Positron Annihilation Spectroscopy Studies In Polymer Blends

Anju Tanwar[1*]

[1*]Department of Physics, M.S.J. College, Bharatpur 321 001, India, E-mail: tanwaranju@gmail.com

*CorrespondingAuthor: - E-mail: tanwaranju@gmail.com

Abstract
Having deep insight into the microstructure, and realizing the correlation between microstructure and properties is very important to the precise construction of high-performance polymeric materials. The promising application in microstructure characterization, much attention has been focused on the effective technique of positron annihilation l spectroscopy (PAS). Positron annihilation lifetime measurements give direct information about the dimension and contents of free-volume holes in amorphous materials. The unique capability of PALS to probe free-volume properties is from the fact that positronium atom is trapped in the atomic-scale holes which have a size ranging from 1 to 10 Å. Positron annihilation spectroscopy (PAS) was performed in polysulfone and poly (methyl methacrylate) blends covering the full range of composition. From the positron results an increase in free volume hole size has been observed which indicates further that there is coalescence of free volumes ofpolysulfone with that of poly(methyl methacrylate) to some extent and phase separation behaviour continues.

1. Introduction

Polymer blends have attracted considerable attention over the past two decades, not only due to its growing industrial application but also for their scientific interest [1]. Among the different physical and chemical properties of polymer blends, miscibility studies have been subject of increasing interest particularly at molecular level. Complete knowledge of the microstructural change at the molecular level is necessary to understand the underlying mechanism of miscibility of blends. However the conventional methods cannot fulfill this need. Positron annihilation has proved to be a new powerful tool to study the microstructural properties of polymers. Many of the macroscopic properties of polymers crucially depend on the microstructure of the subnanometer local free volume holes that arise as a consequence of the irregular molecular packing in these materials. It is now widely accepted that the free volume properties are closely related to polymer chain dynamics which plays an important role on the mechanical, electrical and transport properties of polymers. A complete understanding of the microstructure of free volume in polymers and polymer blends is very important. Most microprobes, such as electron spin resonance (ESR), small angle X-ray diffraction and photochromic fluorescence, can not provide direct information about the microstructure of free volume holes. PALS has emerged as a unique and potent probe for characterizing the free volume properties of polymers [2–8] and polymer blends [9–10].

In recent years, PAS has been successfully used to determine the free-volume, void, and layer properties in polymeric systems. The basic principle of using PAS in polymers is based on the fact that the positron and Ps are preferentially localized in pre-existing defects, including free volume ($\sim 0.1-1$ nm) and voids (>1 nm) in polymeric systems. The annihilation parameters (e.g., positron annihilation lifetime) are directly related to the integrals of positron and electron wave functions.Uses and advancements of PALS in polymer science rely on a good understanding of the fundamental properties of Ps and of molecules and their interactions, the chemical and physical aspects of materials, and advances in instrumentation.

In a polymer matrix thermalized positrons can form positronium (Ps), the bound state that will be localized in free volume holes. The positronium (Ps) atom can be in one of two allowed states : para–positronium (p–Ps), if spins are aligned antiparallel, singlet state, or ortho–positronium (o–Ps), if parallel, triplet state [11]. In PAS of polymers three lifetimes are commonly observed in the lifetime distribution, $\tau_1 \sim 0.15$ ns, which comeswhich comes mostly from the annihilation of p-Ps, $\tau_2 \sim 0.3- 0.5$ ns, from free positron annihilation and $\tau_3 \sim 2$ns from pick – off annihilation of p-Ps. The lifetime τ_3 is related to

the size of the intermolecular spaces i.e. free volume holes in the polymer structures. The lifetime τ_2 is associated with the interactions of positrons with valence or core electrons of the constituent atoms, and τ_1 is close to the intrinsic p-Ps annihilation. The annihilation characteristics of o–Ps reflect the microstructural information of the free volume. The results for o–Ps lifetime (τ_3) and its probability (I_3) are related to the free volume hole size, fraction, and distribution. Free–volume hole sizes, fractions, and distribution in a variety of polymers have been reported using PAS method [12–13]. In polymer blends, some PAS results have been reported [14–15]. Miscibility studies of PEO/PMMA blends have been investigated by many researchers [16–17]. Machado *et. al.* have reported a window of miscibility for PEO/PMMA blends around 20–30 wt % of semi crystalline PEO [17]. Change in free volume has been reported in miscible and immiscible blends [18–19]

Poly (methyl methacrylate) is a transparent thermoplastic material that is often used in place of glass. It has got vast applications including medical sciences. Polysulfone is tough, rigid, high-strength transparent thermoplastic polymer retaining its properties between -100^0C and $+150^0$ C. It is a good membrane material. Its membranes are used in applications like hemodialysis, waste water recovery, food and beverage processing, and gas separation. We have prepared blends of PMMA and PSF. In this paper, we report positron annihilation lifetime spectroscopy (PALS) in polysulfone, poly (methyl methacrylate) and polysulfone / poly (methyl methacrylate) polymer blends.

2. Experimental
Sample preparation
polysulfone supplied by Gharda Chemicals Ltd. Bharuch, Gujarat (India) and poly (methyl methacrylate) or (PMMA) supplied by HiMedia Laboratories Pvt. Ltd., Mumbai (India) were used for the study.

Thin films of PMMA, Polysulfone and polysulfone / poly (methyl methacrylate) blends were prepared by solution cast method. Blends of polysulfone / poly (methyl methacrylate) in the ratio, 10:90, 30:70, 50:50, 70:30, 90:10 were prepared. For preparing blends of polysulphone and PMMA in variable proportions, the granules of PMMA and Polysulfone were dissolved in common solvent i.e. dichloromethane, and stirred thoroughly for a few hours to ensure mixing. The

solution was then put into flat–bottomed Petri dishes floating on mercury. The solvent was allowed to evaporate slowly over a period of 10–12 h. The films (thickness ~ 100 μ m) so obtained were peeled off and dried in vacuum for 24 h in order to ensure the removal of the solvent. The cast films of polysulfone / poly (methyl methacrylate) blends were opaque in the entire composition range.

Positron Annihilation spectroscopy (PAS)
The positron annihilation lifetimes of polymer samples and blends were determined by detecting the prompt γ–ray (1.28 Mev) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ–rays (0.511 Mev). The positron source was sandwiched between two identical stacks of four layers of sample film. The PAL spectra were obtained using conventional fast–fast coincidence spectrometer with a time resolution of 290 ps as monitored by using a ^{60}Co source. PATFIT–88 program [20] was used for discrete term analysis to obtain τ_i (i = 1, 2, 3) and I_i (i = 1, 2, 3) values. Finite term analysis decomposes a PAL spectrum into 2 to 3 terms of negative exponential the longest lifetime ($\tau_3 \approx$ 1–3 ns) is due to ortho–positronium (o–Ps) annihilation. In the current PAL method, we employed the results of o–Ps lifetime to obtain the mean free–volume hole radius by the following semi empirical equation.

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

where τ_3 (o–Ps lifetime) and R (hole radius) are expressed in ns and A^0 respectively. R_0 equals R + ΔR where ΔR is the fitted empirical electron layer thickness (=1.66 A^0). The microvoid volume (V_f) is given as

$$V_f = 4/3\ \pi R^3 \quad ......(2)$$

The hole fraction is empirically determined by

$$f_v = C\left(\frac{4}{3}\pi R^3\right).I_3 \quad ......(3)$$

where I_3 is the intensity (in %) of o–Ps and C is empirically determined to be ~0.0018 [21].

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 [22]. Fast Comptec constant fraction differential discriminators (CFDDs) were used for selecting energy and providing timingsignal independent of the rise time and amplitude of the anode signal from the PM tubes to time to amplitude converter (TAC) (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. Detectionof the 1.27 MeV gamma quanta provides the start signal for a TAC. The stop signal is generated on detection ofone ofthe 0.511 MeV gamma quantas. If 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 spectrometer is shown in figure 1.

3.Results and discussion
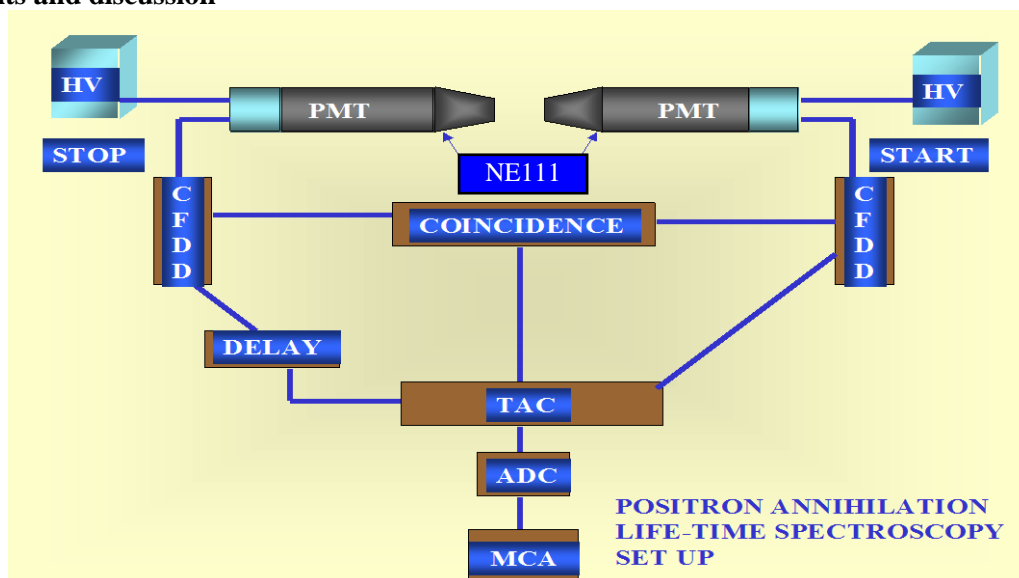
Figure 1:*Positron Annihilation Lifetime Spectroscopy Setup*

PAS measurements
PAS results for the virgin samples and blends are listed in table 1. Our results of virgin samples of PMMA and Polysulfone are consistent with the existing results for polymers [23]. To our knowledge PALS results for polysulfone / poly (methyl methacrylate) for these compositions are not reported in the literature. The longest lifetime τ_3 is due to o–Ps annihilation. The o–Ps lifetime and intensity I_3 are the parameters that vary as functions of the chemical structure of polymers and the composition of polymers. They are used to evaluate the free–volume hole properties. The results of hole radii, hole volume and fractions for Polysulfone, PMMA and polysulfone / poly (methyl methacrylate)blends are reported in table 2.

Table 1 Lifetime and intensities of virgin and blend polymers

PSF/PMMA	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)
0/100	0.159±0.01	0.350±0.01	2.099±0.01	38.5±3.1	43.8±2.9	17.7±0.1
10/90	0.156±0.01	0.360±0.01	2.111±0.01	40.1±2.5	42.1±2.4	17.7±0.1
30/70	0.162±0.01	0.371±0.01	2.124±0.01	44.9±2.5	38.3±2.4	16.7±0.1
50/50	0.149±0.01	0.362±0.01	2.157±0.01	36.5±2.1	45.7±2.0	17.8±0.1
70/30	0.174±0.01	0.401±0.01	2.158±0.01	46.4±2.3	36.2±2.2	17.3±0.1
90/10	0.173±0.01	0.392±0.01	2.176±0.01	40.9±2.4	41.4±2.4	17.7±0.1
100/0	0.179±0.01	0.386±0.01	2.207±0.01	38.7±2.9	42.9±2.8	18.4±0.1

Table 2 PALS parameters τ_3 and I_3 for PSF/PMMA blends and calculated R, V_f and f_v according to eqs (1), (2) and (3)

PSF/PMMA	τ_3 (ns)	I_3 (%)	R (Å)	V_f (Å³)	f_v (%)
0/100	2.099±0.01	17.7±0.1	2.94	106.4	3.38
10/90	2.111±0.01	17.7±0.1	2.95	107.5	3.41
30/70	2.124±0.01	16.7±0.1	2.97	109.7	3.28
50/50	2.157±0.01	17.8±0.1	2.99	111.9	3.55
70/30	2.158±0.01	17.3±0.1	2.99	111.9	3.46
90/10	2.176±0.01	17.7±0.1	3.01	114.2	3.62
100/0	2.207±0.01	18.4±0.1	3.04	117.6	3.88

The hole size results show that PSF has larger size free volume holes in comparison to PMMA. The larger volume of τ_3 in PSF than in PMMA could be interpreted in terms of molecular structure and its packing in the polymer, larger values of V_f and f_v in PSF than in PMMA are due to presence of four aromatic rings in PSF which creates more free space in molecular packing of polymer chains than in PMMA. The local free–volume hole properties of polymers in blends are very important for local packing and segmental arrangements.

The results for the lifetime and intensity of o–Ps, τ_3 and I_3 as a function of weight percent of PSF in blends are shown in figure 2. Free volume hole radii, volume and fractions as calculated using eqs 1, 2 and 3 in a spherical hole model are shown in figure 3. The variation of the o–Ps lifetime τ_3 in the blend with increasing percentage of PSF as shown in figure 2 increases, with increasing PSF concentration, suggesting that the Ps cavity becomes larger as the PSF concentration is increased.
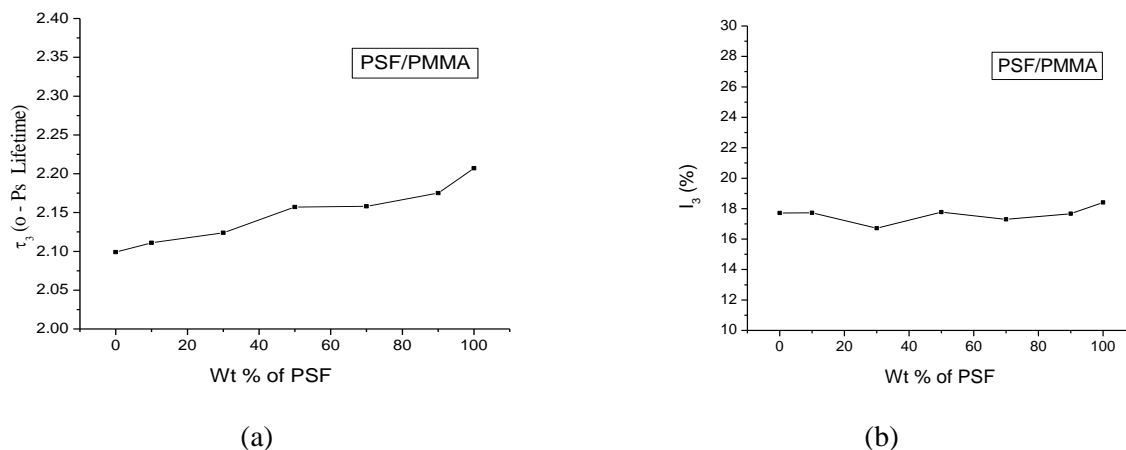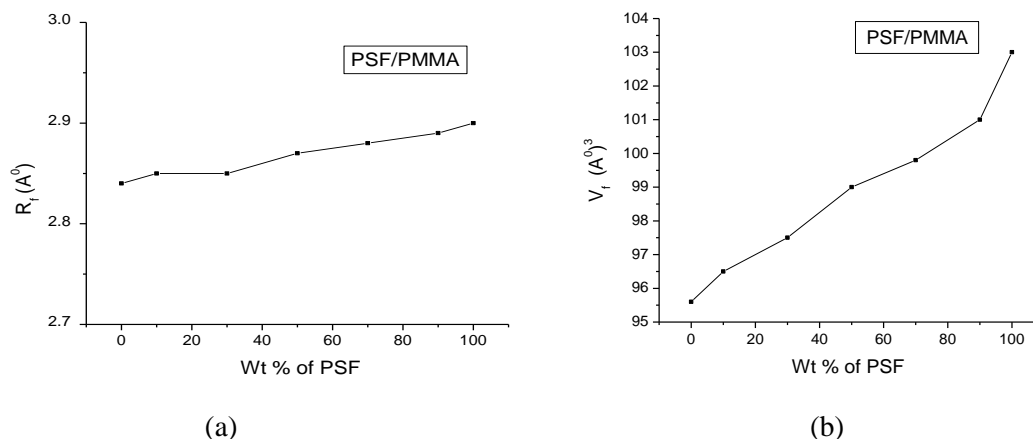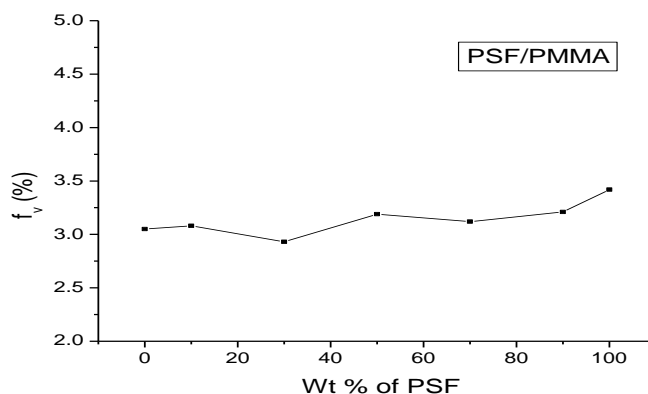

(a)   (b)

Figure 2. o–Ps lifetimes and intensities of PSF/PMMA blends vs wt % of PSF.

(a)   (b)

(c)

Figure 3. Hole radius (R_f), hole volume (V_f) and fractions of free volume in PSF/PMMA blends vs wt % of PSF.

From figure 3 we find that R increases almost linearly with increasing concentration of PSF in the blends. Increase in the free volume indicates immiscibility in the blends. In contrast to the variation of the lifetime, the o–Ps intensity I_3 exhibits a complex behaviour. Slight decrease in I_3 values for corresponding increase in τ_3 values may have resulted from agglomeration of free volume holes. Figure 3b shows increase in mean free volume (V_f) of the free volume holes in PSF/PMMA blends with increasing composition of PSF in the blends. This behaviour suggests the formation of immiscible blends for the compositions investigated. Machado et. al. have observed decrease in mean free volume (V_f) in PMMA/PEO polymer blends with increasing PEO concentration, up to a limit value near 20–30 wt % of PEO forming miscible blend in this interval [17]. They found window of miscibility around 20–30 wt % of PEO. However no window of miscibility has been observed for PSF/PMMA blends.

Figure 3c shows the variation of fractional free volume, f_v, in the blends, which is complex in nature. Complicated variation of f_v has been reported for the immiscible blends [23]. The complicated variation of free–volume hole fractions in immiscible blends observed by PALS technique is a result of the high sensitivity of the o–Ps atom not only to free–volume holes but also to any interfacial spaces, such as those created between boundaries of two phases. A complicated variation of f_v in PSF/PMMA immiscible blends results from the trapping and detrapping of Ps between free–volume holes and interface. It has been postulated that I_3 value is a measure of the crystallinity in the sample and that, in a 100 %

crystalline polymer, the o–Ps formation probability approaches zero [16]. I_3 values for the PSF/PMMA blends are non zero indicating amorphous nature of blends. Amorphous nature of blends is also confirmed by XRD measurements of the samples.

4. Conclusion

Analysis of PALS results for polysulfone / poly (methyl methacrylate) blends shows change in free volume with varying composition of PSF in the blends. Increased free volume has been observed in the blends. The PAS results indicate that polysulfone / poly (methyl methacrylate)blends are immiscible. PAS techniqueis very helpful in the microstructural analysis of polymeric systems. These studies will help in using these blends in various applications.

References
1. Utracki L A (1989) Polymer alloys and Blends, Hanser, Munich
2. Jean Y C (1990) Microchem. J. 42:72
3. Maurer F H J, Schmidt M (2000) Red. Phys. Chem. 58:509
4. Fang J, Tanaka K, Kita H, Okamoto K, Ito Y (2000) J. Polym. Science : Part B : Polymer Physics 38:1123
5. Dlubek G, Stejny J, Lupke T, Bamford D, Petters K, Hubner C, Alam M A, Hill M J

(2002) J. Polym. Sci. : Part B : Polym. Phy. 40:65

6. Dlubek G, Pionteck J, Kilburn D (2004) Macromol. Chem. Phys. 205:500

7. Kansy J, Consolati G, Dauwe C (2000) Rad. Phy. Chem. 58:427

8. Bartos J, Kristiak J (1999) J. Phys :Condens. Matter 11:A371

9. Chen Z Q, Uedono A, Suzuki T, He J S (2003) J. of Radioanalytical and Nuclear Chemistry 255:291

10. Felix M V, Consolatia G, Velazqueq R, Castano V M (2006) Polymer 47:265

11. Scharader D M, Jean Y C (1998) Eds. Positron and Positronium Chemistry, Elsevier : Amsterdam

12. Dlubek C, Lupke T, Fretwell H M, Alam M A, Wutzer A, Radush H J (1998) Acta Polymer 49:236

13. Wate S, Acharya N K, Bhahada K C, Vijay Y K, Tripathi A, Avasthi D K, Das D, Ghughre S (2005) Rad. Phy. Chem. 73:296

14. Chen Z Q, Uedeno A, Li Y Y, He J. S. (2002) Jpn. J. Appl. Phys. 41:2146

15. Kobayashi Y, Wang C L, Hirata K (1998) Physical Review B 58:5384

16. Wastlund C, Maurer F H J (1997) Macromolecules 30:5870

17. Machado J S, Silva G G, Soares L S (2000) J. Polym. Sci. : Part B : Polym. Phys. 38:1045

18. Hill A S, Zipper M D, Tant M R, Stack G M, Jorden T C and Shuttz A R (1996) J. Phys :Condens Matter 8:3811

19. Ravikumar H B, Ranganathaiah C, Kumaraswamy G N, Thamos S (2005) Polymer 46:2372

20. Kirkegaard P, Eldrup M (1989) Riso National Laboratory, Rosklide, Denmark :81

21. Yang H, Jean Y L (1997) Materials Science Forum 255–257:40

22. Sen P, *Positron and Positronium Chemistry*, Ed. Y. C. Jean, World Scientific (1990) 109.

23. Suzuki T, Shunquing He, Shantarovich V, Kando K, Hamada B, Masto M, Ma L, Ito Y (2003) Rad. Phys. Chem. 66:161

24. Liu J, Jean Y C, Yang H (1995) Macromolecules 28:5774Yang H, Jean Y L (1997) Materials Science Forum 255–257:40