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Original Research Article

Investigation of Free-Volume dependence on Temperature, Aging and Moisture in Epoxy and Polyester Polymers by Positron Annihilation Lifetime Spectroscopy

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Abstract:
The Positron annihilation technique (PAT) has been widely recognized and applied for the study of various materials over many years, including metals, alloys, molecular solids, semiconductors and other technologically significant substances. Among its variants, positron annihilation lifetime spectroscopy (PALS) has proven particularly effective in studying polymeric materials, owing to its sensitivity to free-volume characteristics. Understanding these free-volume properties provides insights into the physical, mechanical, and thermal behaviour of polymers. This study presents PALS measurements on cured epoxy and polyester resin polymers, examining how positron lifetime parameters vary with temperature, physical aging, and moisture absorption. Analysis of the lifetime spectra was performed using 'PATFIT' software along with 'CONTIN' algorithm. The longest lifetime component (τ_3), together with its intensity (I_3), associated with the size and spatial distribution of voids/free-volume holes within the polymer matrix, respectively, exhibited notable changes under different conditions. We interpret these variations as resulting from changes in the free- volume hole (FVH) characteristics present in the polymer matrix.

Keywords:
Positron annihilation, Free-volume, Glassy Polymers, ortho-Positronium lifetime, Glass transition temperature, Physical aging

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Introduction

The connection between free volume and atomic motion in polymers and related substances has been a longstanding topic of scientific investigation. Early work by Fox & Flory (1951,1950) and Doolittle (1951), followed by contributions from Liu et al. (1993) and other researchers, established free- volume (FV) as a key model for understanding how molecules move and how materials behave in their liquid and glassy phases. Since then, a major aim in polymer science has been to determine how molecular relaxation processes are linked to free-volume (FV) features. At the outset, FV was regarded largely as a theoretical construct as researchers lacked practical methods to observe it directly. The primary difficulty stemmed from the extremely small size of these transient voids—often only a few angstroms across—and their ultrashort lifetimes, typically around 10^{-13} seconds. Conventional characterization methods, including X-ray diffraction, STM, SEM, neutron diffraction and AFM are mainly capable of detecting relatively static surface morphology or cavities greater than roughly 10 Å. As a result, they are not suitable for detecting the transient, sub- nanometre FV sites that exist within polymer matrices.

According to Liu et al. (1993) Positron annihilation spectroscopy (PAS) in polymeric materials has the ability to determine local FVH properties. Using this approach, Jean (1990) and Schrader & Jean (1988) injected positrons into the sample and measured the annihilation lifetimes associated with both 'free' and 'bound' Positronium (Ps) states. As discussed by Lui et al. (1993), "due to their charge, positrons and Ps" are pushed away from the ionic cores of polymers and accumulate in electron-deficient regions, such as voids or FV cavities. According to Ferrell (1956), this trapping may also result from electron exchange repulsion between Ps and surrounding molecules, which further drives Ps into these open- volume regions. The annihilation photons primarily originate from these localized sites, providing insight into the free-volume structure. This interpretation is supported by experimental studies of Jean (1993), Haldar et al. (1996) and others (Yang et al., 2015; Wang et al., 2003), where positron lifetimes vary systematically with factors such as temperature, pressure, and physical aging.

Upon entering a material, a positron can either annihilate with an electron directly or exist as short-duration bound species termed as '*positronium'* (Ps) before annihilation. When an electron undergoes annihilation with a positron without forming any intermediate state, the process is referred to as '*direct annihilation'*, typically resulting in a lifetime of 100–500 picoseconds. In molecular solids and liquids, however, positrons often pair with electrons to form Ps.

As previously noted by Castelli (2012), Ps appears either as a singlet state ($^1S_0$) *para-positronium* (p-Ps) -with the electron and positron spins oriented oppositely (↓↑), or as a triplet configuration ($^3S_1$) *ortho-positronium* (o-Ps)-in which their spins are aligned parallel (↑↑). According to Tao (1972), p-Ps undergoes decays into a pair of photons having an average lifetime of about 125 to 130 picoseconds, while o-Ps decay has a significantly longer average lifetime of approximately 1.47 $x10^{-7}$ sec into three photons. In condensed matter, the state of the positronium atom can transform from the ortho- to the para-state

due to collisions with the surrounding medium. This transition leads to a faster decay through 2γ-annihilation. Such transitions are collectively known as *quenching processes*. Kato et al. (2020) reported that quenching leads to a reduction in the o-Ps pick-off annihilation lifetime, typically between 1 and 10 nanoseconds.

As noted by Lue et al. (2008), a small size of the Positronium (Ps) probe, ~ 1.59 Å, PAS is particularly well-suited for detecting free-volume holes (FVH) in the angstrom range, as well as molecular motions occurring over timescales of 10^{-10} seconds and longer. Unlike many conventional techniques, PAS can effectively probe these nanoscopic voids without significant interference from the bulk of the material. In molecular systems, Ps formation predominantly occurs in regions of free-volume (FV), where the o-Ps component with longer lifetime provides us the advantage that it is directly connected to the size of the neighboring void (Consolati et al., 2023). As o-Ps becomes confined within FVH, the measured lifetime serves as a sensitive indicator of hole dimensions (Consolati et al.,2023).

Today, PAS, particularly its lifetime variant (PALS), is established as a quantitative technique for polymer characterization. According to Consolati et al. (2023), in addition to estimating the dimensions and fraction of FVH, it also reveals detailed information regarding their spatial distribution in the 1–10 Å region. In this study, we utilize PALS to investigate the size and spatial distribution of FVH in cured epoxy and polyester resin polymers under different conditions.

According to earlier studies by Consolati et al. (2023) and Kaushik (2011), cured epoxy and polyester resin polymers are classified as glassy polymers, characterized by their glass transition temperatures (Tg) which is above room temperature. Interpretation of Tg is crucial for their practical applications, as the mechanical properties of polymers significantly degrade above this threshold, leading to reduced toughness and mechanical stability as noted by Yang et al. (2015) and Odegard & Bandyapadhyay (2011). The behaviour of glassy polymers is closely linked to their molecular packing density, often expressed from the viewpoint of FV. Below Tg, FV is essentially "frozen," with limited molecular mobility. As the temperature approaches Tg, the free volume increases to a critical level, enabling greater molecular motion. Above Tg, the polymer enters a ‘Visco-elastic state’, where FV rapidly increases with temperature until it eventually approaches the melting point.

One significant concern with these polymers is their degradation over time, which can result from chemical bond rupture or physical changes in their microstructure (Wang et al., 2003; Kaushik, 2011; Odegard & Bandyapadhyay, 2011; Merrick et al., 2020). Wang et al. (2003), and others (Kaushik, 2011; Odegard & Bandyapadhyay, 2011) noted that glassy polymers are often considered as super-cooled liquids that have solidified into a non-equilibrium state. Over time, they undergo structural relaxation, also known as physical aging, as they gradually move toward thermodynamic equilibrium (Yang et al. 2015; Wang et al., 2003; Kaushik, 2011). Merrick et al. (2020) noted that “Physical aging is accompanied by changes in the polymer's free volume, including a decrease in the

dimensions and a new distribution of FVH. In light of this, we investigated the aging behaviour of our polymers under different conditions.

Another crucial factor influencing the mechanical performance of glassy polymers is moisture/water absorption. Moisture, in any form, as noted by Gordo et al. (2013), can gradually penetrate the polymer matrix, occupy FV spaces and act as a plasticizer. This softening effect compromises the structural integrity and overall performance of the polymer. In light of this, we have investigated the changes in free volume resulting from moisture absorption under various situations.

Although several PALS studies have been conducted on cured epoxy polymers, focusing on aspects such as temperature dependence, physical aging and moisture absorption [Yang et al. 2015; Wang et al., 2003; Odegard & Bandyapadhyay, 2011; Merrick et al., 2020; Nakanishi et al., 1988), similar investigations on cured polyester polymers are rare (Kaushik, 2011). In this study, we perform a comprehensive and simultaneous PALS analysis for both polymer types, enabling a detailed and quantitative comparison of their behaviour with respect to temperature dependence, physical aging and moisture absorption. According to the explanations provided by Schrader & Jean (1988) and

Jean (1993), "the pick-off annihilation of o-Ps lifetime (τ_3), measured by PALS, inversely depends on the integrated overlap of positron (ρ^+) and electron (ρ^-) densities at the point of annihilation". Jean (1990) and Tao (1972) proposed a simplified model where a Ps atom is confined within a potential well of spherical nature having radius R_0 with infinitely high barriers. Using this quantum mechanical framework, Nakanishi et al. (1988) and Mills (1981) formulated a 'semi-empirical' expression that links the experimentally obtained o-Ps lifetime (τ_3) with the radius (R) of the FVH distributed within the polymer network. The equation below presents the relation described in their work (Nakanishi et al., 1988); Mills, 1981).

$$\tau_3 = 0.5\left[1 - \frac{R}{R_0} + \frac{\sin 2\pi(R/R_0)}{2\pi}\right]^{-1} \quad (1)$$

where $R_0 = R + 1.66$ in Å and τ_3 is in ns (10^{-9} sec).

A careful evaluation of the PAL spectrum is necessary to extract reliable physical information. For this work, the spectra were primarily interpreted using a discrete-component lifetime fitting approach, while a continuous-distribution method was applied in selected cases.

In the discrete-component lifetime fitting approach, the spectral data were analyzed using the computer program PATFIT (Jean, 1990; Schrader & Jean, 1988; Kirkegaard et al., 1981). During analysis, the PAL spectra were resolved into three distinct lifetime components. The first and shortest component ($\tau_1 \approx 0.12$ ns) is associated with the annihilation of p-Ps. The second component, with an intermediate lifetime of about $\boldsymbol{\tau_2 \approx}$ 0.40 ns, reflects annihilation events involving free positrons or positron–molecule interactions. As reported by Wang et al. (2003), the third and longest component ($\tau_3 \geq 0.5$

ns) corresponds to pick- off annihilation of o-Ps**,** while trapped in free-volume cavities.

The longest lifetime component**,** τ_3, serves as the basis for estimating the mean size of the FVH using equation (1). In addition, the intensity parameter I_3 reflects the relative abundance of these free volume sites. To quantify the fractional free-volume (f_v) in polymeric systems, Wang et al. (1990) and Jean (1994) proposed a relationship similar to that expressed below:

$$f_v = A \times V_t \times I_3 \quad (2)$$

Here, V_t denotes the FV magnitude (in Å³) obtained from τ_3 using equation (1), and **A** represents a proportional constant. As discussed by Cheng et al. (2009), constant **A** typically lies between 0.001 and 0.002, which is linked to the material's volume expansion coefficient.

FVH in polymers is typically distributed over a range of sizes rather than a single characteristic size. PAL spectra are evaluated through the continuous- lifetime approach using the CONTIN program developed by Gregory & Zhu (1990) to extract the lifetime distribution, particularly that of o-Ps lifetime, which reflects the heterogeneous nature of the polymer matrix. By analysing this lifetime distribution, one can determine both FVH size variation and their concentration within the material.

Experimental Methodology

The epoxy specimens were fabricated by mixing the resin, diglycidyl ether of bisphenol-A (DGEBA), with triethylene tetramine (TETA) as the curing agent in a weight ratio of 10:1. The mixture was cured at ambient temperature for a duration of 24 hours. After curing, the hardened sheet was sectioned into small square pieces, each approximately 1 cm × 1 cm in size.

The polyester specimens were produced by polymerizing unsaturated styrenated alkyd resin in the presence of methyl ethyl ketone peroxide (MEKP, 1 wt%) as the catalyst and cobalt octoate (0.5 wt%) as the accelerator. The mixture was initially cured at 343 K for 12 hours, after which it underwent two additional heat-treatment stages: 4 hours at 393 K followed by 2 hours at 413 K. Once fully cured, the resulting laminate was trimmed into small sections of approximately 1 cm × 1 cm.

PAL experiments were performed at 298 K using a standard fast–fast coincidence spectroscope setup similar to the arrangement reported by Ramani et al. (1993). A ^{22}Na source with an activity of 15 μCi served as the positron source. The system's timing resolution, evaluated from the prompt curve of a ^{60}Co source, was found to be approximately 0.32 ns (FWHM). For temperature- dependent studies, the source–sample assembly was housed in a specially designed cell, with temperature controlled by a microprocessor-based programmable temperature controller (Indotherm

MPC 500) accurate to ±1 K. PAL spectra were collected between 293 K and 473 K, typically at intervals of around 10 K increments, for both heating and cooling cycles. Each spectrum was recorded with a minimum of about 5×10^6 counts to ensure statistical reliability.

As mentioned previously, each PAL spectrum was fitted using a three- component lifetime analysis with the assistance of the PATFIT package (Kirkegaard et al., 1981). For selected epoxy spectra, further examination was performed using procedures similar to those reported by Gregory & Zhu (1990) was carried out in which "annihilation rates probability distribution function" (PDF), $\lambda\alpha(\lambda)$ as a function of annihilation rate λ, was extracted using the CONTIN algorithm (Gregory & Zhu, 1990) described earlier and employed by others (Haldar et al., 1996).

To understand the changes brought about by physical aging, epoxy samples were aged at 393 K for 100 hours, while cured polyester samples were aged at 433 K for 100 hours under vacuum conditions. Post-annealing, the specimens were brought back to ambient temperature using various cooling rates, including furnace cooling and quenching in water or liquid nitrogen. PALS measurements were then performed on these quenched samples at regular intervals at room temperature.

To study moisture absorption, a specially designed glass vessel with two interconnected arms was used. One arm held the polymer sample, while the other contained water. Both arms were individually evacuated before opening the valve connecting them, allowing water vapor to saturate the sample chamber and provide the necessary moisture for absorption. Additionally, water absorption experiments were conducted by directly immersing the samples in water. Positron lifetime spectra were recorded at various absorption intervals, namely 15 min, 30 min, 1 hr, 2 hr, 4 hr, and 16 hr.

Results and Discussions

Temperature-dependence of positron lifetime parameters in epoxy and polyester resin polymers

Figure 1(a) and Figure 1(b) presents the positron lifetime spectra for epoxy and polyester samples respectively recorded at 293K and 473K, highlighting significant spectral changes that occur with temperature. The variation of the o-Ps lifetime (τ_3) with temperature is plotted in Figure 2(a), while the corresponding changes in its intensity (I_3) are shown in Figure 2(b) for epoxy materials. A similar plot of τ_3 and I_3 for the polyester sample is shown in Figure 3. In case of epoxy sample, during the cooling cycle, the values of τ_3 closely retrace the path observed during heating. Because τ_3 and I_3 are strongly associated with the FV characteristics of polymeric materials, the subsequent discussion will focus on their variations.

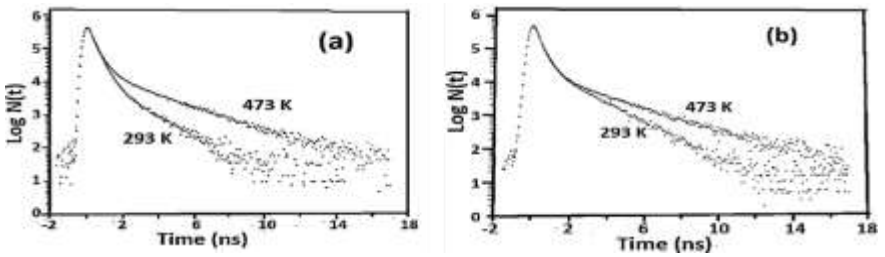


Figure 1. Positron lifetime spectra at two separate temperatures in our samples: (a) epoxy and (b) polyester

Using equation (1), the value of τ_3 was converted into the FVH radius, **R** (Deng et al., 1992). The corresponding hole volume was then determined using the formula $V_f = \frac{4\pi R^3}{3}$ and these values appear on the right-side scale of Figures 2(a) and 3(a). Previous PALS studies on epoxy polymers cured with different agents (Deng et al., 1992; Jean et al., 1986) reported τ_3 and I_3 values consistent with those obtained in this work.

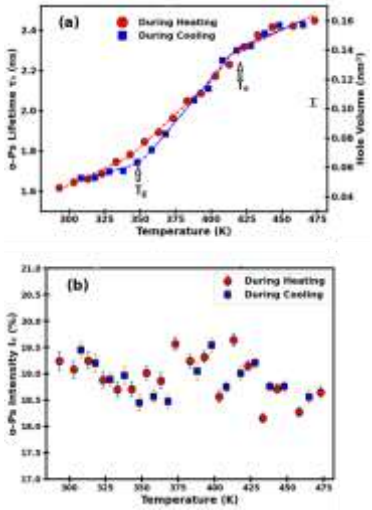


Figure 2. Variation with temperature of (a) the annihilation lifetime (τ_3) and (b) the associated intensity (I_3) of o-Ps in epoxy samples.

The plot of ortho-positronium lifetime (τ_3) versus temperature (T) for the epoxy sample (Figure 2a) reveals three separate regions based on changes in the slope of the curve. A pronounced change occurs around 350 K, especially during cooling, where τ_3 begins to increase more steeply with temperature. This inflection point has been termed as glass transition temperature 'T_g' (≈ 350 K) by Jean et. al. (1986), which has been confirmed by 'Differential Thermal Analysis' (DTA) performed by us. Below 'T_g', the polymer remains in a rigid, glassy form, whereas above 'T_g', the material becomes rubber-like (Merrick et al.,

2020).

Figure 2(b) illustrates that the I_3 intensity stays almost unchanged throughout the temperature range studied, indicating that the concentration of FVH remains largely constant. Consequently, the observed increase in total free volume is mainly due to an expansion in the size of these cavities, as τ_3 is directly linked to their dimensions.

At a temperature of around 420 K, sometimes referred to as the onset temperature T_e, another variation in the gradient of the τ_3 versus temperature curve is noted. Similar trends have been recorded in other polymers by Deng et al. (1992) and others (Jean et. al., 1986; Valsange et al., 2024). However, the origin of this second transition is unclear, as it is not supported by DSC or DTA measurements of this system. It may indicate a softening process in the polymer, somewhat analogous to the melting behaviour observed in crystalline solids. This temperature T_e is well below the decomposition temperature for our epoxy composition, which is above 480 K.

We now turn to the PALS results for the cured polyester resin sample, specifically the lifetime and intensity parameters of o-Ps (τ_3 and I_3), focusing on their temperature dependence as shown in Figure 3. The variation of τ_3 with temperature closely resembles that observed in the epoxy sample, except that no second transition around T_e was detected in this case. A noticeable variation in the gradient of the τ_3 versus temperature plot occurs around 350 K, which may indicate a phase transition similar to the glass transition noted by Valsange et al. (2024), although this could not be confirmed by our DTA analysis.

At room temperature, the I_3 value for the polyester sample is approximately 7%, significantly lower than that observed in the epoxy sample (~19 %). However, I_3 increases steadily with temperature, reaching about 17% at 473 K. This temperature-dependent behaviour of I_3 is in sharp contrast to that of the epoxy sample, for which no significant variation in I_3 was observed. This discrepancy may be attributed to structural difference, notably, epoxy is largely amorphous, while polyester exhibits a semi-crystalline structure, a network of amorphous or partially crystalline regions (Valsange et al., 2024) with a higher degree of molecular alignment at room temperature, resulting in smaller initial free-volume space.

As the temperature increases, this ordered structure may begin to break down, introducing more free volume and leading to an increase in I_3. At sufficiently high temperatures, the material may have transformed to a fully disordered state. The corresponding variation in FVH size, calculated from τ_3, is also shown in Fig. 3(a).

Figure 4 presents the temperature-related variation of the fractional relative free volume, following the approach of Chen et al. (2010), F_r (defined as $F_r = I_3 \times V_f$) for the cured epoxy and polyester samples. This is somewhat similar to equation (2), commonly used for free-volume fraction calculations, except for the multiplying factor A. For the epoxy sample, the variation in F_r closely follows the trend observed for τ_3, indicating that the free volume changes are primarily resulting from an increase in hole size. In contrast, the polyester

sample exhibits a much larger variation in F_r within the temperature range of 350–473 K, resulting from simultaneous increases in both I_3 and V_f.

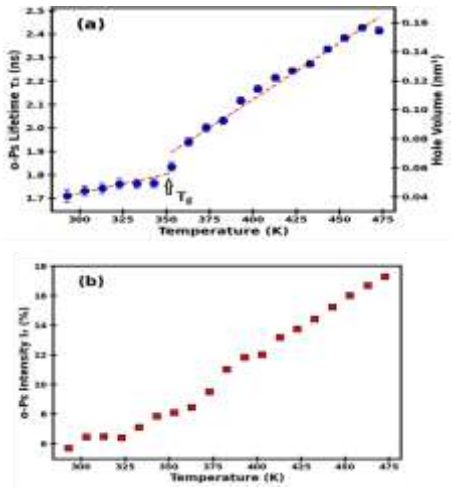


Figure 3. Variation with temperature of (a) the annihilation lifetime (τ_3) and (b) the associated intensity (I_3) of o-Ps in polyester samples.

The temperature-dependent positron lifetime spectra for the epoxy polymer were also processed with CONTIN to derive the PDF, $\alpha(\lambda).\lambda^2$. A close agreement was noticed among the peak positions of the lifetimes obtained from the CONTIN program and those determined through the PATFIT analysis. Figure 5(a) displays the lifetime distribution functions (PDF) plotted against the o-Ps lifetime at some selected temperatures for our epoxy sample.

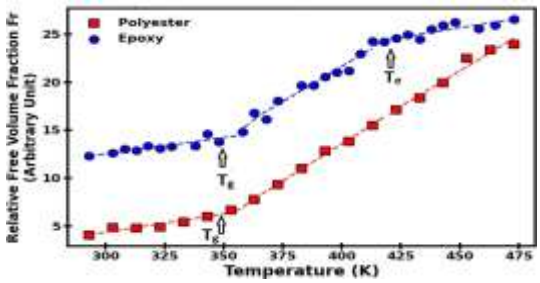


Figure 4. Variation with temperature of fractional relative free-volume Fr (= I_3V_f) in epoxy (blue dots) and polyester (red squares) samples

It can be observed that the lifetime distributions become broader with increasing temperature, indicating a wider range of o-Ps lifetimes at higher thermal conditions. Based on the measured distributions, the probability density function of free-volume hole

radius f(R), was derived following the method described by Gregory & Zhu (1990) and Jean & Deng (1992), which is depicted in Figure 5(b). The distributions generated from the analysis are relatively symmetric and exhibit significant broadening at elevated temperatures, reflecting broader distribution in FVH sizes.

Study of structural relaxation and physical aging

Physical aging is a slow and prolonged process that may take up to 100 years to reach equilibrium [Consolati et al., 2023; Kaushik, 2011). As has been previously noted (Consolati et al., 2023), after annealing at temperatures above their respective glass transition temperatures (T_g), both samples were cooled to temperatures below T_g. This rapid cooling effectively "freezes" the equilibrium free-volume distribution established at high temperature. Once below T_g, the polymer system gradually attempts to attain a new stable state configuration consistent with the lower temperature. However, this relaxation process is extremely slow due to the significantly reduced segmental movement of polymer chains within the glassy phase, where the accessible FV is restricted. Since τ_3 and the associated I_3 of o-Ps are sensitive indicators of FVH size and its distribution, this slow redistribution is expected to manifest in the temporal variation in the positron decay parameters**.**

The impact of aging time on o-Ps lifetime parameters for epoxy and polyester samples, under three cooling rates, are shown in Figures 6 and 7, respectively. The trends observed for τ_3 and I_3 are consistent across all cooling rates, indicating that the effect of physical aging follows a similar pattern regardless of the cooling method. From this behaviour, it can be inferred that physical aging primarily affects the free-volume hole density over time, while the hole size (related to τ_3) remains relatively unchanged. Moreover, the rate of aging was found to decrease over time, indicating that the polymer gradually relaxes toward a new equilibrium state, which would require a long duration to attain fully. A similar trend has also been reported by Hsu,Chai-Wen et al. (2015) and others (Wang et. al., 2003).

Notably, in the polyester sample, faster quenching results in higher values of both τ_3 and I_3 than the corresponding values for as-prepared samples at room temperature. Moreover, we also find that τ_3 and the associated I_3 of o-Ps annihilation are significantly higher for liquid nitrogen quenched samples as compared to furnace cooled or water quenched samples. This can be well understood considering the fact that rapid cooling induces a higher degree of structural disorder, which becomes frozen into the material, resulting in an increased amount of free volume and its fraction.

Water/moisture absorption studies

Changes in τ_3 and I_3 during water/moisture absorption for epoxy and polyester samples are illustrated in Figures 8 and 9, respectively. Each sample was exposed to different absorption conditions, as previously described. These plots illustrate how water uptake influences the FV characteristics in both polymer systems over time.

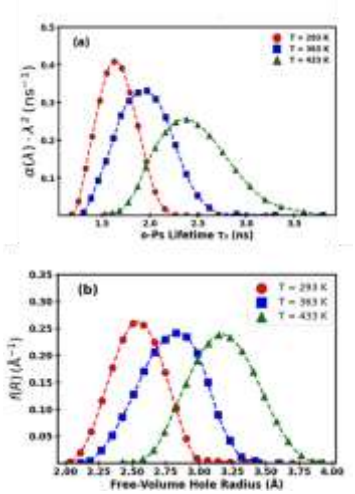


Figure 5 (a) o-Ps annihilation lifetime distribution for epoxy polymer at three selected temperatures obtained by CONTIN analysis; (b) The probability density function of free-volume hole radius f(R) at three different temperatures (corresponding to the o-Ps lifetime distributions presented in Fig. 5(a)).

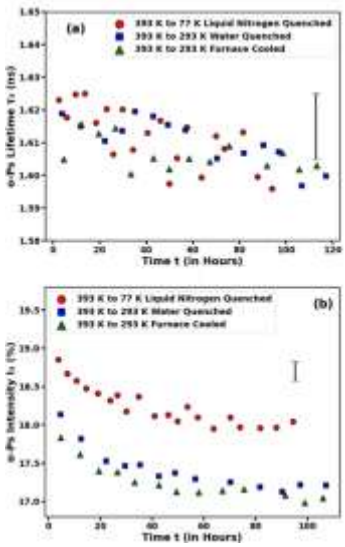
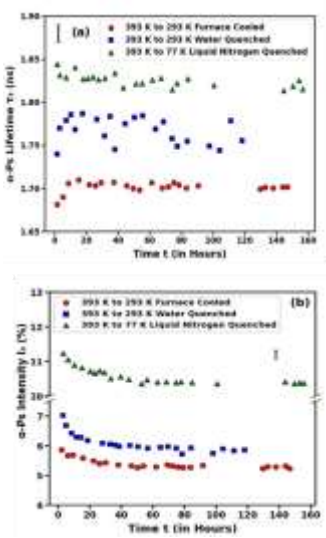


Figure 6. Impact of physical aging on (a) τ_3 and (b) I_3 over the aging time for epoxy samples cooled at different rates

The measured τ_3 remains approximately unaffected by the absorbed water content in both polymers, whereas I_3 shows a gradual decrease with increasing absorption time before stabilizing at a constant level. The average τ_3 values are about 1.6 ns for epoxy and 1.7 ns for polyester, which, according to equation 1, correspond to “spherical” voids with average radii of 2.4 to 2.5 Å—closely matching the kinetic diameter of a water molecule (~3 Å). As moisture penetrates the polymer, water molecules increasingly occupy the FV region, limiting the space accessible for positron annihilation. The observed variations in τ_3 and I_3 as the polymer absorbs moisture are associated with the entrapment of water molecules (Gordo et al., 2013) in the polymer’s FV and ‘intermolecular’ spaces. Under comparable conditions, the epoxy polymer exhibited a more pronounced reduction in I_3 than the polyester polymer, which can be ascribed to its relatively higher initial free-volume fraction. Furthermore, epoxy is intrinsically hygroscopic, while polyester resins are comparatively hydrophobic, contributing to the difference in behaviour. The magnitude of change was also greater at elevated temperatures, possibly because of the greater amount of accessible FV and/or due to the higher diffusion coefficient of water molecules, which enhances both the rate and depth of penetration into the polymer matrix



. **Figure 7.** Impact of physical aging on **(a)** τ_3 and **(b)** I_3 over the aging time for polyester samples cooled at different rates

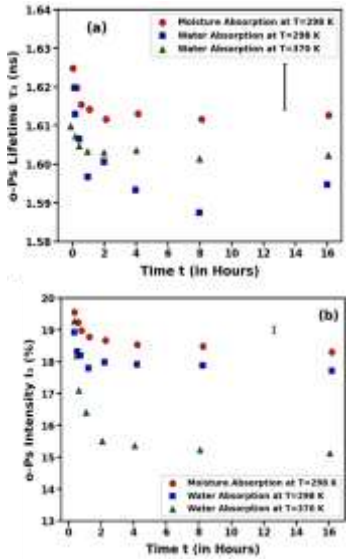


Figure 8. Effect of moisture/ water absorption on (a) τ_3 and (b) I_3 plotted against the moisture uptake time in epoxy sample

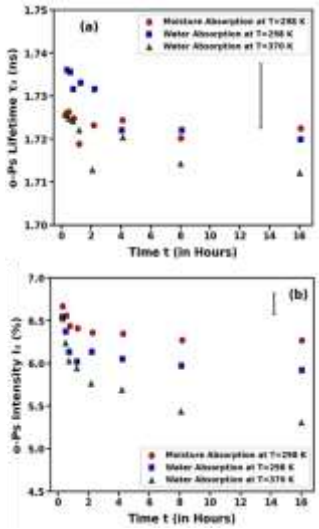


Figure 9. Effect of moisture/ water absorption on (a) τ_3 and (b) I_3 plotted against the moisture uptake time in polyester sample

Conclusions

PALS measurements were conducted to characterize the free-volume properties of the epoxy and polyester materials. The temperature variation of the positron annihilation lifetime (τ_3) and the associated intensity (I_3) was investigated to determine changes in free-volume hole size (V_f) over the temperature range of 293–473 K. Both polymers exhibited a pronounced increase in V_f around their glass transition temperature (T_g). This behaviour was explored and discussed in detail. Additionally, positron lifetime measurements during physical aging revealed systematic changes over time that were consistent regardless of the cooling rate applied to the samples. Finally, the role of water absorption on the o-Ps lifetime and the associated intensity was examined, showing more significant changes when absorption occurred at an elevated temperature of 370 K.

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