in real time during crystallization of *cis*_{1,4} polyisoprene samples [5]. Positron annihilation lifetime spectroscopy was used to estimate the size and number density of free volume sites in copolymer of styrene and butadiene rubber [6]. PALS combined with DSC was applied to characterize the nanoscale free volume in butadiene acrylonitrile copolymer (NBR) polyethylene (PE) blends [7].

The aim of this work is to study the nanoscale free volume in natural rubber using PAL technique combined with DSC and X-ray diffraction.

2. Experiment

2.1. Sample: Natural Rubber

Samples that used in the present study was coming from on tree source, Hevea rubber tree (*Hevea brasiliensis*) which is the only plant species being cultivated for commercial production of rubber in the world. The samples are classical flat specimen 10 mm in length, 5 mm in width and 1 mm thickness.

2.2. Positron Annihilation Technique

Positron lifetime measurements were performed for natural rubber using a conventional fast-fast coincidence spectrometer with a time resolution of 300 ps (FWHM). A positron source ²²Na was prepared by depositing about 20 μC of NaCl solution on kapton foil (7μm thick), then sandwiched between two identical measured samples. The two samples including the positron source were fixed on the cooling finger of a closed cycle Helium cryostat (air cooled compressor model 8200). The cold head (model 22) of this cooling system includes design features optimized specifically for the positron annihilation measurements. The sample was cooled indirectly, using static helium exchange gas inside the sample chamber. The temperature was controlled by a Lakeshore temperature controller (model 321), which could maintain the temperature of the samples to within 0.1 K. The polymer sample was cooled down to the selected temperature, (ranging from 100 °C to 40 °C) and then the positron lifetime spectrum was recorded at the given temperature. The lifetime spectra were resolved into four components using the LT 9.0 program [8], which allows both discrete and log normal distribution of annihilation rate $\lambda=1/\tau$. The finite-

term analysis is a method used for the determination of the mean size and fraction of free volume holes. Whereas the continuous lifetime analysis yields a distribution of the o-Ps annihilation rate $\lambda_4=1/\tau_4$, the size distribution of free volume holes can be calculated.

In the finite-term analysis, the experimental lifetime spectrum $Y(t)$ is expressed as convolution of the instrument resolution function $R(t)$ with a finite number (n) of negative exponentials plus a background (B) [9], where:

$$Y(t) = R(t) * \left(N_t \sum_{i=1}^n \alpha_i \lambda_i e^{-\lambda_i t} + B \right) \quad (1)$$

hence N_t is the normalized total counts, λ_i is the annihilation rate ($=1/\tau_i$) and ($\lambda_i \alpha_i$) is the intensity. The fitting parameters λ_i and α_i (with $i = 1, 2, 3, 4$) were obtained using the least-square fit to the experimental lifetime spectrum $Y(t)$ in Eq. (1).

Lifetime analysis decomposed the PAL spectrum into four different states of positron annihilation; the shortest-lived component τ_1 with intensity I_1 was attributed to the annihilation of p-Ps. The intermediate components τ_2 with intensity I_2 and τ_3 with intensities I_3 were mainly due to the positrons trapped in the defects present in the crystalline regions and crystalline-amorphous interphase regions [10]. The longest component lifetime τ_4 with intensity I_4 was due to the pick-off annihilation of o-Ps in the amorphous region of the polymer matrix [11].

According to the model proposed by Tao [12] and Eldrup et al. [13], the o-Ps lifetime τ_4 is related to the size of the free volume in which the o-Ps annihilates. Positronium (Ps) is assumed to be localized in a spherical potential well having an infinite potential barrier of radius $R_o (= R_h + \delta R)$ with an electron layer. The average radius of the free volume holes (R_h), can be determined from the following relation [14]:

$$\tau_4 = 0.5 \left[1 - \frac{R_h}{R_h + \delta R} + \frac{1}{2\pi R_h} \sin\left(\frac{2\pi R_h}{R_h + \delta R}\right) \right]^{-1} \quad (2)$$

where δR is the thickness of the electron layer. The assumption is that the lifetime of the o-Ps in the electron layer is the spin-averaged Ps lifetime of 0.5 ns [13, 15]. $\delta R = 1.66 \text{ \AA}$ was determined by fitting Eq. (2) with experimental τ_4 values of molecular materials with known hole sizes. The free volume size V_h was calculated as $V_h = 4\pi R_h^3/3$, where as the relative fractional free volume $fv = V_h I_3$.

Since the free volume hole radii are likely to exist in a distribution, the o-Ps lifetime is expressed as a distribution rather than as discrete values. In the continuous lifetime analysis, a PAL spectrum is given in a continuous decay as:

$$Y(t) = R(t) \left(N_t \int_0^{\infty} \lambda \alpha(\lambda) e^{-\lambda t} dt + B \right) \quad (3)$$

The integral in parenthesis is simply a Laplace transformation of the function $\lambda \alpha(\lambda)$, where $\alpha(\lambda)$ is the probability density function of the annihilation rate $\lambda = 1/\tau$ [16].

2.3. Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) was used to measure the glass temperature (T_g), the crystallization transition temperature (T_c) and the melting temperature (T_M). The crystalline melting point of a polymer corresponds to a change in the state from a solid to a liquid is represented as endothermic peak in a DSC curve. In addition, to determine the melting point and heat of fusion from DSC, the width of the melting range was indicative of the range of crystal size and perfection. Isothermal crystallization could occur at a range of temperatures below T_M and above T_g .

2.4. X ray diffraction

Philips powder diffractometer of X'pert (MPD) system with Bragg-Brentano para focusing of reflection geometry technique and graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.709 \text{ \AA}$) was applied in the studied samples. A fixed divergence slit of 1° and a receiving slit of a height 0.1 mm were used. Soller slits of 0.04 rad was used in both the incident and diffracted beam. Data were collected over the range $0^\circ \leq 2\theta \leq 90^\circ$ in 0.03° steps with a counting time 10s. The collected data range gives an accessible scattering vector magnitude (k) of about 16.0. This value provides a reasonable resolution in both the inverted space (K-space) and also the real space (R-space).

2.5. Tensile deformation

Deformation of the samples was obtained by using the tensile apparatus in situ with the PAL spectrometer. The positron annihilation experiment was started after the rubber sample was stretched to (300%), then held at a constant elongation during the positron annihilation measurements.

3. Results and Discussion

3.1. Annihilation of free positrons

Figures 1(a,b) and 2(a,b) show the variation of the second (τ_2 , I_2) and third (τ_3 , I_3) lifetime components versus the temperature which are associated with annihilation of free positrons in the crystal domains and interface, respectively. The lifetime components (τ_2 and τ_3) show similar variation trend where one can observe a weak increase below T_g (-70°C) and a stronger increase above T_g up to -30°C . In addition, the two lifetimes show a weak variation till the melting temperature T_M (30°C). However, the population of the crystal and interface domains, which are represented by (I_2 and I_3) respectively, show opposite variation trends at -30°C whereas I_2 increases from 55% to 65% and I_3 decreases from 18% to 3%. This may be due to the combination of some small size defects to form new defects with bigger sizes and low fractions.

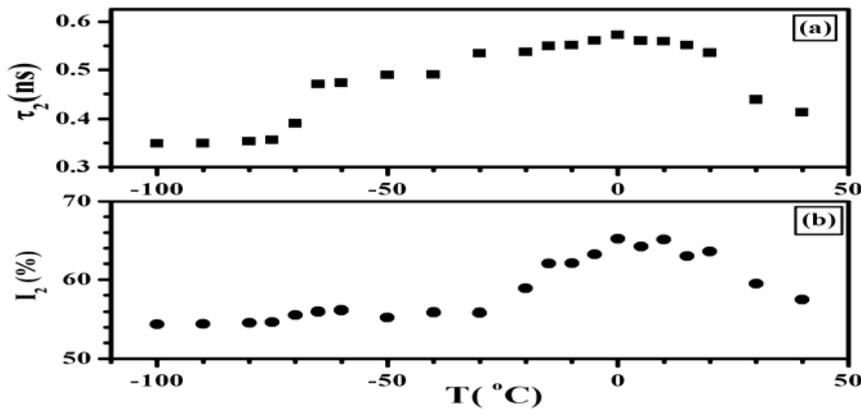


Fig. (1 a,b): The temperature variation of the second lifetime components, (τ_2 , I_2) in natural rubber.

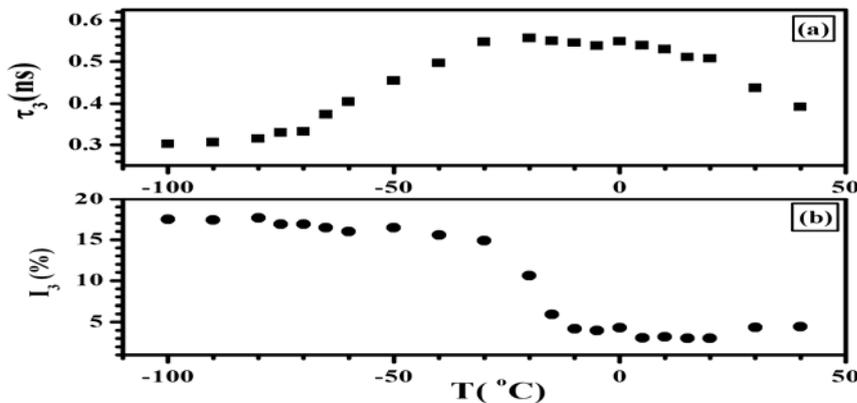


Fig. (2a,b): The temperature variation of the third lifetime components, (τ_3 , I_3) in natural rubber.

3.2. Ortho positronium annihilation in free volumes

Figure 3(a,b) shows the temperature variation of the o-Ps lifetime components (τ_4 , I_4) for natural rubber versus temperature. It provides information on the microstructure changes in amorphous region of polymers [11]. The lifetime (τ_4) is ranging from 1.5 to 3.5 ns and its intensities (I_4) ranging from 18 to 28%. The measurements conclude that:

- At low temperature ($T < T_g$), the o-Ps lifetime components (τ_4 and I_4) do not vary considerably with temperature because all motions including molecules and chains at this temperature are completely froze [17].
- During the isothermal measurements, the temperature variation show an intermediate transition point ($T_o = -20^\circ\text{C}$) above the glass temperature (T_g) and before the melting temperature (T_M) which can be attributed to less stable crystalline phase.
- The steepest change in τ_4 and I_4 with temperature occurs at (T_g) and liquid transition (T_o) temperature. This is due to the main-chain segmental motion and the increase of mobilization in polymer matrix. This can increase the free volume size in the amorphous domain and consequently increase the o-Ps lifetime (τ_4) from 1.5 to 3.5 ns and its fractions (I_4) from 18 to 28%.
- Above T_M , polymers are in a real liquid state having a relaxation time that is comparable to o-Ps lifetime. In this state, Ps creates a large new open space, called Ps-bubble, which has a size of few angstroms. Therefore τ_4 tends to decrease and I_4 to increase [18].

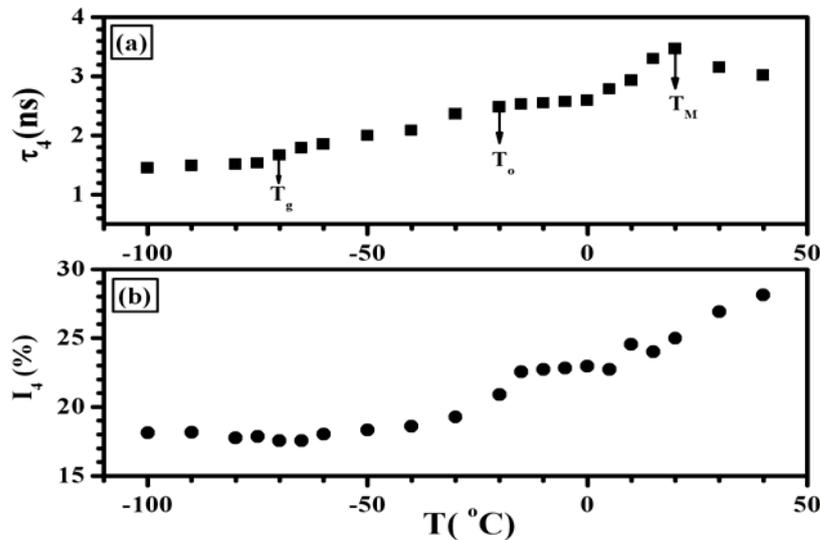


Fig. (3a,b): The temperature variation of the o-Ps lifetime components, (τ_4 , I_4) in natural rubber.

3.3. Thermal expansion coefficient:

To analyze the transition point (T_o), the free volume fractions (f_v) were estimated as a function of temperature according to the following equation:

$$f_v = 0.025 + (T-T_g) \alpha_f. \tag{4}$$

where α_f is the thermal expansion coefficient for free volume. The results are listed in Table (1).

Table (1): Comparison of free volume expansion coefficient α_f and volume expansion coefficient.

Temperature	$T < T_g$	$T > T_g$	$T > T_M$	Volume expansion coefficient
α_f	$5.9 \times 10^{-3} \text{ K}^{-1}$	$74 \times 10^{-3} \text{ K}^{-1}$	$25 \times 10^{-3} \text{ K}^{-1}$	$6.6 \times 10^{-4} \text{ K}^{-1}$

From Table (1), one can observe that: α_f in free volume is about more than one order of magnitude higher than the normal thermal expansion coefficient of rubber. It indicates a strong evidence of Ps trapping in free volume sites, which exists only in the amorphous domains. Therefore, the increase of I_4 from 18 to 28%, Fig. (3b), can be assigned to the increase in amorphous domains with temperature. Also, Fig. (4) indicates that: Below T_g , all motions including molecules and chains are completely frozen [17] where f_v is constant. Above T_g the matrix becomes rubbery and the chain mobility increases with temperature, thus increasing the fractional free volume content. In addition, an intermediate transition point at $T_o = -20^\circ\text{C}$ before the melting point could be resolved. This transition indicates the presence of a less stable crystalline phase. At the melting point $T_M = 30^\circ\text{C}$, the free volume fraction (f_v) reaches maximum.

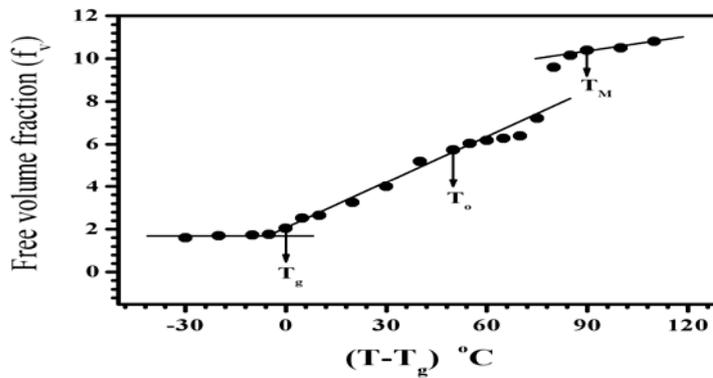


Fig. (4): The temperature variation of free volume fractions (f_v).

3.4. Free volume distributions

Figure (5) shows the variation of the free volume size distribution as a function of temperature. Below T_g , the free volume distribution shows an average volume of $45A^{03}$. Whereas above T_g , the distribution is shifted to larger free volume size $149A^{03}$ at the transition temperature T_o and reaching a maximum value of $252 A^{03}$ at T_M . The distribution size is shifted to a lower free volume size at $T>T_M$, reaching $199 A^{03}$ at $40^\circ C$ where the polymer becomes in a real liquid state.

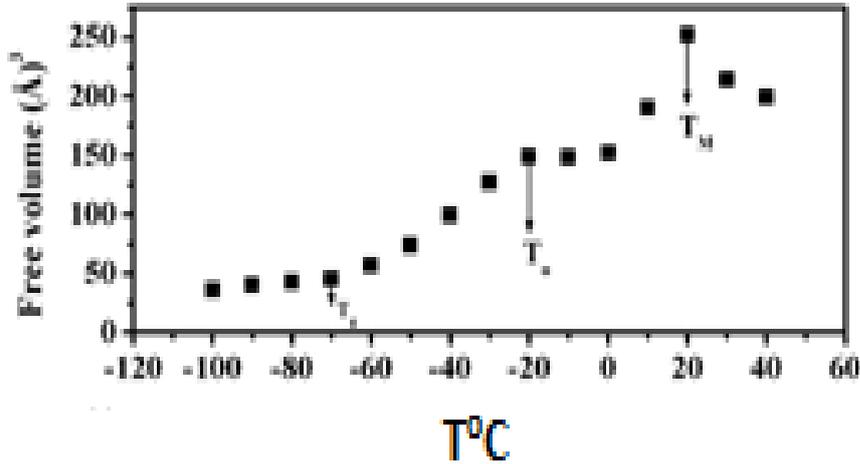


Fig. (5): Free volume hole size at different temperatures in natural rubber.

3.5. DSC Measurements:

DSC was performed to characterize the T_g and T_M of natural rubber Fig (6). The T_g value deduced from PAL measurements was found to be few degrees different from that obtained by DSC. This is due to the fact that, the duration of PAL measurement is (3. 4) hours whereas DSC measurement is less than a minute. Thus the longer time may affect the relaxation of molecular chains and show a temperature difference.

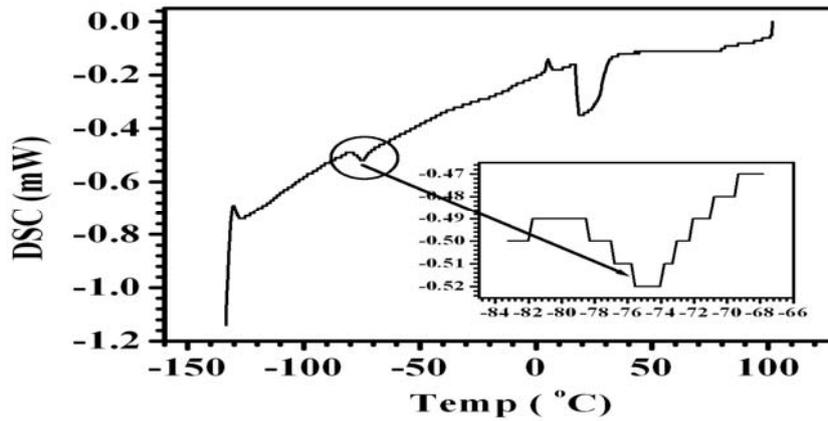


Fig. (6): DSC scans of natural rubber.

3.6. X ray diffraction

The XRD data reveal the formation of amorphous phase of the prepared rubber samples at low angles ($10\text{--}35^\circ$) Fig (7). The formed humps are broadening with the increase of temperature in the range of ($-30\text{--}60^\circ\text{C}$). In an intermediate region ($42\text{--}45^\circ$), a set of crystalline peaks are observed with the temperature range ($-30\text{--}60\text{C}^\circ$). A new sharp observed peak was depicted at ($2\theta = 50.5^\circ$) with the same position for all samples. Finally, a weak crystalline peak was revealed at ($2\theta = 74^\circ$) for all the investigated samples. One can conclude that in agreement with (PAL) results, and the thermal expansion coefficient measurements for free volume, XRD measurements as a function of temperature detected the variation of the mobile domains. Whereas the temperature increases, the peak height of the crystalline decreases. The broadening which was indicated to amorphous domain increases which means that the free volume increases with temperature.

3.7. Tensile Deformation

After stretching the sample to (300%), the positron annihilation measurements at room temperature during 1200 minutes did not show a steep change in the lifetime (Fig 8). This is may be because the measurements was constant at room temperature and below T_M which shows that the sample crystallinity is still stable. Tensile deformation of the rubber sample at room temperature did not show any effect on the positron annihilation measurements, after stretching the sample to 300%.

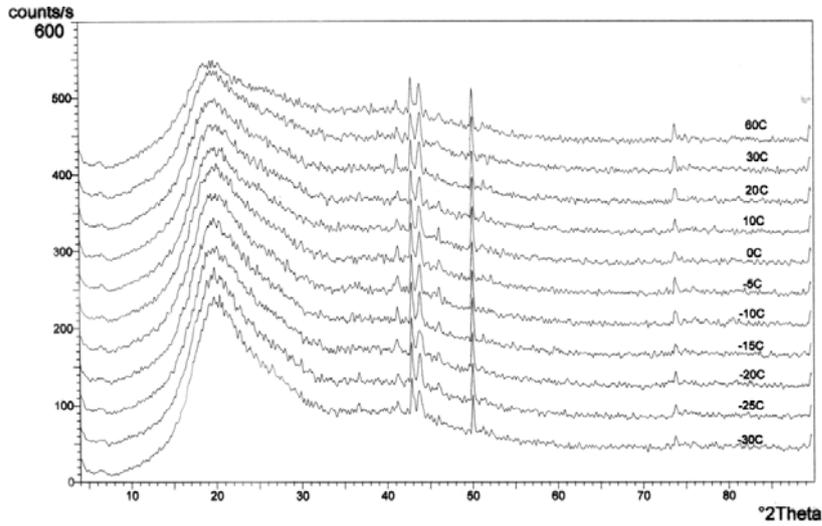


Fig. (7): XRD of natural rubber.

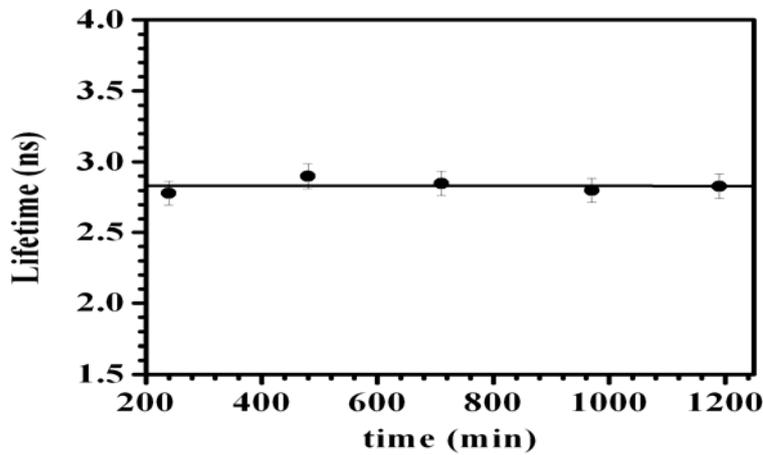


Fig. (8): Tensile deformation of natural rubber.

4. Conclusion

1. The positron lifetime spectra in natural rubber show four components, the small two components ($\tau_2 = 0.35\text{-}0.55$ ns) and ($\tau_3 = 0.3\text{-}0.55$ ns) are attributed to free positron annihilation in the interstitials of the matrix and at interface. Whereas the large component ($\tau_4 = 1.5 - 3.5$ ns) is due to o-Ps annihilation in free volumes.
2. Ortho-positronium (o-Ps) annihilation is able to probe the variation of free volume properties with temperature in amorphous domains with size ranging from 42\AA^3 to 252\AA^3 in the temperature range from the glass temperature to the melting temperature.

3. The expansion coefficient of free volume is found to be more than an order of magnitude higher than the volume expansion coefficient, indicating strong evidence of Ps trapping in free volume sites in amorphous domains.
4. Above T_g , the temperature variation of free volume indicates the presence of an intermediate transition point before the melting point which can be attributed to a less stable crystalline phase.
5. In agreement with DSC and XRD measurements, PAL gives the same temperatures for T_g and T_m and the nano free volume variation with temperatures.

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