Micro-Structural Properties Of Polymers By PALS - A Review

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Abstract
In recent years the positron annihilation lifetime spectroscopy (PALS) has been developed as a useful tool in probing the microscopic and local properties of polymers. One of the great successes in this area of research is the determination of micro-structural properties of the defects, such as free volume and holes, on an atomic scale (2-20 Å) in polymers. It has been demonstrated that the positron annihilation lifetime spectroscopy (PALS) is capable of determining size, distribution, fraction and an isotropic structure of holes and free volume in polymers and polymer blends.

Keywords: PALS; microscopic; free volume; holes; micro-structural

Introduction
The positron is a very special probe in the area of materials science research. Unlike conventional probes such as neutrons, photons, and electrons, the positron is a strong interacting probe [1]. The process of positron–electron annihilation is governed by the interaction at the zero ranges, i.e., the overlap between the positron and the electron at the same position. The interaction of the positron with its anti–particle, the electron, is so strong that the scientific information from annihilation is not only comprehensible but contains the most complete physical information. From past four decades, a novel method, positron annihilation lifetime spectroscopy (PALS), has been developed to determine micro-structural and interfacial properties of a wide variety of materials [2-8]. PALS is scientifically very rich. This probes the most fundamental information on matter. In recent years, PAS has been successfully used to determine the free-volume, void, and layer properties in polymers [9-13] and polymer blends [14-15].

The high sensitivity of PALS in probing defect properties arises from the fact that the positronium atom (Ps)–an atom consisting of a positron and an electron- is preferentially localized in atomic-scale free volume and holes. When positrons are trapped in open–volume defects, such as vacancies and their agglomerates, the positron lifetime increases with respect to the defect–free sample. This is due to the locally reduced electron density of the defect. Thus, a longer lifetime component, which is a measure of the size of the open volume, appears. The strength of this component, i.e., its intensity, is directly related to the defect concentration. In principle, both items of information, i.e., the kind and concentration of the defect under investigation can be obtained independently by a single measurement.

Development of drug delivery vehicles and imaging agents using polymeric materials, especially polymer nanoparticles, continues to grow. In these systems the free volume sites are important for controlling the uptake, storage, separation and release of the molecules of interest. So in order to optimise their performance, extensive characterisation of their free volume is essential. PALS is particularly useful as a qualitative tool for measuring the effect of processes on the porosity in materials.

Positron annihilation lifetime spectroscopy
The annihilation of positrons in condensed matter provides a unique way of obtaining information about the internal structure of material. This information is transmitted through γ-rays, emitted when the positron is annihilated in the material. The PALS has been used here for microstructural study of the polymer blends.
The conventional positron lifetime measurement is possible since a γ–quanta with energy of 1.27 MeV is emitted almost simultaneously with the positron in the ^{22}Na source. The positron energy, which extends up to 511 keV, decreases in the sample within a few picoseconds by non–elastic interactions. The mean positron penetration depth of this so–called thermalization process is of the

order of 100 μm. The thermalization time usually amounts to a few picoseconds. It is thus small compared with the positron lifetime and can be neglected. On reaching thermal energies, the positron diffuses in the periodic lattice potential before it is possibly trapped in a lattice defect. The diffusion length is in order of 100 nm. This distance determines the number of atoms to be probed for positron traps during the positron lifetime. Hence, the diffusion length strongly determines the sensitivity of the positron method to detect defects.

During thermalization and at nearly thermalized stage, a positron may capture an electron from the environmental molecules and form positronium (Ps), a bound state of positron and electron similar to a hydrogen atom. Therefore, during its lifetime, the positron may exist in both positron and Ps states in molecular solids. The polymeric materials contain local free volume, which have the size of few Å. These are the favourable sites where positron and Ps atoms are localized prior to annihilation [15]. This is schematically shown in the figure 1.

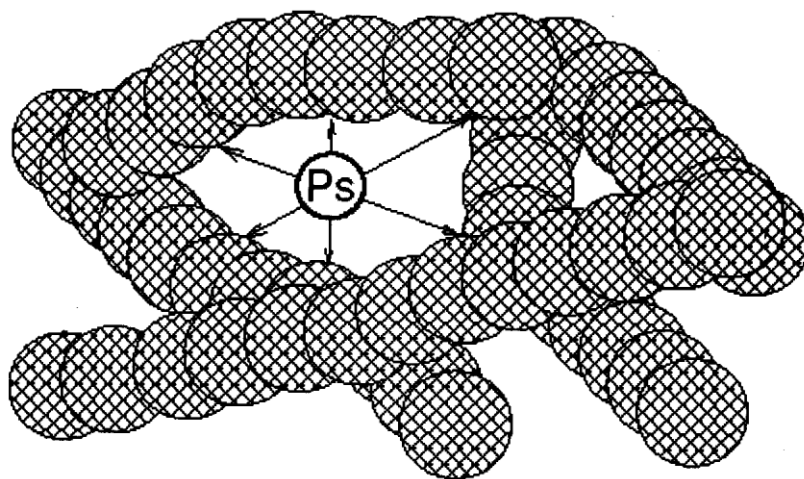Because two spin orientations are possible for an electron–positronium, (p–Ps) where the

Figure 1: Ps localisation and annihilation in a hole of the (excess) free volume

spins are antiparallel, has an intrinsic self–annihilation lifetime of 125 ps, decaying into two γ– rays of 0.51 MeV ($=mc^2$). *Ortho*–positronium (o–Ps), with parallel spin orientation, annihilates into three γ–rays with an intrinsic lifetime of 142 ns in vacuum. o–Ps and p–Ps are formed normally in the ratio of 3:1. The lifetime of the o-Ps confined in the local free volume of the polymer lies typically between 2 to 5×10^{-9} s [16–17].

The positron in the polymeric material has following possible states at the time of annihilation: (i) free (delocalized) and/or localized positron state and (ii) free and/or localized Ps state. The localization sites are free volume holes, which are more favourable sites than the bulk for positrons and Ps. The Ps probes only free volume regions and not interfered by the bulk properties of the polymeric material [18].

The positron lifetime of a single event can be measured by detecting the time difference between the birth γ –quanta of the β^+–decay in the source and one of the annihilation γ –quanta of energy of 511 keV. The activity of the source must be sufficiently low in order to ensure that on average only one positron is in the sample. This avoids the intermixing of start and stop quanta originating from different annihilation events. A special "sandwich" arrangement of foil source, samples, and detectors guarantees that all positrons emitted from the source are penetrating the sample material. The γ –rays are converted by scintillator–photo multiplier detectors into analog electrical pulses. The pulses are processed by discriminators. Their output pulses start and stop a time–to–amplitude converter as an "electronic stopwatch". The amplitude of the output pulse is proportional to the time difference between the birth and the annihilation γ –quanta and, thus, represents a measure of the positron lifetime. The single annihilation event is stored after analog–digital conversion in the memory of a multi–channel analyzer. The channel numbers represent

the time scale. In order to obtain the complete lifetime spectrum, more than 10^6 annihilation events are recorded.

The lifetime spectrum of the polymeric material is conventionally described by a sum of discrete exponentials:

$$N(t) = \sum_{i=1,n} I_i e^{-\lambda_i t} \quad (1.1)$$

Where n is the number of exponential terms, I_i and λ_i, represent the number of positrons (intensity) and the annihilation rate respectively for the annihilation from the ith state. The positron annihilation rate, τ_i, is the reciprocal of positron mean lifetime, λ_i. It is an overlap integral of the positron density, ρ_+ and the electron density, ρ_- at the site of annihilation:

$$\lambda = constant \times \int \rho_-(r)\rho_+(r)dr \quad (1.2)$$

Where constant is normalization constant.

The PAL spectrum is fitted with a finite number of component terms, n, using different computer codes [19–20]. For amorphous polymers $n=3$ is selected to fit the observed lifetime spectrum.

The PAL spectrum expressed in equation (1.1) as a discrete distribution of lifetime can also be expressed as a continuous distribution of lifetime against intensity. In that case, the summation in equation (1.1) is replaced by an integral.

$$N(t) = \int \lambda \alpha(\lambda) e^{-\lambda t} \quad d\lambda \quad (1.3)$$

Where $\lambda \alpha(\lambda)$ is the probability density function (*pdf*). The *pdf* is obtained by deconvoluting experimental curve with exact instrumental resolution function and inverting in Laplace transform [15].

The lifetime of o-Ps annihilating by pick-off process is determined by the overlap of Ps wave function with bulk electrons of surrounding medium and the o-Ps lifetime becomes dependent on physical size of trap. Thus, the PAL method can be used to probe the free volume in amorphous media. The relation between free volume size and the o-Ps decay rate, λ_3, is given by Tao-Eldrup [12, 15] model, assuming that the Ps is trapped in a spherical hole with radius R_0 $(=R+\Delta R)$ having an infinite potential barrier. This model has one free parameter, ΔR, which is determined to be 1.66Å by fitting to data taken in well characterized small pore materials such as zeolites [16] and has been shown to be quite material independent. The o-Ps lifetime as a function of free volume radius R is given by

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}sin\frac{2\pi R}{R_0}\right)^{-1} \quad (1.4)$$

Where $R_0 = R+\Delta R$. The correlation between, τ_3 and free volume (spherical) is shown in figure 1
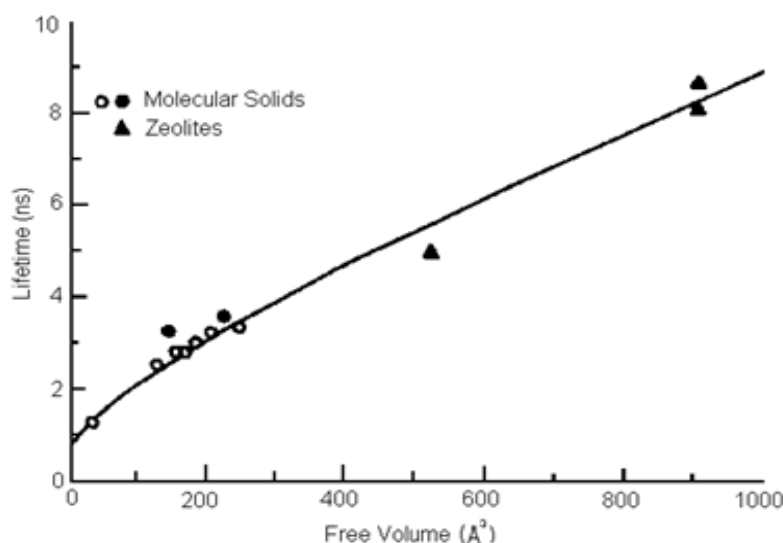

Figure 2: A correlation curve between the observed o-Ps lifetime and the volume of the free volume holes. The solid line is the best fit using equation (1.4) with $\Delta R =1.656$Å. The data points are the measured o–Ps lifetimes in molecular systems with known pore size [24].

Measurements

The positrons for the lifetime measurements were obtained from the radioactive decay of ^{22}Na isotope, which is the most commonly used source of positrons. The ^{22}Na isotope gives a relatively high positron yield of 90.4% and has several other advantages. The appearance of 1.27 MeV γ–quanta almost simultaneously with the positron, the easiness of its handling for laboratory work, comparatively large half-life (2.6 years) and low cost make this isotope the most useful source material in positron research [14].

The positron lifetime was registered as a time difference between the emission of the 1.27 MeV γ-quanta generated almost simultaneously with the positron and one of the 0.511 MeV annihilation γ-quanta.

The source was prepared by evaporating ∼ 5 μ Ci of aqueous ^{22}NaCl salt on a thin (∼ 8 μ m) rhodium foil. The source foil must be thin in order

to reduce the background of 0.511 MeV annihilation quanta. The positron source is sandwiched between the two identical samples of the material, the thickness of which must be sufficient enough (>100 μ m) to absorb all the positrons [15].

The positron annihilation lifetime (PAL) spectra were obtained using conventional fast-fast coincidence system. The fast NE111 plastic scintillators in truncated conical geometry coupled to RCA 8575 photomultipliers were used. The conical shape of the scintillators improves the light collection process. Fast Comptec constant fraction differential discriminators (CFDDs) were used for selecting energy and providing timing signal independent of the rise time and amplitude of the anode signal from the PM tubes to time to amplitude converter (TAC)
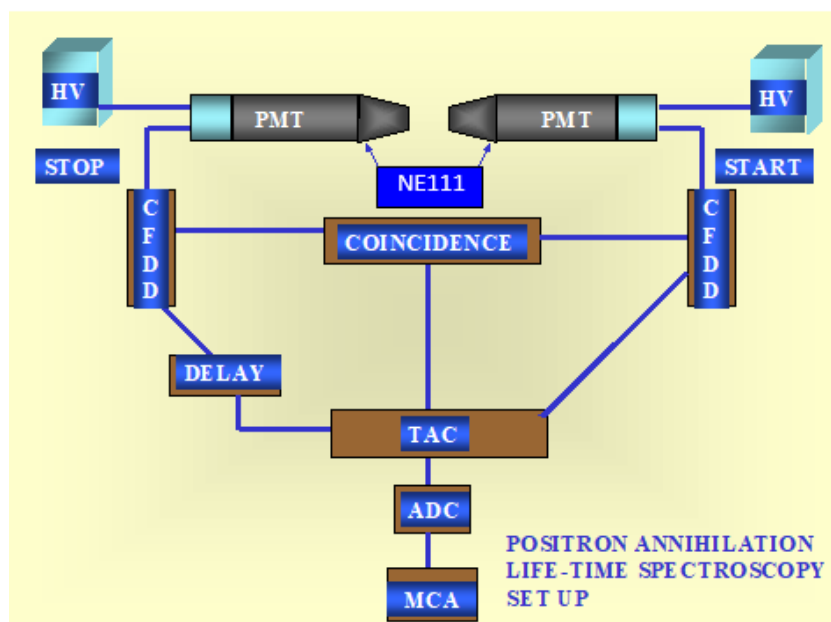

Figure 3: Positron Annihilation Lifetime Spectroscopy Setup

(Ortec 457). The windows of the CFDDs in start and stop arms were adjusted for 1.27 MeV start and 0.511 MeV stop signals respectively. Detection of the 1.27 MeV gamma quanta provides the start signal for a TAC. The stop signal is generated on detection of one of the 0.511 MeV gamma quantas. If legitimate gamma-gamma coincidences are observed, a pulse whose amplitude is proportional to the time interval between start and stop signals, is sent from the

TAC to a multi-channel analyzer (MCA) where it is stored in the appropriate time channel. The block diagram of the positron lifetime spectro-meter is shown in figure 3

The uncertainty in the measurement of lifetime was estimated by observing the distribution of time intervals when ^{22}Na source is replaced by ^{60}Co, which emits two γ-rays almost simulta-neously. The full width of this prompt distribution at half maximum was ∼ 400 ps [9]. The PALS

setup at IUC-DAE Consortium for Scientific Research Kolkata with a better time resolution of ~290 ps is widely used by researchers. [14].

Free volume studies

Positron lifetime spectra in polycarbonate has been measured as a function of temperature and time [26]. *Ortho*– positronium (o–Ps) life time remained constant with prolonged measuring time, but its intensity decreased and increased with time at room temperature and low temperatures, respectively. Marques *et. al.* [27] have studied free volume parameters in polyurethane membranes and they have shown that hole size and overall free volume in bisoft segment polymer membranes, as obtained by positron annihilation, are correlated to gas permeation properties. The temperature dependence of mean size of local free volume (holes), v_h, of two differently plasticized poly (vinyl/chloride)s have been studied [28]. The hole volume at 100 K was estimated to be 0.07 nm^3 and its value increased above, for temperature above T_g, to ~ .18 nm^3. Dlubek *et. al.* [29] have used PALS technique for studying inter diffusion in blends of chemically different polymers. Wate *et. al.* [30] have studied the change in free volume in ion–irradiated polycarbonate membranes and observed increase in average free volume with ion fluence in low fluence regime and recorded decrease in free volume for higher fluence. They have attributed the increase in average free volume to chain scission along the tracks and the decrease to random cross linking of scissioned segments.

Ravi Kumar *et. al.* [31] have observed increase in free volume hole size and its concentration with the increase in ethylene propylene diene monomer (EPDM) content of the Poly (trimethylene-terephthalate)/ EPDM blends which is attributed to coalescence of free volumes of EPDM with that of poly trimethylene terephthalate (PTT).

Free volume measurements using positron annihilation lifetime spectroscopy (PALS) have been done in PTT and EPDM blends with and without addition of a compatibilizer precursor EPM–g–MA. These incompatible blends are characterized by a two–phase morphology, narrow interphase and poor physical and chemical interactions across the phase boundaries [32]. The temperature dependence of the average free volume hole size and its distribution in blends of poly (methyl methacrylate) and poly (ethylene

oxide) have been studied by positron annihilation lifetime spectroscopy [33]. Dlubek *et. al*. [34] have studied the local free volume in blends of Acrylonitrile–Butadiene–styrene copolymer and polyamide.

Pham *et. al*. [35] studied porosity of synthetic polymer nanoparticles using PALS.
A series of poly (styrene/divinyl benzene) particles with diameters in the range of 100 to 500 nm were synthesized and then carefully chemically treated using the sulfonation process, to increase their porosity. The particles were characterised by Scanning Electron Microscopy (SEM), light scattering and PALS. Light scattering gave larger size for the treated particles, reflecting the hydration effect and therefore the increase in porosity. PALS spectra of untreated and treated particles gave four and three life-time components, respectively. Analysis by PASCUAL version 1.3.0 program indicated there was a reduction in the intensity and the type of the micropores in the treated particles. They expressed that PALS is a sensitive tool for detecting changes in microporosity in particles.

Conclusion

PALS is nowadays an established technique to study the size of atomic and sub nanometer-sized holes in various materials. In amorphous polymers, these holes appear due to the structural (static or dynamic) disorder and constitute the (excess) free volume. A large series of homo- and copolymers have been investigated for hole sizes in polymer blends as a function of the composition or heat treatment. It is a useful technique for studying interdiffusion in blends of chemically different polymers. Miscibility of polymers have also been studied by positron annihilation lifetime spectroscopy. PALS has proved to be a sensitive technique to measure the micro-structural properties.

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