STUDY OF FREE VOLUME IN POLYMER BLENDS BY PALS

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Abstract

Blends of polysulphone (PSF) and poly (methylmethacrylate) (PMMA) have been prepared by using solution cast technique. The change in free volume in the blends of polysulphone and poly (methylmethacrylate) is characterized by Positron Annihilation Lifetime measurements. Here we are showing the change in free volume density in the blends. The increase in intensity (I_3) component in blend of PSF and PMMA shows the increase in free volume density. Optical micrographs of the blends have been taken to get an insight of the morphology of the blends. The resulting blends of PMMA and PSF are found to be of immiscible category.

Keywords: [Positron Lifetime, Free volume, Immiscible blend, Optical micrograph]

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1. Introduction:

Positron annihilation lifetime spectroscopy (PALS) has been widely applied to study vacancies in metals and intermolecular spaces in polymers. It has emerged as a powerful tool for measuring the size, number and size distribution of free volume holes in polymers [1-4]. In a polymer matrix thermalized positrons can form positronium (Ps) that will be localized in free volume holes. There are two ground states of Ps, Para-positronium (p-Ps), where the spins are antiparallel, has an intrinsic self annihilation lifetime of 125 ps, decaying into two gamma rays of .511 Mev. Ortho-positronium (o-Ps), with parallel spin orientation, annihilates into three gamma rays with an intrinsic lifetime of 142 ns in vacuum. O-Ps and p-Ps are formed normally in the ratio of 3:1[5].

The annihilation characteristics of ortho positronium (o-Ps) reflect the microstructural information of the free volume. The lifetime and intensity of this component can be translated into hole size and density of holes [6]. The annihilation of o-Ps in the spherical free volume hole is described by simple quantum mechanical model of spherical potential well with an electron layer thickness of R. The semi empirical relation between radius of the free volume hole R and o-Ps lifetime is given by:

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

Where τ_3 and R (hole radius) are expressed in ns and A^0, respectively. R_0 equals $R+\Delta R$ where ΔR is the fitted empirical layer thickness (1.66 A^0) . The microvoid volume (V_f) is given by $4/3\pi R^3$.[7]
 Kobayashi *et al.* concluded that I_3 is proportional to the concentration of free volume cavities. The Ps intensity is influenced by many factors, such as the structure of the molecules, the number of intermolecular spaces, the chemical composition, the degree of polymerization, and radiation effects [8]

Chen et al observed irradiation effects in polycarbonate by PALS [9]. They studied the temperature dependence of the Ps annihilation parameter and found a sharp decrease in o-Ps intensity at approximately 100 K. Dlubek et al have used PALS technique for studying inter diffusion in blends of chemically different polymers (10). Wate et al. 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 [11].

Polymer blends provide many useful properties which combine the properties of individual components. They can exhibit higher performance at a lower cost. Therefore they have been attracting increasing attention in recent years [12]. Blends can be of miscible or immiscible category depending on the individual polymers used. We have prepared blends of polysulfone and polymethylmethacrylate with varying composition as 90 : 10, 80 : 20 and 60 : 40. Blend membranes have been prepared by solution cast technique. Positron annihilation lifetime measurements have been done for polysulfone, polymethylmethacrylate and their blends. Here we are reporting the change in free volume density in the blends of PSF and PMMA.

2. Experimental:

The lifetime measurements have been performed using a conventional slow- fast coincidence spectrometer with plastic scintillation crystals having a time resolution about 270 ps. A Na^{22} source (20μci) deposited on rhodium foil was sandwitched between the stacks of 4 layers of polymer blends of PSF and PMMA. Measurements have been done in air at room temperature. BaF_2 scintilators coupled to Philips XP 2020 photo multipliers were used in fast timing. BaF_2 is attractive due to its high atomic number and relative high density of 4.88 g/ cm^3 which were favorable properties for high photo peak detection efficiency for gamma rays. ORTEC constant Fraction differential discriminators were used for selecting energy and providing time signals to Time to amplitude converter. The time resolution (FWHM) of prompt spectra was 400 ps.   The lifetime of positron is measured by observing the time difference between two gamma quanta signaling the birth and death of the positron. The birth signal is a gamma ray emmited simultaneously with the positron from the source nucleus (1.28 Mev for the Na^{22} isotope) and the death signal is the 0.511 Mev annihilation quanta. Optical micrographs were taken by optical microscope at magnification of 40 x 10.

3.Results and discussion:
 (a) Positron annihilation lifetime spectroscopy
In the PALS of polymers, three lifetimes are commonly observed in the lifetime distribution $\tau_1 \sim 0.15$ ns, which 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 o-Ps. The lifetime τ_3 is related to the size of the intermolecular spaces 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). In the present investigation for discrete term analysis the PATFIT-88 [13] program was used. The positron annihilation lifetime data is given in table 1. The component τ_2, attributed to free annihilation of positrons is 378 ps for pure PSF and 376 ps for pure PMMA, which matches well with the reported values for polymers (14). We observed that there was not much change in the values of this component for the blends of PSF and PMMA. There is no effect of blending on τ_1 values. The long lived component τ_3, which is very sensitive to structural changes in the polymer, directly correlates to the free volume hole size. The intensity of this component contains information about free volume hole concentration. In pure PSF, the o-Ps lifetime τ_3 is 1684 ps and its intensity is 12% while in PMMA, the o-Ps lifetime is 1700 ps but intensity is 8%. In PSF/PMMA blends the lifetime τ_3 is between that of PSF and PMMA. We find that as content of PMMA goes on increasing in PSF/PMMA blend the intensity goes on increasing. This result suggests that the free volume properties have changed as a result of blending PSF with PMMA. The optical micrographs clearly shows that blend of PSF/PMMA are of immiscible category having separate phases. Therefore o-Ps will form and annihilate in both the phases. Increase in the I_3 in the blends of PSF/PMMA is attributed to increase in free volume density in the blends.

Sample PSF+PMMA	τ_2 (ps)	I_2 %	τ_1(ps)	I_1 %	τ_3 (ps)	I_3 %
100%+ 0%	378	59.10	150	28.60	1684	12.29
(90%+10%)	380	57.10	150	28.60	1680	14.29
(80%+20%)	382	57.10	150	24.60	1676	18.29
(60%+40%)	389	53.10	150	26.60	1668	20.29
0%+100%	376	61.1	147	30.60	1700	8.29

Table1

(b) Morphology of the blends

Micrographs taken by optical microscope of blends of PSF/PMMA are shown in figure 1. As seen in the figure 1, blend 90:20 i.e. PSF is 90 % and PMMA is 20%, we are showing that there is not a single phase instead PMMA separates from PSF into spherical blocks.
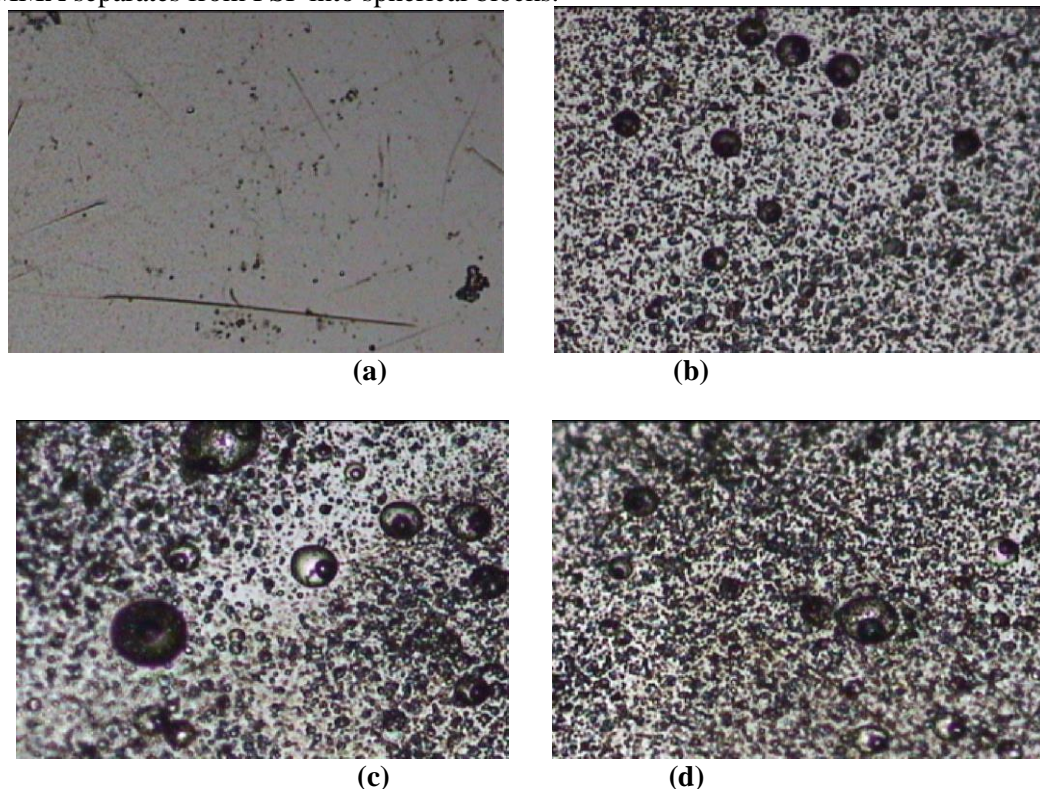

(a)   **(b)**

(c)   **(d)**

Figure 1. Optical micrographs of PSF / PMMA blends (a) 100:0 (b) 90 : 10 (c) 80 :20 (d) 60 :40

In the blend PSF and PMMA are phase separated. As we go on increasing the amount of PMMA in the blend the number of spherical blobs goes on increasing. The micrographs of blends,80:20 and 60:40 taken by optical microscope clearly depicts the same, as it is clear from morphology of blends that PSF and PMMA are forming immiscible blends. Fayt et al for the polystyrene and polybutadiene blends have reported earlier [15].

4. Conclusion:

1. It is concluded from the above analysis of positron lifetime in PSF/PMMA   blends that on increasing the concentration of PMMA in the host PSF the freee volume increases, i.e confirms from third lifetime (τ_3) component and intensity componet(I_3).

2. Increase in I_3 shows increase in free volume density in the blends. It seems that more voids have been created at the phase boundaries of PSF and PMMA in PSF/PMMA blends, which are responsible for increase in o-Ps intensity.

3. Optical micrographs clearly suggest that blends of PSF/PMMA in the ratio 90:10, 80:20 and 60:40 are immiscible.

References

1. Jean Y C, Microchem.J.42 (1990) 72
2. Aly Hasan Emad, American Journal of Applied Sciences 8(2) (2011)147-155
3. Hughes D J etal, Journal of Physics: Conference Series,443(2013)012045
4. Han Xiaobing , Nanomaterials 12 (2022)4161
5. Positron and Positronium Chemistry, ed. D.M. Schrader and Y.C. Jean, Elsevier, Amsterdam, 1998
6. Ferreira Marques M.F. et al, Rad.Phys. Chem. 68 (2003) 573-576.
7. Kumar R., et al, Rad. Measurements 36(2003) 151-154
8. Kobayashi Y., et al, Macromolecules 22(1989) 2302
9. Chen Z Q, et al Jpn. J. Appl. Phys. Vol. 40(2001) 5036-5040
10. Dlubek G, et al, Rad. Phys. Chem. 68 (2003) 369-373
11. Wate S,et al, Rad. Phys. Chem. 73 (2005) 296-301
12. Utracki L A, Polymer Alloys and Blends (Hanser,Munich 1989)
13. Kirkegaard P and Eldrup M,Riso National Laboratory, Rosklide, Denmark,1989,81-92
14. 14.Suzuki T,et al, Rad. Phys. Chem. 66 (2003) 161-166
15. 15. Fayt R,et al J. Polym. Sci,Polym . Chem. Ed. 23 (1985) 337