Extracting the Free Volume and Hole Fraction of Based Polymers under Positron Annihilation Lifetime Spectroscopy Technique

Saygin M. Nuri [1]
Nada M. Hassan [1]
Ronak S. Bagelany [2]

[1] Department of Physics, College of Education for Pure Sciences, Kirkuk University, Kirkuk, IRAQ
[2] Department of Mathematics, College of Education for Pure Sciences, Kirkuk University, Kirkuk, IRAQ

In this study, the polymer structures of PMMA, SAN and SMA polymers were examined from bulk to surface by positron energy. The polymers were analyzed by Positron Annihilation Lifetime Spectroscopy (PALS), the latest technique for studying the structure of polymers. The most important parameters of PALS technique are orthopositronium lifetime τ_3 (o-Ps) and orthopositronium intensity I_3 (o-Ps), These parameters help us to measuring the free volumes and hole fraction of the polymers, these physical parameters play important role in innovation new polymers. The free volume and holebility ratio measured with the PALS technique as a function of electronic density. The minimum and maximum values of free volume were determined in PMMA and SAN, the minimum and maximum values of holebility ratio were determined in SMA and PMMA respectively.

Keywords: Positron annihilation; Polymers; Spectroscopy; Lifetime
Received: 23 March 2025; **Revised:** 26 May 2025; **Accepted:** 2 June 2025

1. Introduction

In this work, the polymers structures of poly(methyl methacrylate) (PMMA), styrene-*co*-acrylonitrile (SAN) and styrene-*co*-maleic (SMA) have potential uses and applications in wide field. To investigate the free volume and holebility ratio for each polymers formed the aim of this study.

Today, PALS is the newest and most effective method used to measure microscopic size of defects in the molecular structure, Additionally, Positron Doppler Broading Annihilation Radiation (DBAR) is among the methods to obtain information about structural change. The Potential uses of polymers (PMMA, SAN and SMA) in many field. It is important to examine it from a scientific perspective, and the aim of this study were to examine these polymers and to extract their physical properties and parameters like free volume, hole fractions and extracting the density profiles how changes from bulk to surface for each polymer. For this purpose, the latest technique in physics, The PALS [1,2]. To studying and extracting the microscopic defects size, free volume and hole fraction as a function of positron energy dependence. The PALS system use for elastic collision with matter, are very important to investigate the physical properties, thermodynamic and mechanical behavior of polymers molecules. The aim of this study is to determine the nanometric scale defects [3] of the molecules of pure PMMA, SAN and SMA polymers, such as the changes in profiles of free volume and hole fractions from the bulk to the surface, how changes the microscopic defects from bulk to surface. The aim is to examine and extracting free volume and hole fraction rates, which are among the most important factors of the density function, to compare the change rates and to provide opportunities for synthesis in further studies.

The electron is negatively charged (e^-) and the positron is positively charged (e^+). Positron magnetic moment and charge value are equivalent to electron. Other parameter properties are almost the same as electron values. The positron is a member of the lepton family and obeys to Fermi statistics [4], one of the basic characteristics of the positron is that it exist in a weak interactions and softer interactions with materials. A stable positron is very difficult to find in nature. Positrons are obtaining by the decay of weak neutron radioisotopes, giving off gamma energy greater than 1.05 MeV, and can be obtained from ^{22}Na [5], which is cheap and has a half-life of about three years.

Within the material, the positron-electron pair can survive for only a few of a nanosecond before being annihilated. A positron can capture an electron and a bonded structure could be formed before the pair annihilates. This neutral structure is called positronium atom (Ps). Ps is often found in molecular structures. Positronium tends to form in free volume and hole fraction [6-11] within matter. According to different combinations of positron and electron, the Ps atom could exist in two basic levels. The positronium atom is at the single level ($^1S_0$), which were called parapositronium (p-Ps), when the spins of the electron and positron are antiparallel, if the spins are parallel to each other, it is found in the ($^3S_1$) triple level called orthopositronium (o-Ps). The p-Ps atoms make up a quarter of all Ps atoms, while o-Ps atoms make up three quarter of all Ps atoms. The lifetime and

extinction events are different for p-Ps and o-Ps, which are explained by quantum electrodynamics. While the lifetime for free p-Ps annihilated with two photons is 0.125 ns, the lifetime for orthopositronium o-Ps annihilated with three photons is a few ns. The positronium (Ps) atom has almost the same structure and wavelength as the hydrogen atom, and its size is twofold Bohar radius) [12].

2. Experimental Part

The most important parameters of the positron annihilation lifetime spectrometry technique shown in Fig. (1) are the orthopositronium lifetime τ_3 (o-Ps) and orthopositronium intensity I_3 (o-Ps) [13,14], determined by analyzing the positron lifetime spectra. The orthopositronium lifetime and orthopositronium intensity data were taken [15] for each polymers within application positron energy of PMMA, SAN and SMA. Then have been calculated the free volume and hole fraction [14,15] parameters for each of polymers under examination were calculated from the Tao-Eldrup model[18] and the values of radius of free volume and hole fractions are listed in tables (1), (2) and (3). The free volume and hole fraction measured depending on the positron energy [16,17]. In this model, the positronium atom (Ps) is considered or assumed to be in an infinite potential well of radius R of the free volume. The following relationship is obtained from the integration of the positronium atom with the overlapping of the surrounding electron density [18] or electron layer $\delta R=R_0-R$, where R represents the free volume hole diameter as a function of orthopositronium lifetime τ_3 (o-Ps).

$$\tau_3(o-p_s)=\frac{1}{2}\left[1-\frac{R}{\delta R-R}+\frac{1}{2\pi}\sin\frac{2\pi R}{\delta R-R}\right]^{-1} \quad (1)$$

with δR=0.1656nm is represent the electronic density parameter or electron layer. The free volume radius of the infinite well potential could be calculated by using Eq. (1) and could express the free volume value calculated from equation as in below

$$<\upsilon_f(\tau_3)>=4\pi R^3/3 \quad (2)$$

Additionally, orthopositronium intensity I_3 (o-Ps) and orthopositronium free volume are linearly proportional with orthopositronium lifetime, The positronium hole fraction h_{ps} and free volume are linearly proportional as a function of orthopositronium lifetime may expressed [19,20] as in below

$$h_{ps}=CI_3\upsilon_f(t_3) \quad (3)$$

where C is a constant and for polymers its value is 0.0018 Å^{-3}. The calculated free volume radius R, positronium hole fraction and free volume values are tabulated in tables (1), (2) and (3) for PMMA, SAN and SMA, respectively

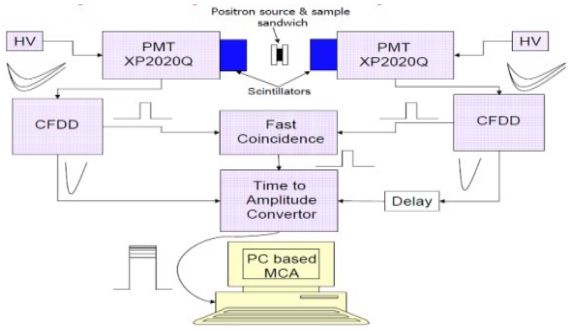

Fig. (1) A schematic diagram of positron annihilation lifetime spectroscopy system

3. Results and Discussion

The longest-lived component, o-Ps lifetime (τ_3) and its intensity (I_3) are obtained from the analysis of the positron lifetime spectra. The o-Ps lifetime can serve as a measure of the free volume size. A positronium (Ps) is considered to have an infinite spherical potential well of radius R. The relation (18) between the radius R and the o-Ps lifetime (τ_3) allows to find the average free volume, in a spherical approximation where $R_0=R+\Delta R$ with ΔR=0.1656nm as an adjustable parameter for a measure of electron layer inside the spherical potential well.

In Fig. (2), the free volume and hole fraction for the PMMA structure are plotted as a function of orthopositronium lifetime τ_3 (o-Ps). The positron energy intensity 3.0-0.3 keV were used to investigate the density gradient profile from the bulk to the surface. The free volume and hole fraction increased when they approached to the surface and were determined as 113.12-89.59 Å^3 and 7.27-3.52, respectively.

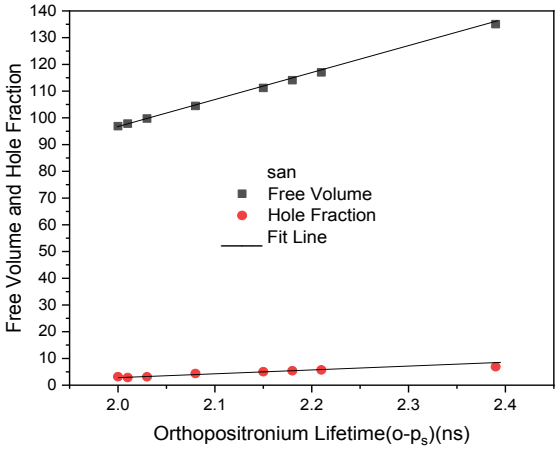

Fig. (2) The Free volume versus τ_3 (o-Ps) for PMMA

In Fig. (3), the free volume and hole fraction for the SAN structure are plotted as a function of orthopositronium lifetime τ_3 (o-Ps). The positron energy intensity 3.0-0.3 keV were used to investigate the density gradient profile from the bulk to the

surface. The free volume and hole fraction increased when they approached to the surface and were determined as 135.04-97.84 Å^3 and 6.88-2.84, respectively.

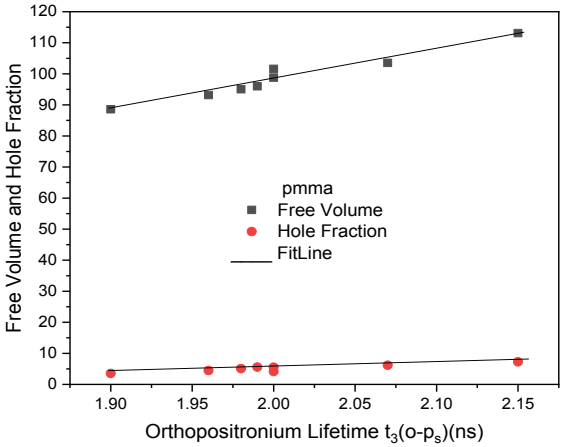

Fig. (3) The Free volume versus τ_3 (o-Ps) for SAN

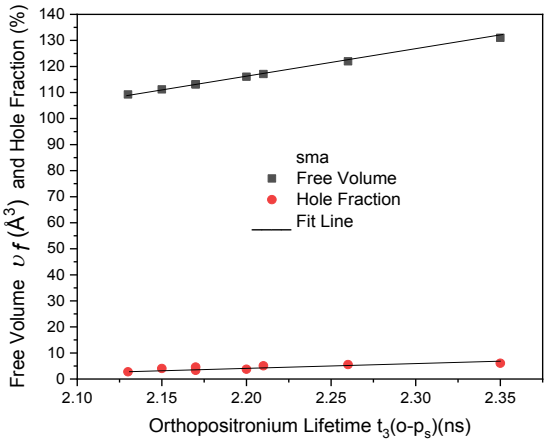

Fig. (4) The Free volume versus τ_3 (o-Ps) for SMA

In Fig. (4), the free volume and hole fraction for the SMA structure are plotted as a function of orthopositronium lifetime τ_3 (o-Ps). The positron energy intensity 3.0-0.3 keV were used to investigate the density gradient profile from the bulk to the surface. The free volume and hole fraction increased when they approached to the surface and were determined as 130.99-109.25 Å^3 and 6.06-2.79, respectively.

In Fig. (5), the hole fraction for the PMMA, SAN and SMA structure are plotted as a function of positron energy intensity 3.0-0.3 keV were used to investigate the gradient profile of hole fraction, as it seems when increase the positron energy intensity the hole fractions decreased in polymers. Figure (6) shows the relation between the orthopositronium intensity I_3 (o-Ps) and positron energy, when increase the positron energy intensity leads to increase the orthopositronium intensity I_3 (o-Ps).

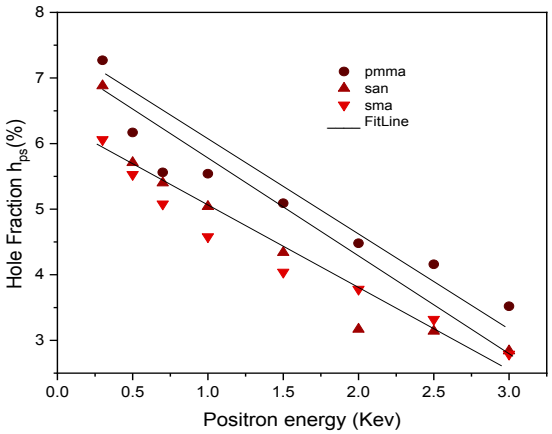

Fig. (5) The hole fraction versus posıtron energy for polymers

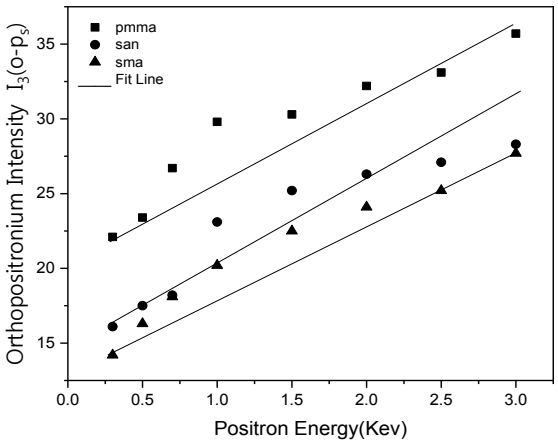

Fig. (6) The I_3 (o-Ps) versus posıtron energy for polymers

In Fig. (7), shows the relation between the orthopositronium lifetime τ_3 (o-Ps) and positron energy, when increase the positron energy leads to decrease the orthopositronium lifetime τ_3 (o-Ps), the physical meaning of this event the electronic density is going to be lesser than interface to surface, electronic density of materials were starting to decrease from interface to surface (electron depth profile). And it were determined that the free volume (***vf***) increasing from interface towards the surface as in Fig. (8).

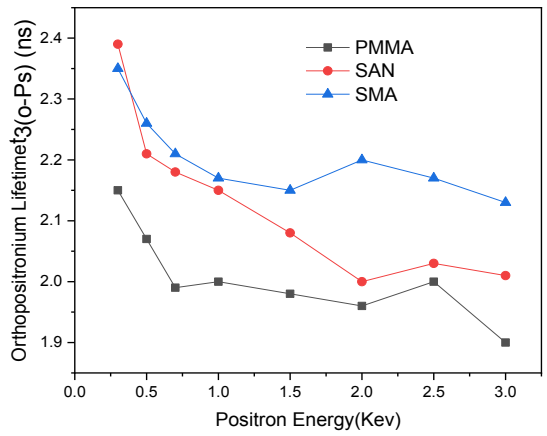

Fig. (7) The Orthopositronium lifetime versus posıtron

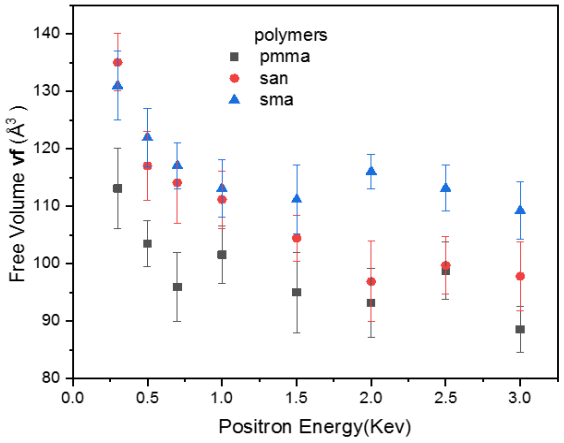

Fig. (8) The free volum versus posıtron energy for polymers PMMA, SAN and SMA

3. Conclusions

In this work, the structure and defect rate of PMMA, SAN and SMA polymers were studied. To know how are change the gradient of free volume and hole fractions from the bulk to the surface in order to extract the interfacial thickness. The parameters orthopositronium lifetime and orthopositronium intensity have been obtained that measured by PALS technique, then had been extracted the free volume radius and hole fraction gradients. It were determined that all three polymers showed an increase in their free volume and hole fraction from the bulk to the surface. This determinations will play a very important role in synthesizing new polymers.

References

[1] Y.C. Jean, P.E. Mallon and D.M. Schrader, **"Principles and Applications of Positron and Positronium Chemistry"**, World Scientific Publishing (NJ, 2003), pp. 1-34, 37-70, 117-137.

[2] S.J. Tao, "Positronium Annihilation in Molecular Substances", *The J. Chem. Phys.*, 56 (1972) 5499-5510.

[3] J.-W. Rhim et al., "Effect of Free Volume on Curcumin Release from Various Polymer-Based Composite Films Analyzed Using Positron Annihilation Lifetime Spectroscopy", *Materials*, 14(19) (2021) 5679.

[4] R. Yasin and S. Kuzeci, "Study of Thermal Effect on Physical Properties of PEG8000/TiO2 Composite Using Positron Annihilation Lifetime Spectroscopy", *Iraqi J. Appl. Phys.*, 19 (2023) 27-32.

[5] M. Eldrup et al., "A Positron-Annihilation Investigation of Defects in Neutron-Irradiated Copper", *Radiat. Effec. Defect S*, 54 (1981) 65-80.

[6] S.K. Sharma and P.K. Pujari, "Role of free volume characteristics of polymer matrix in bulk physical properties of polymer nanocomposites: A review of positron annihilation lifetime studies", *Prog. Polym. Sci.*, 75 (2017) 31-47.

[7] S.K. Sharma et al., "Investigation of nanolevel molecular packing and its role in thermo-mechanical properties of PVA–fMWCNT composites: positron annihilation and small angle X-ray scattering studies", *Phys. Chem. Chem. Phys.*, 16 (2014), 1399-1408.

[8] S.K. Sharma et al., "Structure at Interphase of Poly(vinyl alcohol)–SiC Nanofiber Composite and Its Impact on Mechanical Properties: Positron Annihilation and Small-Angle X-ray Scattering Studies", *Macromolecules*, 48 (2015) 5706-5713.

[9] U. Yahsi et al., "On the Ionic Conductivity of Polymer Electrolytes in Terms of Hole Fraction", *J. Polym. Sci. B: Polym. Phys.*, 46 (2008) 2249-2254.

[10] A. Yumak Yahsi, A. Almashayek and U. Yahsi, "Dielectric relaxation time of PVAc in terms of hole fraction calculated from the theory of Simha-Somcynsky", *Polymer*, 295 (2024) 126753.

[11] F. Sahin-Dinc et al., "The Effect of Hole Fraction on Viscosity in Atactic and Syndiotactic Polystyrenes", *Int. J. Thermophys.*, 36 (2015) 3239-3254.

[12] P. Kirkegaard et al., "Program System for Analyzing Positron Lifetime Spectra and Angular-Correlation Curves", *Computer Phys. Commun.*, 23 (1981) 307-335.

[13] S. Kuzeci et al., "Free – volume analysis of the structural and dielectric properties of PMMA/TeO_2 composites via positron annihiltion lifetime spectroscopy", *J. Alloys Comp.*,1004 (2024) 175938.

[14] S.M. Nuri, S.R. Hasan and H.A. Mohammed, "The Therml Effect of PLA and PLA/Curcumin Composite Properties under Positron Annihilation Lifetime Spectroscopy", *Iraqi J. Sci.*, 62 (2021) 3407-3416.

[15] J. Algers et al., "Free Volume and Density Gradients of Amorphous Polymer Surfaces As Determined by Use of a Pulsed Low-Energy Positron Lifetime Beam", *Macromolecules*, 37 (2004) 4201-4210.
[16] Z. Yu et al., "Molecular weight-dependence of free volume in polystyrene studied by positron annihilation measurements", *J. Polym. Sci. B: Polym. Phys.*, 32 (1994) 2637-2644.
[17] A.U. Kaya et al., "Structural and dielectrical properties of PMMA/TiO_2 composites in terms of free volume defects probed by positron annihilation lifetime spectroscopy", *Polym. Polym. Compos.*, 29 (2020) 107-116.
[18] M. Eldrup, D. Lightbody and J.N. Sherwood, "The temperature dependence of positron lifetimes in solid pivalic acid", *Chem. Phys.*, 63 (1981) 51-58.
[19] D.K. Pradhan, R.N.P. Choudhary and B.K. Samantaray, "Studies of dielectric relaxation and AC conductivity behavior of plasticized polymer nanocomposite electrolytes", *Int. J. Electrochem. Sci.*, 3 (2008) 597-608.
[20] Y.Y. Wang et al., "Positron-Annihilation in Amine-Cured Epoxy Polymers - Pressure-Dependence", *J. Polym. Sci. B: Polym. Phys.*, 28 (1990) 1431-1441.

Polymethylmethacrylate (PMMA)

Table (1) PALS parameters as orthopositronium lifetimes and orthopositronium intensities in terms of low positron energy of polymethylmethacrylate. τ_1 is taken as 125 ps as fixed in all calculation

E (keV) (±0.003)	τ_3 (ns) (±0.01)	I_3 (%) (±0.3)	R (Å) (±0.01)	h_{ps} (%) (±0.11)	vf (Å^3) (±0.11)
3.0	1.90	22.1	2.755	3.52	88.59
2.5	2.00	23.4	2.849	4.16	98.78
2.0	1.96	26.7	2.812	4.48	93.18
1.5	1.98	29.8	2.830	5.09	95.03
1.0	2.00	30.3	2.849	5.54	101.60
0.7	1.99	32.2	2.840	5.56	95.97
0.5	2.07	33.1	2.912	6.17	103.51
0.3	2.15	35.7	2.983	7.27	113.12

Polystyrene-*co*-acrylonitrile (SAN)

Table (2) PALS parameters as orthopositronium lifetimes and orthopositronium intensities in terms of low positron energy of polystyrene-*co*-acrylonitrile. τ_1 is taken as 125 ps as fixed in all calculation

E (keV) (±0.003)	τ_3 (ns) (±0.01)	I_3 (%) (±0.3)	R (Å) (±0.01)	h_{ps} (%) (±0.11)	vf (Å^3) (±0.11)
3.0	2.01	16.1	2.858	2.84	97.84
2.5	2.03	17.5	2.876	3.14	99.72
2.0	2.00	18.2	2.849	3.17	96.90
1.5	2.08	23.1	2.921	4.34	104.46
1.0	2.15	25.2	2.982	5.04	111.18
0.7	2.18	26.3	3.008	5.40	114.10
0.5	2.21	27.1	3.034	5.71	117.03
0.3	2.39	28.3	3.182	6.88	135.04

Polystyrene-*co*-maleic (SMA)

Table (3) PALS parameters as orthopositronium lifetimes and orthopositronium intensities in terms of low positron energy of polystyrene-*co*-maleic. τ_1 is taken as 125 ps as fixed in all calculation

E (keV) (±0.003)	τ_3 (ns) (±0.01)	I_3 (%) (±0.3)	R (Å) (±0.01)	h_{ps} (%) (±0.11)	vf (Å^3) (±0.11)
3.0	2.13	14.2	2.965	2.79	109.25
2.5	2.17	16.3	3.000	3.32	113.13
2.0	2.20	18.1	3.025	3.78	116.06
1.5	2.15	20.2	2.982	4.04	111.18
1.0	2.17	22.5	3.000	4.58	113.13
0.7	2.21	24.1	3.034	5.08	117.09
0.5	2.26	25.2	3.076	5.53	121.97
0.3	2.35	27.7	3.015	6.06	130.99

