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Positron Annihilation Lifetime Spectroscopy for the Characterization of Ion Induced Modification

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The irradiation of polymeric materials with Swift Heavy Ions (SHI) results in to the change of their free volume properties that have strong correlation with their macroscopic properties. Positron Annihilation Lifetime Spectroscopy (PALS) provides direct information about the dimension, content and hole size distribution of free volume in polymers. The paper describes PALS technique for the measurement of positron annihilation lifetime spectra using fast fast coincidence technique. Studies on Swift Heavy Ion induced modification in polymers have been carried out by characterization through PALS.

Key Words: Ion induced modification, Positron annihilation

INTRODUCTION

Energetic ions play a crucial role in synthesis, modification (nano size) and characterization of materials. They offer unique possibilities in these fields since a single ion may deposit a large energy density in the solid (upto 100 keV/nm) within a well-localized small volume surrounding the ion path (of the order of 10 nm in dia). Polymers have wide industrial, scientific and technological applications and thus need a basic understanding of their material properties. Interest in ion beam modification of the polymers has increased in recent years, prompted by the ion induced improvements in the mechanical, chemical, optical and electrical properties of various polymeric substrates[1,2]. The availability of heavy ion beams from the accelerators has brought new impetus to the field of ion beam modification as dramatic modifications in polymeric materials have been observed as a result of irradiation of polymers with Swift Heavy Ions (SHI). Some of the modifications by incident ions have been attributed to the scissoring of the polymer chains, breaking of covalent bonds, promoting the cross-linkages, carbon cluster formation, liberation of volatile species and even the formation of new chemical bonds in some cases[3,4]. The effectiveness of these modifications produced in the polymer depends on the structure and the ion beam parameters (energy, fluence, mass, charge) and the nature of the target material itself.

The existence of free volume holes in polymers has been postulated for more than four decades. A key problem in this regard is to relate the macroscopic properties of polymer to atomic scale (a few Å) free volume holes. The damage produced in the form of latent tracks by heavy ions results into the change of free volume properties of the material, which have strong correlation with its macroscopic properties[5]. There are no. of techniques useful in defect/free volume investigation, none of which, however can provide all the information required in the definitive study. It is desirable to utilize techniques which are defect specific, non destructive and unrestrictive in application and which allow for depth selectivity. Positron annihilation spectroscopy possesses a unique combination of these attributes[6].

Positron annihilation spectroscopy in polymers

Positron Annihilation Spectroscopy (PAS) has become well established as probably the most effective and successful technique for the direct examination of the free volume in polymers.

Unlike other methods used to determine free volume in polymers, PAS is capable of determining the local hole size and free volume fractions in polymers without interfering significantly with the bulk of the polymers. PAS has also been developed to be a quantitative probe of the free volume. Not only does the technique probe the free volume size and fractions of free volume, but it also gives detailed information on the distribution of free volume hole size in the range from 1 to 10 Å. The Positron annihilation spectroscopy is a family of three experimental techniques: Positron annihilation lifetime spectroscopy (PALS), Doppler broadening spectroscopy (DBS) and Angular Correlation of Annihilation Radiation (ACAR) .The three methods of positron annihilation are shown in Fig. 1. All these techniques have been applied to polymers.

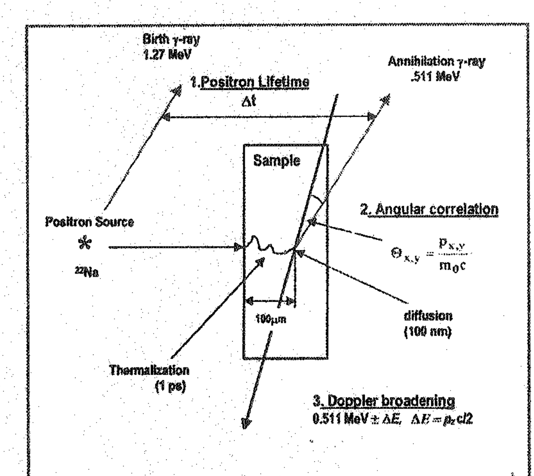

Figure : Three methods of positron annihilation

Fig. 1

Positron annihilation lifetime spectroscopy (PALS)

PALS is capable of determining size distribution, fraction, and free volumes in polymers. The atomic scale free volume holes are detected on the basis that positronium (Ps) atoms are formed and localized in the free volume holes[6,7]. When energetic positrons from a radioactive source are injected into a condensed medium they first slow down to thermal energies in a very short time of the order of 1 ps. Finally, after living in thermal equilibrium the positron annihilates with an electron from the surrounding. The average lifetime of positrons is the characteristic of each material and varies from 100 to 500 ps. During the slowing down process or near thermalisation state a positron may pick up an electron from the environmental molecules and form a bound state, the so-called Ps atom. Therefore, between the time of thermalisation and the time of annihilation the positron exists in both positron and positronium state in molecular substances.

In a polymeric material, a few percent of free volume fraction exists at a size of few Å. These are the favorable sites where positron and Ps atoms are localized before annihilation and thus positron and positronium have sufficient chance to sense the existence of such holes. Thus one expects that annihilation signals be mainly from the positron and Ps annihilation in free volume holes. Ps atom has two spin states: (i) *para*-positronium (*p*-Ps), spin zero (↑↓), lifetime in vacuum 125 ps, decays into two gammas and (ii) *ortho*-positronium (*o-Ps*), spin one (↑↑), lifetime in vacuum 142 ns, decays into three gammas. The *o-Ps* lifetime in condensed matter is considerably smaller than the vacuum value of 142 ns, because of pick-off annihilation of positrons by surrounding electrons. Nevertheless, this lifetime is longer than the lifetime of other positrons in the same material, because the electron in the *o-Ps* partially shields its positron from the electrons with antiparallel spins, which would annihilate it more rapidly. Polymers with large free volumes form a favorable environment for *o-Ps* atoms that can survive as long as 4 ns.

The value of the lifetime of this component, as well as the relative intensity gives valuable information about free volume in polymeric materials.

Positron lifetime spectrometer

Positron annihilation lifetime spectrometer at the Inter University Consortium for Department of Atomic Energy Facilities (IUC-DAEF), Kolkata Centre with a time resolution of *ca.* 280 ps was used for measurements. The positrons for the lifetime measurements were obtained from the radioactive decay of ^{22}Na isotope that is the most commonly used source of positrons. ^{22}Na decay to the excited state of ^{22}Ne by emission of positron and a neutrino.

$$^{22}\mathrm{Na} \rightarrow {}^{22}\mathrm{Ne} + e^{+} + \gamma$$

^{22}Na decays through positron emission and by electron capture to the first excited state at 1274 keV of ^{22}Ne. This excited state goes to the ground state by the emission of a 1274 keV gamma ray with a half-life $\tau_{1/2}$ of 3 x 10^{-12} s. Thus positron emission is almost simultaneous with the emission of 1274 keV gamma ray while the positron annihilation is accompanied by two 511keV gamma rays. The measurements of the time interval between the emission of 1274 and 511 keV gamma rays can yield the lifetime 'τ' of positron annihilation. ^{22}Na isotope gives a relatively high positron yield of 90 % and has several other advantages. The appearance of 1.27 MeV γ quantum 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.

For lifetime or Doppler measurements, the simplest way to guide the positrons into the samples, is to use a sandwich configuration as in Fig. 2 below:

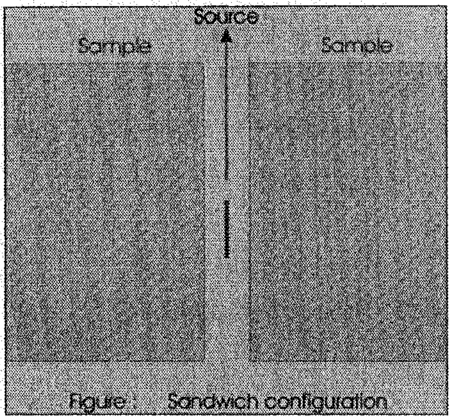

Fig.-2

The source should be very thin so that only a small fraction of the positrons annihilate in the source. Radioactive material can be deposited directly on the samples or separation foil can be used to allow the use of the source repeatedly. The source was prepared by evaporating 5 µCi of aqueous ^{22}NaCl salt on a thin (*ca.* 8 µm) rhodium foil. The positron source was sandwiched between two identical samples of the material, the thickness of which was sufficient enough to absorb all the positrons. In the present study the samples were in the form of films of different thickness. Therefore, the source was sandwiched between the two identical stacks of layers of sample films to make the thickness of the stack *ca.* 400 µm.

PAL spectra were obtained using fast-fast coincidence system. The fast BaF_2 scintillators in truncated conical geometry coupled to Phillips XP 2020 photo multipliers were used. The conical shape of the scintillators improves the light collection processes. ORTEC 583 Constant Fraction Differential Discriminators (CFDD) 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) (ORTEC 567). 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 photon provides the start signal for a TAC. The stop signal is generated on detection of one of the 0.511 MeV annihilation gamma photons. 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 lifetime spectrum of the polymeric material is conventionally described by a sum of discrete exponentials: $N(t)=\sum I_i e^{-\lambda i\, t}$

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 PAL spectrum is fitted by a finite number of component terms, n, using the compute codes.

For polymers, n = 3 is selected to fit the observed lifetime spectrum. A typical positron lifetime spectrum in polytetrafluroethelene, commercially known as Teflon is shown in Fig. 3.

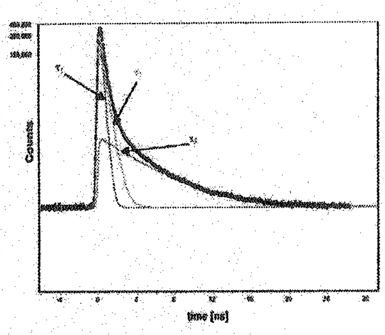

Figure : A typical lifetime spectrum of Teflon (polytetrafluoroethelene)[47].

Fig. 3

The three components, which appear in the lifetime spectrum, are attributed to the annihilation of *p*-Ps, free positrons (not Ps) and *o-Ps*. Shortest component, τ_1 *ca.* 0.13 ns with intensity I_i = 7-20 % is attributed to *p*-Ps. Intermediate component, $\tau2$ = 0.4-0.5 ns and intensity I_2 = 40-60 %, is attributed to the direct annihilation of positrons. The longest component, τ_3 = 2-5 ns and intensity between 10-30 %, is attributed to *o-Ps* annihilation in free volumes. The *o-Ps* lifetime is found to sensitively depend on the size of the free volume.

Nano-void detection by PAL

Free volume radius R is obtained by first considering *o*-Ps trapped into a spherical volume with radius R_0, providing infinite potential barrier. The Schrodinger equation is solved to obtain the positronium wave function for the centre of mass motion of *o*-Ps in the ground state. The *o*-Ps pick-off annihilation rate is then calculated through a semi-empirical approach, by assuming a homogeneous electron layer with a thickness of $\Delta R = R_0 - R = 0.166$ nm adjacent to the wall and calculating the overlap of positronium wave function with the electron layer. Accordingly, the following expression may be obtained, which relates *o*-Ps pick-off lifetime, τ_3 and free volume radius, R[8-10].

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi} Sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1}$$

where τ_3 and R (hole radius) are expressed in ns and Å respectively. R_0 equals $R + \Delta R$ where ΔR is the fitted empirical layer thickness (= 1.66 Å). The micro-void volume (V_f) is given by $4/3\pi R^3$. Further, the fractional free volume F_v may be estimated from the following empirical relation[11].

$$F_v = C\, V_F\, I_3$$

where, V_f is free volume and the scaling factor; C is a structural constant evaluated from an independent isochronal experiment and is determined empirically to be *ca.* 0.0018[12].

EXPERIMENTAL

Various polymers such as CR-39, CR-39(DOP) and Makrofol polycarbonates, Polyamide Nylon-6 and Polystyrene, *etc.* were irradiated with different Swift Heavy Ions of different energies from Pelletron accelerator at Nuclear Science Centre (N.S.C.), New Delhi, Variable Energy Cyclotron, Kolkata and Universal Linear Accelerator, UNILAC (Heavy Ion Accelerator) at GSI (Gesellschaft fur Schwerionenforschung) Darmstadt, Germany.

Data acquisition and analysis

The positron lifetime spectroscopy data were analyzed by fitting three lifetime components by finite term lifetime analysis using PATFIT-88 program[12]. It decomposes a PAL spectrum into 2-5 terms of negative exponentials. In polymers, 3 lifetime results give the best χ^2 (< 1.1) and most reasonable standard deviations[13]. The lifetime values and intensities for PN-6 and PES are tabulated in Tables 1 and 2. The longest-lived component, τ_3, is attributed to the *o*-Ps atoms in free volumes of amorphous regions of polymer *via* the pick-off annihilation.

RESULT AND DISCUSSION

As an example Tables 1 and 2 present the data obtained for Polyamide Nylon-6 samples irradiated with C^{5+} ion of 70 MeV at Pelletron accelerator, NSC, New Delhi.

TABLE-1

LIFETIME AND INTENSITIES OF UNIRRADIATED AND IRRADIATED POLYAMIDE NYLON-6 POLYMER

Fluence (ions/cm^2)	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)
Unirradiated	0.20	35.96	0.39	46.30	1.71	18.56
9.3×10^{11}	0.17	31.18	0.38	51.78	1.69	18.29
3.7×10^{12}	0.17	32.75	0.37	50.23	1.68	17.89
1.8×10^{13}	0.17	32.46	0.37	50.52	1.67	17.65
3.7×10^{13}	0.16	29.28	0.36	50.21	1.62	17.01

The long-lived component τ_3, which is very sensitive to structural changes in the polymer is attributed to *o*-Ps pick-off annihilation in free volume. In PALS, it is the *o*-Ps lifetime that is directly correlated to the free volume hole size. The intensity of this component contains information about free volume hole concentration[6]. The energy transfer by the ion leads to radical formation, bond scission and cross-linking of polymer chains. The dominance of scission or cross-linking depends essentially on the polymer and energy loss per unit path length or linear energy transfer (LET). For low LET, spurs develop far apart and independently; the deposited energy tends to be confined in one chain (not in neighboring chain) leading to scission[14-16]. In case of high electronic LET, spurs overlap, the probability of two radical pairs to be in neighboring chains is increase and cross-linking is facilitated. The scission causes increase in the free volume whereas the cross-linking causes decrease in the free volume.

TABLE-2
THE LIFETIME PARAMETERS OF *o*-Ps AND RADIUS OF FREE VOLUME HOLE(R) AND FRACTIONAL FREE VOLUME (F_V) IN POLYAMIDE NYLON-6 POLYMER

Fluence (ions/cm^2)	τ_3 (ns)	I_3 (%)	R (Å)	V_f (Å^3)	f_V
Unirradiated	1.71	18.56	2.57	71.32	2.38
9.3×10^{11}	1.69	18.29	2.55	69.91	2.30
3.7×10^{12}	1.68	17.89	2.54	69.66	2.24
1.8×10^{13}	1.67	17.65	2.53	69.17	2.20
3.7×10^{13}	1.62	17.23	2.48	64.40	1.99

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