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RESEARCH ARTICLE

EFFECT OF TEMPERATURE, PHYSICAL AGING, AND MOISTURE ABSORPTION ON POSITRON LIFETIME PARAMETERS IN CURED POLYESTER RESIN STUDIED BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Abstract

The positron annihilation method has been widely applied to study an extensive range of materials such as metals, alloys, molecular solids, and numerous other technologically important systems. Among the different experimental methods, positron annihilation lifetime spectroscopy (PALS) has proven to be particularly effective in polymer studies because its high sensitivity to free-volume environments within the polymer. Examining these free-volume features provides crucial information regarding the physical, mechanical, and thermal responses of polymeric materials. In this study, PALS experiments were conducted on a cured polyester resin to explore the responses of the positron lifetime parameters to temperature variations, physical aging, and moisture uptake. The lifetime spectra were processed using PATFIT analysis software. The third lifetime component (τ_3) and its corresponding intensity (I_3), associated with the size and density of the free-volume sites showed clear variations under these different conditions. The observed trends were interpreted in relation to the modification of the free-volume structure within the polymer network.

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Introduction: -

The interplay between the atomic mobility and free volume in polymers and related materials has long been a subject of scientific interest. The theoretical framework of free volume, used to interpret the molecular dynamics and the corresponding physical responses of materials in their glassy and liquid states, was first established by Fox and Flory (1951,1950), expanded by Doolittle (1951), and further developed by Liu et al. (1993). Since then, a central objective in polymer research has been to quantify the relationship between the molecular dynamics and free-volume (FV) characteristics. At first, the concept of free volume (FV) was viewed as mostly theoretical because it seemed impossible to measure it directly. The challenge stemmed from the fact that these voids exist on the scale of only a few angstroms and persist for extremely short time, around 10^{-13} seconds or more. Standard characterization methods, including STM, SEM, X-ray diffraction, neutron diffraction, and AFM, are limited to observing static surfaces or voids greater than roughly 10 Å in size. As a result, these techniques are unable to detect fleeting, sub-nanometer free-volume cavities that are characteristic of polymeric materials.

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Positron annihilation spectroscopy (PAS) has become a powerful technique for probing free-volume hole (FVH) characteristics of polymers, as noted by Liu et al. (1993). Positron annihilation occurs when a positron, the antimatter counterpart of an electron, encounters an electron, leading to mutual annihilation of both particles. Their combined rest mass is transformed into energy, which is most commonly released as a pair of high-energy gamma photons emitted in opposite directions to satisfy the conservation of energy and momentum. When a positron enters a material, it may annihilate immediately with an electron or form a transient bound state prior to annihilation. If no intermediate state is formed, termed as direct annihilation, it generally produces lifetimes on the order of 100–500 ps. In contrast, in molecular liquids and solids, positrons commonly pair with electrons to create a short-lived bound entity known as 'positronium' (Ps). This basic physical phenomenon underpins important applications in both medical diagnostics, such as positron emission tomography, and materials research through positron annihilation spectroscopy. In these techniques, the characteristic energies and temporal correlations of the emitted gamma photons provide detailed insights into the location and nature of the annihilation process, enabling the identification of structural features and defects.

In PAS, first demonstrated by Jean (1990) and Schrader and Jean (1988), positrons are injected into the material, and their annihilation lifetimes in both free and trapped states, including positronium (Ps), were recorded. Because positrons and Ps carry a positive charge, they are naturally repelled by the polymer ion cores and are therefore inclined to migrate toward microscopic free-volume cavities that correspond to regions of lower electron density. Ferrell (1956) explained that electron-exchange repulsion between Ps and neighboring molecules further promotes its localization in these open-volume sites. The annihilation photons largely originate from these regions, enabling direct insight into the free-volume architecture. Comparable observations were documented in earlier and later investigations conducted by Jean (1990, 1994), Haldar and co-workers (1996), Wang and colleagues (1990), and Yang and co-authors (2015), who reported systematic variations in positron lifetimes with changes in temperature, pressure, and physical aging.

As outlined by Castelli (2012), positronium can exist in two possible spin alignments, the singlet configuration, known as 'para-positronium' (p-Ps, $^1S_0$), where the electron and positron possess opposite spins (⇃↾), and the triplet state, termed 'ortho-positronium' (o-Ps, $^3S_1$), in which the spins are parallel (↿↾). Tao (1972) reported that p-Ps typically annihilates into two photons with an average lifetime of roughly 125–130 picoseconds, whereas o-Ps survives much longer, with a characteristic three-photon decay lifetime of about 1.47×10^{-7} seconds. Within the condensed phases, interactions with surrounding molecules can induce the spin-state transition of ortho-positronium to its para state. This conversion pathway results in a quicker two-gamma annihilation event, which is broadly referred to as quenching. According to Kato et al. (2020), such quenching mechanisms shorten the effective o-Ps pick-off lifetime, which generally falls in the range of 1-10 nanoseconds. The lifetime of ortho-positronium (o-Ps) exhibits a strong dependence on its environment. This sensitivity underlies its effectiveness as a probe of free volume and material composition.

According to Lue et al. (2008), the extremely small dimension of the positronium (Ps) species, approximately 1.59 Å, makes positron annihilation spectroscopy (PAS) highly effective for identifying free-volume holes (FVH) on the angstrom scale, as well as molecular motions occurring on timescales of 10^{-10} s or longer. Free volume represents the additional volume relative to an ideal, densely packed structure and manifests as microscopic voids whose size and distribution vary with temperature and density. These gaps facilitate molecular mobility and structural rearrangements, which play a particularly important role in the flow and relaxation behavior of amorphous materials. In contrast to many traditional characterization methods, PAS can explore these minute cavities with minimal influence from the surrounding bulk material. Studies by Consolati et al. (2023) show that, in molecular materials, Ps is preferentially created within free-volume regions, where the long-lived o-Ps component is particularly valuable because its lifetime correlates directly with the size of the adjacent void. When o-Ps becomes trapped in an FVH, their observed lifetime acts as a highly sensitive measure of the hole dimensions (Consolati et al., 2023).

Positron annihilation spectroscopy (PAS), particularly its lifetime measurement (PALS), has become a widely recognized quantitative tool for examining polymer structures. As noted by Consolati et al. (2023), beyond determining the dimension and proportion of FVH, the method can also provide insight into how these voids are distributed on a scale of 1–10 Å. This investigation used PALS to analyze the dimensions and concentration of FVH in cured polyester resin systems subjected to various experimental conditions. Earlier investigations by Consolati et al. (2023) and Kaushik (2011) indicate that cured epoxy and polyester resins fall under the category of glassy polymers, distinguished by glass transition temperatures (T_g) above ambient conditions. Understanding T_g is essential for their practical use, since polymer mechanical performance declines markedly once this limit is exceeded, resulting in diminished toughness and structural integrity, as reported by Yang et al. (2015) and Odegard and Bandyapadhyay (2011). The response of glassy polymers is strongly influenced by their molecular packing efficiency, which is often described in terms of free volume (FV). Below T_g, the available FV remains largely immobile and molecular motion is minimal. As the material approaches T_g, the FV grows to a level that permits increased segmental mobility. Once the temperature exceeds T_g, the polymer transit into a viscoelastic regime, during which FV rises rapidly with temperature until it approaches the melting region.

Significant research attention has been directed toward understanding the physical aging processes in polymeric materials. The occurrence of physical aging in polymers has been reported for more than two decades but it has only recently become the focus of widespread research (Wang et al., 2003; Kaushik, 2011; Odegard & Bandyapadhyay, 2011; Merrick et al., 2020). The major issues associated with these polymers is their degradation over extended periods, which can result from the breaking of chemical bonds or alterations in their internal microstructure. Glassy polymers are commonly described as supercooled liquids that have transitioned into solid, non-equilibrium condition. Over time, they experience a gradual structural reorganization, known as physical aging, as the material slowly approaches thermodynamic equilibrium (Odegard and Bandyapadhyay, 2011; Gordo et al., 2013). This aging phenomenon is generally accompanied by changes in free-volume characteristics, such as a decrease in void dimensions and rearrangement of free-volume sites.

The situation is most often demonstrated using the volume vs. time curve observed for amorphous polymers as they are cooled from a completely melted condition through the glass transition temperature, T_g, to lower temperature (Hill, 1999). In amorphous polymers and amorphous phases of semicrystalline materials, rapid cooling below the glass transition temperature (T_g) traps polymer chains in non-equilibrium states, leading to an excess volume that depends on the cooling rate (Hill, 1999). Accordingly, a systematic study of polymer aging was conducted under varying conditions.

Moisture uptake is another critical parameter that influences the mechanical behavior of glassy polymers. Water molecules slowly penetrate the polymer network, where they reside in free-volume cavities and function as plasticizing agents (Gordo et al., 2013; Lue et al, 2008; Wang et al., 2003). This interaction leads to material softening, resulting in a decline in mechanical stability and performance. The present work examined the impact of moisture absorption under varying environmental conditions on the free-volume properties of these polymers.

Although numerous PALS investigations have addressed the effects of temperature, physical aging, and moisture absorption in cured epoxy systems (Davis and Pethrick, 1998; Wang et al., 2003; Yang et al., 2015; Gordo et al., 2013), similar investigations on cured polyester polymers are relatively scarce (Kaushik, 2011). In this study, a detailed PALS evaluation of cured polyester resins was been performed to bridge the existing gap, offering a quantitative evaluation of the free-volume evolution under varying thermal conditions, aging processes, and moisture exposure.

In positron annihilation lifetime spectroscopy (PALS), the experimentally measured positron lifetime (τ) is influenced by the extent of spatial overlap between the positron (ρ^+) and electron (ρ^-) density distributions at the annihilation site (Schrader and Jean, 1988; Jean, 1993). To describe positronium localization in condensed matter, Tao (1972) proposed a quantum mechanical model in which positronium (Ps) is confined within a spherical potential well of radius R_0 featuring infinitely large potential barriers. On the basis of this model, a widely adopted semi-empirical relation was subsequently formulated, also known as Tao–Eldrup model, establishing a direct correlation between the o-Ps lifetime (τ_3) and the radius (R) of FV cavities distributed within the polymer matrix (Mills, 1981; Nakanishi et al., 1988).

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

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

A thorough analysis of the positron annihilation lifetime (PALS)spectrum is crucial to ensure meaningful physical interpretation. Quantitative interpretation of PAL spectra is typically achieved through finite-component lifetime analysis. In this method, the experimental spectra are decomposed using a least-squares fitting routine to extract the annihilation rates, $\lambda_i = 1/\tau_i (i = 1,2,3,4)$, together with their associated intensities I_i. Such analyses are commonly performed using the PATFIT computational package (Kirkegaard et al., 1989). In this study, the PAL spectra were resolved into three separate lifetime components. The shortest component ($\tau_1 \approx 0.12$ ns) was associated with the intrinsic annihilation of singlet para-positronium (p-Ps). The lifetime of the intermediate duration ($\tau_2 \approx 0.40$ ns) corresponds to free positron annihilation with electrons in the bulk matrix, while the longest lifetime ($\tau_3 \geq 0.5$ ns) arises from the pick-off annihilation of ortho-positronium (o-Ps) localized within the FV cavities. Parameter $\tau_3$is subsequently employed to determine the mean free-volume hole size using Eq. (1), and its intensity I_3 provides information on the relative population and spatial distribution of these cavities. Moreover, free-volume fraction (f_v) of the polymer can be estimated using a semi-empirical relation proposed by Wang et al. (1990) and Jean (1994):

$$f_v = A \times V_t \times I_3 \tag{2}$$

where V_t denotes the free-volume hole size (in Å³) derived from τ_3, and A is a proportionality constant representing the o-Ps formation probability. The value of A, typically in the range of 0.001–0.002, was obtained from the volumetric thermal expansion coefficient of the polymer.

Experimental Methodology: -

Sample preparation: -

Polyester specimens were prepared by curing unsaturated styrenated alkyd resins using methyl ethyl ketone peroxide (MEKP, 1 wt%) as the initiator and cobalt octoate (0.5 wt%) as the accelerator. Curing was performed at 70 ^{0}C for 12 h, followed by post-curing at 129 ^{O}C for 4 h and at 140 ^{O}C for 2 h to ensure complete crosslinking. The cured laminates were cut into 1 cm × 1 cm samples for positron annihilation measurements.

Temperature-dependence of Positron annihilation lifetime measurements: -

Positron annihilation lifetime (PAL) spectra were recorded at 25 ^{O}C using a standard fast–fast coincidence spectrometer setup equipped with a ^{22}Na positron source with 15 μCi activity. The spectrometer's time resolution, evaluated from the prompt spectrum of a ^{60}Co source, was 0.32 ns (FWHM). Temperature-dependent measurements were carried out by mounting the source–sample assembly in a custom-designed heating cell controlled by a microprocessor-based temperature controller (Indotherm MPC 500) with an accuracy of ±1 ^{O}C. Lifetime spectra were collected over a temperature range of 20–200 ^{O}C at intervals of approximately 10 ^{O}C. Each spectrum contained at least 5×10^6counts to ensure adequate statistical precision. The spectra were analysed using the PATFIT program and resolved into three lifetime components.

Physical aging experiments: -

To investigate the physical aging effects, cured polyester samples were annealed under vacuum at 150 ^{O}C for 100 h. Following annealing, the samples were cooled at different cooling rates, namely furnace cooling, water quenching, and liquid-nitrogen quenching. PAL measurements were subsequently conducted at room temperature at regular time intervals to monitor the aging-induced changes.

Moisture absorption studies: -

Moisture uptake experiments were conducted using a specially designed glass apparatus consisting of two interconnected chambers, one containing the polymer specimen and the other filled with water. Both chambers were evacuated independently before opening the connecting valve, allowing water vapor to diffuse into the sample chamber. Additional absorption studies were performed by directly immersing the samples in water at 20 ^{O}C and 97 ^{O}C. The positron lifetime spectra were recorded after exposure times of 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, and 16 h under each condition.

Results: -

Temperature-dependence of positron lifetime parameters: -

Fig.1. compares the positron lifetime spectra of the polyester specimens measured at 20 ^{O}C and 200 ^{O}C, revealing clear temperature-induced changes in the spectral shape. The evolution of the ortho-positronium lifetime (τ_3) and its relative intensity (I_3) with the temperature are shown in Fig. 2. Under the assumption of spherical free-volume cavities, the semi-empirical expression in Eq. (1) is used to derive the average hole radius (R) from the measured τ_3 values. The corresponding FVH size was subsequently calculated as $V_f = \frac{4}{3}\pi R^3$, with the values displayed on the secondary axis in Fig. 2(a).

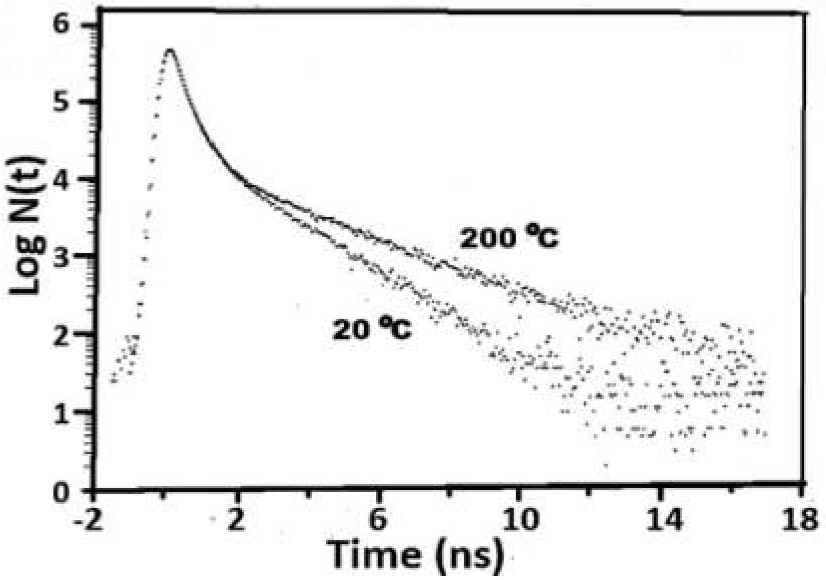

Figure 1. PALS spectra of the polyester sample recorded at two temperatures.

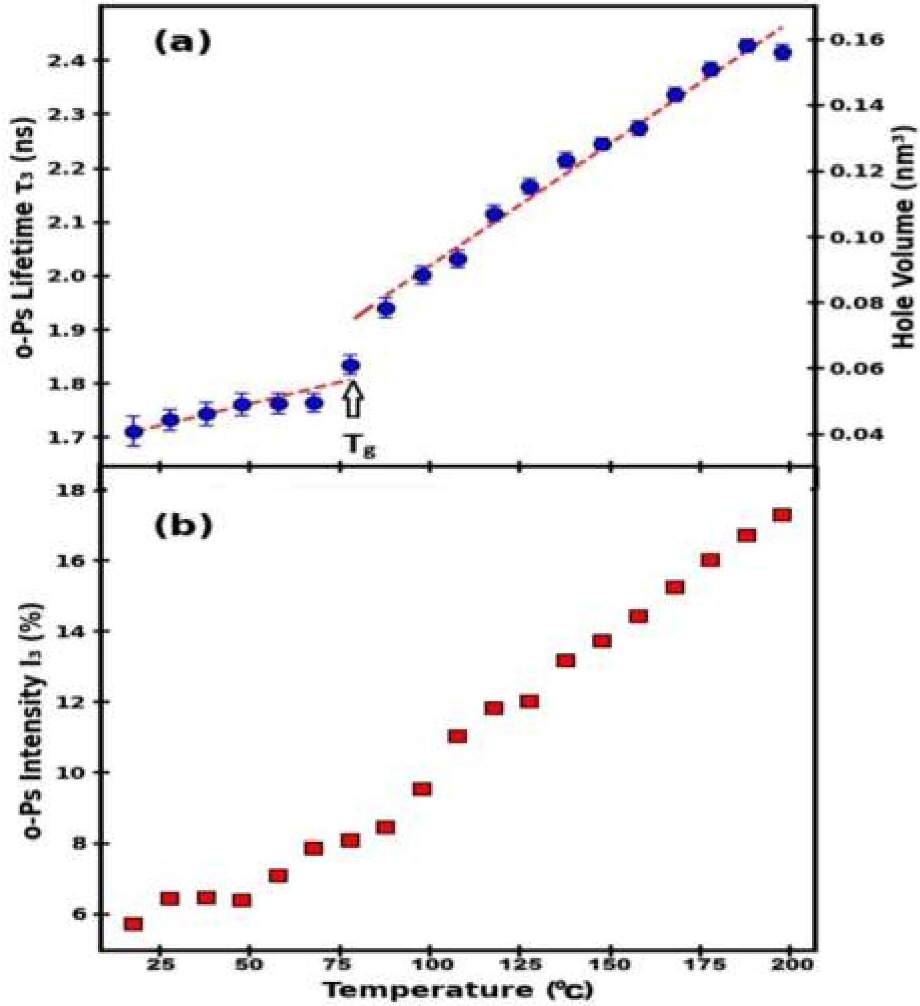

Figure 2. Temperature-dependent behavior of (a) τ_3 (o-Ps lifetimes) and I_3 (o-Ps intensity) in the polyester sample

The variation of τ_3 with temperature, shown in Fig. 2(a), reveals two well-defined regions separated by a marked change in slope near 77 ^{0}C. Above this temperature, τ_3 increases at a significantly faster rate, suggesting the onset of glass transition, identified here as T_g = 77 ^{O}C. In the lower-temperature regime, the material exhibited typical glassy behavior, whereas at temperatures exceeding T_g, the polymer transitioned from the glassy to the rubbery state. At ambient temperature, the intensity I_3 of the polyester sample is approximately 7%. As the temperature is raised, I_3 increases monotonically, attaining a value of nearly 17% at 200 ^{O}C. Considering that value of A is one in Eq. (2), the temperature dependence of the relative free-volume fraction $F_r(= I_3 V_t)$, based on the data in Fig. 2, is shown in Fig. 3. A significant increase in F_r was observed between 77 °C and 200 °C, arising from the simultaneous enlargement of free-volume cavities and an increase in their number density.

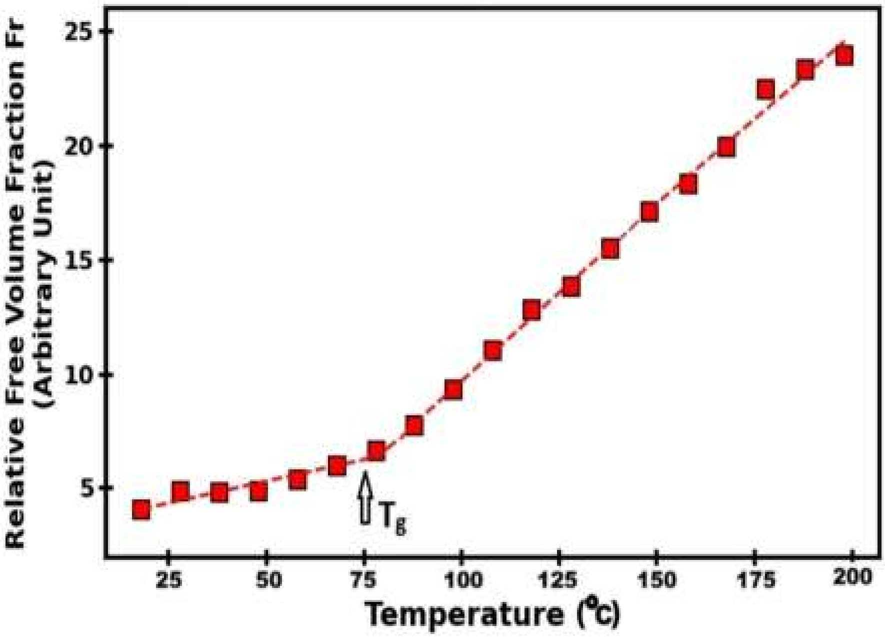

Figure 3. Temperature dependence of the relative free-volume fraction $F_r(= I_3 V_t)$ in the polyester sample, derived from Fig. 2.

Study of structural relaxation and physical aging: -

Fig. 4. presents the evolution of the o-positronium lifetime parameters of the polyester sample plotted against the aging time for three distinct cooling methods. Irrespective of the cooling rate employed, τ_3 and I_3 exhibit comparable temporal trends, suggesting that the qualitative features of physical aging are largely independent of the cooling history. Under certain cooling conditions, the τ_3 values remain essentially invariant throughout the observation period, whereas I_3 shows a slight but systematic decline with increasing aging time. In addition, the decrease in I_3 becomes progressively less pronounced at longer aging durations, indicating a deceleration of the aging kinetics.

It was observed that samples subjected to higher cooling rates exhibited larger values of both τ_3 and I_3 at room temperature when compared with the as-prepared material. In particular, specimens quenched in liquid nitrogen displayed markedly higher o-Ps lifetimes and intensities than those cooled more slowly in a furnace or quenched in water. Fig.5. illustrates the dependence of o-Ps intensity (I_3) on the logarithm of the aging time. In all cooling conditions, I_3 exhibits an approximately linear dependence on log(t).

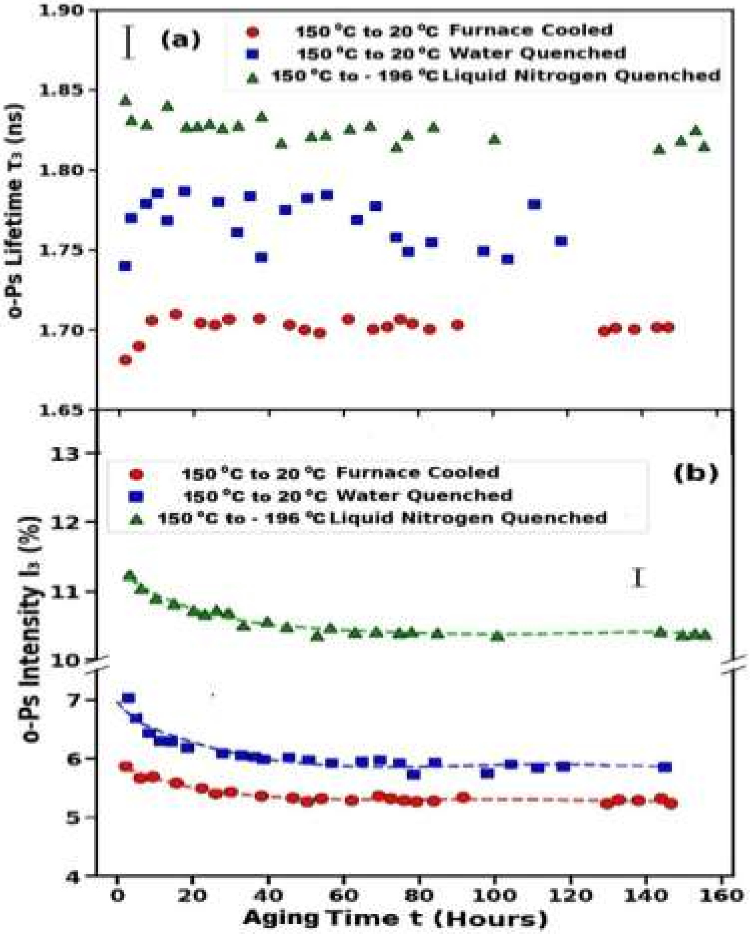

Figure 4. Time evolution of (a) τ_3 and (b) I_3 during physical aging of polyester samples cooled at different rates.

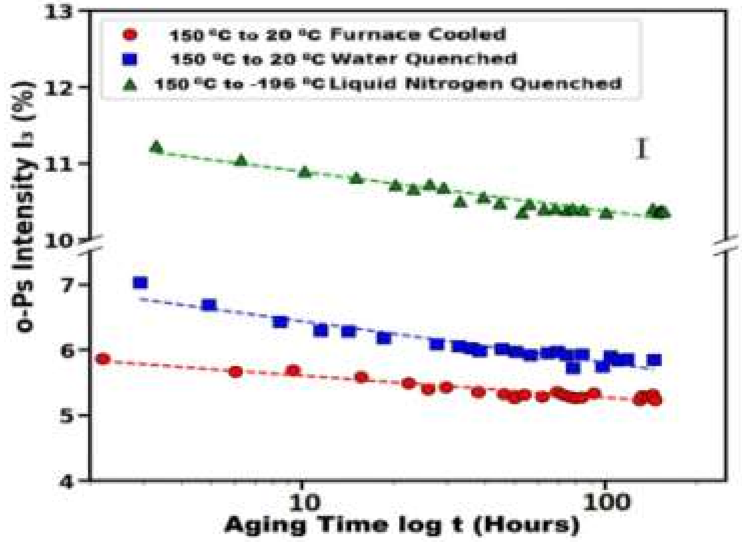

Figure 5. Effect of physical aging in polyester samples cooled at different rates on I_3 as a function of log (t).

Water/moisture absorption studies: -

Fig. 6. depicts the temporal evolution of the measured o-Ps lifetime values, τ_3 and I_3 for polyester samples subjected to moisture exposure under different absorption conditions, as outlined earlier. The results demonstrated the impact of water uptake on the polymer free-volume characteristics of the polymer as a function of exposure time. While τ_3 remains essentially insensitive to the duration of moisture absorption across all samples, a progressive reduction in I_3 is observed with increasing absorption time, followed by the attainment of a steady-state value. The mean τ_3 value is approximately 1.72 ± 0.015 ns, which, based on Eq. (1), corresponds to free-volume cavities with an effective spherical radius of approximately 2.5 ± 0.02 Å. Fig.7 presents the dependence of the o-positronium intensity (I_3) versus the logarithm of moisture absorption time, derived from the data shown in Fig. 6(b). The data points exhibit an approximately linear dependence of I_3 on log(time) over the investigated absorption period, as indicated by the best-fit straight line.

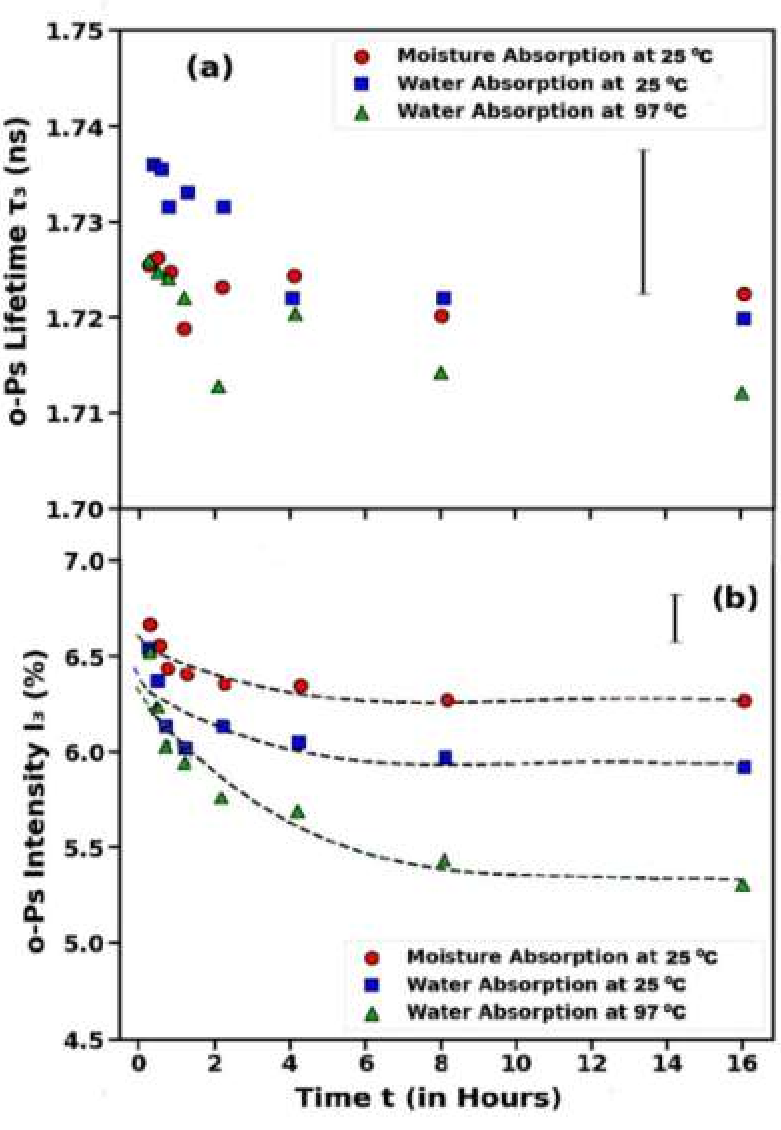

Figure 6. Influence of moisture/water absorption on the o-positronium lifetime parameters of polyester: (a) τ_3 and (b) I_3 as a function of absorption time under different exposure conditions.

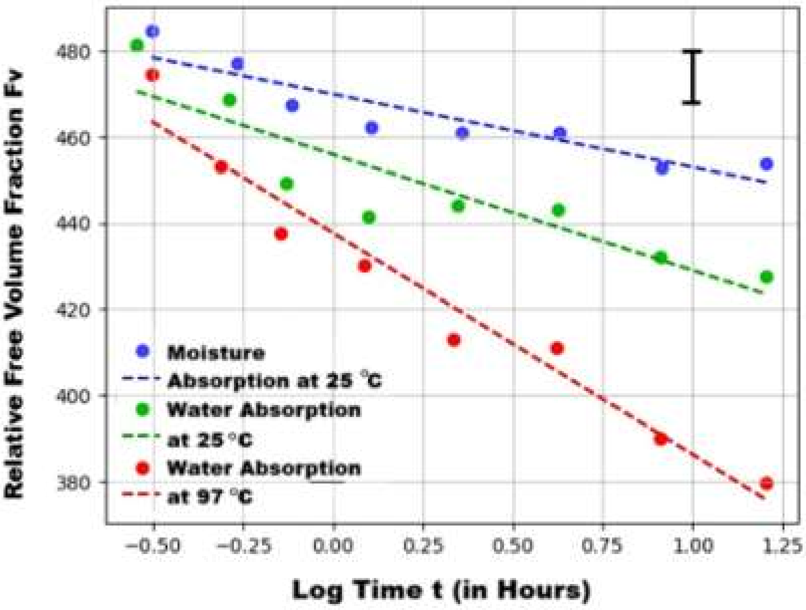

Figure 7. Dependence of o-positronium intensity (I_3) on the logarithm of moisture absorption time for the polyester sample, corresponding to Fig. 6(b), showing the best linear fit.

Discussion: -

Effect of Temperature on Free-Volume Evolution in Polyester: -

Because both the τ_3 and I_3 parameters are closely linked to the free-volume structure of polymers, the analysis that follows primarily examines their temperature-dependent behavior. At ambient temperature, the intensity I_3 of the polyester sample was approximately 7%, which is substantially lower than the values commonly reported for epoxy systems (~20%) (Jean et al., 1986; Deng and Jean, 1993).As mentioned above, with an increase in temperature, I_3 increases steadily, reaching an approximate value of 17% at 200 ^{O}C. This trend indicates an approximately 2.4-fold increase in the population of free-volume cavities. The temperature sensitivity of I_3 stands in contrast to epoxy polymers, where I_3 remains largely invariant with temperature (Deng and Jean, 1993). Consequently, the overall growth in free volume observed in the present system arises from the combined effects of cavity expansion, reflected in τ_3, and an increase in cavity concentration, as indicated by I_3.

This contrasting behavior can be explained by the differences in the polymer morphology. Epoxy systems are predominantly amorphous, whereas polyesters possess a semi-crystalline structure comprising amorphous regions interspersed with partially ordered domains (Valsange et al., 2024; Deng et al., 1992). Studies have shown that o-Ps formation occurs exclusively within the amorphous regions of the polymers. Although the o-Ps lifetime (τ_3) remains largely insensitive to crystallinity, its intensity (I_3) decreases systematically with increasing crystalline content, reflecting a reduction in the number of available free-volume sites rather than a change in their size. The linear dependence of I_3 on crystallinity confirms that positronium does not probe crystalline domains and allows independent assessment of crystallinity. Thus, at room temperature, the higher level of chain packing and molecular ordering in polyester limits the availability of free-volume sites, resulting in relatively smaller initial cavity sizes. As temperature increases, thermal agitation progressively disrupts this ordered arrangement, leading to the formation of additional free volume and a corresponding rise in the o-Ps intensity I_3. At sufficiently elevated temperatures, the polymer structure approaches a highly disordered state.

Physical Aging and Structural Relaxation of Free-Volume in Polyester: -

Physical aging in polymers refers to the reversible rearrangement of molecular packing that occurs without the rupture or formation of chemical bonds. This phenomenon occurs over extended timescales and may require several decades to reach equilibrium (Consolati et al., 2023). As reported by Consolati et al. (2023), when a polymer is thermally treated beyond its glass transition temperature (T_g) and subsequently quenched to temperatures below T_g, the free-volume configuration characteristic of the high-temperature state becomes kinetically trapped, that is, the polymer retains a non-equilibrium free-volume state characteristic of the higher temperature and hence a higher specific volume than its equilibrium value, creating excess free volume. Once in the glassy regime, the system slowly evolves toward a new thermodynamic equilibrium that is appropriate for a lower temperature (Struik, 1978). This process is inherently sluggish because of the severely restricted segmental motion the of polymer chains within the glassy phase, where accessible free volume is scarce.

Because the ortho-positronium lifetime (τ_3) and its associated intensity (I_3) are highly sensitive to both the dimensions and population of FV cavities, the gradual structural relaxation accompanying physical aging is expected to manifest as time-dependent variations in these positron annihilation parameters (Hill, 1999; Cheng et al., 2009). Our observations imply that physical aging predominantly influences the density of FV cavities, as indicated by changes in I_3, while their average size, as reflected by τ_3, is hardly affected. The gradual reduction in the aging rate further supports the notion that the polymer undergoes slow structural relaxation toward a new thermodynamic equilibrium, which is expected to extend over prolonged timescales. Comparable aging behaviour has been reported in earlier positron annihilation studies on polymer systems (Hsu, Chai-Wen et al., 2015; Wang et al., 2003; Deng et al., 1992). This behavior arises because rapid quenching suppresses the structural relaxation during cooling, thereby trapping a higher level of molecular disorder within the polymer matrix. This frozen-in disorder enhances both the available free volume and relative free-volume fraction. Since I_3 exhibits an approximately linear dependence on log(t), as illustrated in Fig. 5, it indicates that the physical aging process follows an exponential decay with time. This logarithmic time dependence is characteristic of diffusion- and relaxation-controlled processes in polymers (Struik,1978).

Effect of moisture absorption on free-volume characteristics: -

The invariance of τ_3 indicates that moisture uptake does not appreciably change the average size of the FV cavities, suggesting that water molecules preferentially occupy pre-existing voids rather than induce cavity expansion or polymer swelling within the investigated time scale. As mentioned above, the free-volume cavities with a radius of approximately 2.5 ± 0.02 Å are, comparable to the kinetic diameter of a water molecule (~3 Å).This dimensional similarity suggests that water molecules introduced during moisture uptake can gradually occupy the existing free-volume sites within the polymer matrix, thereby limiting the number of cavities available for positronium formation. Consequently, the observed decrease in I_3 with absorption time can be attributed to the filling of intermolecular voids by water molecules (Gordo et al., 2013), despite the inherently hydrophobic nature of polyester resins. Thus, the reduction in I_3 reflects a decrease in the number of positronium-forming sites rather than a modification of cavity geometry, consistent with competitive occupation of FV holes by water molecules. Furthermore, the magnitude of the o-Ps intensity (I_3) decrease is more pronounced at elevated absorption temperatures, which may be associated with enhanced free-volume availability and/or increased diffusivity of water molecules, enabling more rapid and extensive penetration into the polymer network (Crank, 1975). Moreover, the attainment of a plateau in I_3 at longer absorption times indicates saturation of accessible free-volume sites, beyond which additional moisture uptake has a negligible effect on positronium formation.

Although polyester resins are generally considered hydrophobic, the presence of polar ester groups and interfacial free-volume regions enables limited but measurable moisture uptake. In contrast to physical aging, where changes are governed by intrinsic structural relaxation, moisture absorption introduces an extrinsic mechanism that selectively reduces the availability of free-volume sites without altering their characteristic size. A similar logarithmic time dependence of o-Ps intensity during moisture absorption has been reported in several polymer systems and is generally associated with diffusion-limited occupation of free-volume sites (Deng and Jean, 1993; Wang et al., 2003). This behavior suggests that the reduction in o-Ps intensity follows a logarithmic time dependence, which is characteristic of diffusion-controlled and relaxation-driven processes in polymer systems. The linear relationship between I_3 and log(time) implies that moisture uptake progressively reduces the number of available positronium-forming free-volume sites, with the rate of reduction slowing at longer times as the system approaches saturation. Such kinetics are consistent with gradual occupation of accessible free-volume cavities by water molecules, followed by a diminishing availability of unfilled sites (Wang et al. 2003). The observed trend further supports the interpretation that moisture absorption primarily influences the population of free-volume holes rather than their average size, in agreement with the near-constant τ_3 values shown in Fig. 6(a).

Summary: -

- Temperature-dependent PALS measurements reveal a distinct change in free-volume behavior near 77 °C, corresponding to the glass transition temperature of polyester.

- Above Tg, the relative free-volume fraction increases due to both enlargement of free-volume cavities and an increase in their number density.
- Physical aging mainly affects the concentration of free-volume cavities, with o-Ps intensity decreasing over time while the cavity size remains nearly unchanged.
- Rapid quenching results in higher initial free volume, reflecting enhanced frozen-in disorder and suppressed structural relaxation.
- Moisture absorption reduces the number of positronium-forming sites without significantly altering cavity dimensions, indicating preferential occupation of pre-existing free-volume cavities by water molecules.

Conclusions: -

Positron annihilation lifetime spectroscopy (PALS) was employed to investigate the free volume in cured polyester polymers. The temperature dependence of the o-Ps lifetime (τ_3) and its intensity (I_3) was analysed to determine the variation in free-volume hole size (V_f) over the temperature range of 20–200 ^{O}C. Polyester polymers exhibited a pronounced increase in V_f above the glass transition temperature (T_g). This behavior 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 effect of water absorption on the ortho-positronium lifetime and intensity was examined, showing more significant changes when absorption occurred at an elevated temperature of 97 ^{0}C.

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Conflict of Interest declaration: -

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