PLT and DBAR Investigations on MPDMAPP Doped PVA/PVP Blend

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Abstract. Poly(vinylalcohol) (PVA)/Poly(vinylpyrrolidone) (PVP) blend films, doped with chalcone derivative (1-(4-methylphenyl)-3-(4-N,N,dimethylaminophenyl)-2-propen-1-one) (MPDMAPP) from 0.025 wt% up to 1 wt% were prepared using solution casting technique. The o-Ps lifetime $\tau_3$ is found to change little, from 1.61 ns at 0.025 wt% dopant concentration to 1.63 ns at 0.5 wt% dopant level, but drops to 1.4 ns at 1 wt% dopant concentration, indicating the onset of phase separation. The S-parameter of DBAR was found to be linearly related to the ortho-Positronium ($o$-Ps) intensity $I_o$. The S-parameter drops significantly from 0.1 wt% up to 1 wt% doping concentration. This is supported by the XRD scans.

1. Introduction
The blending of different polymers, and doping polymers with organic molecules, are strategic routes to improve the performance of polymeric materials [1-2]. The properties of polymeric blends are mainly dependent on the characteristics of the parent homo-polymers, the blend composition and the polymer-polymer miscibility [3]. Poly(vinylalcohol) (PVA) and poly(vinylpyrrolidone) (PVP) are perfectly compatible and miscible polymers; via the hydrogen bond interactions between the carbonyl groups of PVP and hydroxyl groups of PVA in the amorphous regions of the blend [4-5]. The chalcone derivatives are organic materials which have attracted attention due to their excellent blue-green light transmittance [6-7]. They are typically polarizable molecules, consisting of $\pi$-conjugated system with donor and acceptor groups.

The main objective of this study is to measure the $o$-Ps lifetime $\tau_3$ and calculate the bulk lifetime $\tau_m$, mean lifetime $\tau_{m_0}$, positron trapping rate $\kappa$ and S-parameter in (1-(4-methylphenyl)-3-(4-N,N,dimethylaminophenyl)-2-propen-1-one) (MPDMAPP) doped PVA/PVP (50:50) blend using Positron Lifetime Technique (PLT) and Doppler Broadening of Annihilation Radiation (DBAR) technique. In molecular media including polymers, the ortho-Positronium ($o$-Ps) localizes (gets...
trapped) in the free volume holes and there is a finite probability that the positron of $\alpha$-Ps bound state may annihilate with a molecular electron of opposite spin, rather than its bound partner [8]. It is known that the positrons are selectively trapped by vacancy type defects, micro-voids, negatively charged ions and radicals. The chromophore dopants in polymers are trapping sites for the positrons, which are created as a consequence of spatially localized dopant ions. This creates lattice distortion, and negatively charged domains that localises the positrons [9-13]. The evolution of defects and positron trapping rates in chalcone chromophore doped miscible blend systems remains unexplored, to the best of our knowledge. DBAR measurements on the other hand can provide information about the polar groups and chemical surrounding of nanoholes in polymers, and helps to investigate the local chemical environment around the positron trapping sites.

2. Experimental

The films of PVA/PVP (50%:50%) blend, doped with MPDMAPP in different concentrations were prepared by solvent casting method using DMF as solvent, as explained in our earlier papers [7, 10]. The details of positron lifetime set up are explained elsewhere [10]. The energy spectrum is recorded using a high purity Germanium (HPGe) detector having resolution of 1.4 keV at 662 keV photopeak of $^{137}$Cs. The width and shape of the 511 keV annihilation line yields the information about the momentum distribution of electrons with which the positrons annihilate. The $S$ and $W$ parameters were obtained by fraction of the counts which appeared at 0 to 4x10$^{-3}$ m.e and 15 to 30x10$^{-3}$ m.e respectively from the centre to the total counts for the annihilation peak. XRD studies were carried out using Rigaku Miniflex-II benchtop X-ray diffractometer with Copper $K_{\alpha}$ radiation of wavelength $\lambda=0.15406$ nm, with graphite monochromator.

3. Results and Discussion

The measured PLT spectra were resolved into three components. The first life time component ($\tau_1, I_1$) is attributed to the self-annihilation of $p$-Ps and the free annihilation of positrons in the bulk. The intermediate lifetime component $\tau_2$, having intensity $I_2$, is considered to be associated with annihilation of positrons trapped by defects present in the crystalline regions and positrons trapped in the crystalline-amorphous interface regions of the polymeric material.

![Figure 1](image_url). Positron lifetime parameters as a function of MPDMAPP doping concentration in PVA/PVP (50:50) blend
The $\phi$-Ps lifetime ($\tau_3$) is a measure of the size of free-volume holes (in the amorphous regions of the polymer). The intensity ($I_3$) is a measure of $\phi$s formation probability, and not the concentration of free volume holes. From Fig 1, we notice that $\tau_3$ remains constant at 1.6 ns from 0.025 wt% doping level (DL) up to 0.5 wt% DL. It however decreases significantly to 1.4 ns at 1 wt% DL. The chalcone MPDMAPP contains methyl group on one side and dimethyl amino group on the other side, the C$_6$H$_4$–N(CH$_3$)$_2$ group acting as donor site due to its strong mesomeric electron releasing behaviour. On the other hand, the methyl group attached to the phenyl ring containing CO group, i.e. CO–C$_6$H$_4$–CH$_3$ acts as an acceptor group. The lone pair of nitrogen in the donor is transferred to the acceptor group to form a highly polar charge transfer state and when such the aromatic compounds are added to polymers, the electrons can be scavenged by these aromatic compounds, mainly because of the CTCs (defects) which are expected to trap the positrons. By accepting two-state positron trapping model [1, 9, 13], the numerical parameters of positron trapping (mean lifetime $\tau_m$, bulk lifetime $\tau_b$ and positron trapping rate $\kappa$) can be calculated using equations (1), (2), and (3).

$$\tau_m = \frac{(I_1 + I_2)}{(\tau_1 + \tau_2)}$$  \hspace{1cm} (1)

$$\tau_b = \frac{(\tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3)}{(I_1 + I_2 + I_3)}$$  \hspace{1cm} (2)

$$\kappa = \left[1 - \frac{1}{\tau_1 / \tau_b}\right]$$  \hspace{1cm} (3)

Figure 2. Variation of bulk lifetime $\tau_b$, mean lifetime $\tau_m$, positron trapping rate $\kappa$ and S-parameter as a function of MPDMAPP doping concentration in PVA/PVP (50:50) blend.

The Fig. 2 shows the variations of bulk lifetime $\tau_b$, mean lifetime $\tau_m$, positron trapping rate $\kappa$ and S-parameter as a function of MPDMAPP doping concentration in PVA/PVP (50:50) blend. The first component $\tau_1$ can be an average due to both the bulk positron lifetime ($\tau_b$) and the Bloch state residence time ($\tau_n$), as a result of which, $\tau_1 < \tau_b$ [13]. It may also be expected that the OH group of PVA should trap the positrons. This is clear evidence of positron trapping at the polar groups and suggests that the positron can act as a sensitive chemical probe of polar structures in chromophore doped polymers. One may expect the negatively charged parts of polar groups in molecular substances to act as trapping centers as well [1].

Figure 3. Variation of o-Ps intensity $I_3$ with S-parameter in MPDMAPP doped PVA/PVP (50:50) blend

Figure 4. XRD patterns of MPDMAPP doped PVA/PVP (50:50) blends
The $S$-parameter is 0.543 for the sample with 0.5 wt% MPDMAPP in PVA/PVP blend. The variation of $o$-Ps intensity relative to the $S$-parameter shows a linear relationship as shown in Fig. 3. The initial trend can be explained as the partial occupation of the larger free-volume holes of by the doping species, thereby inhibiting $o$-Ps formation for highest dopant concentration. The $o$-Ps lifetime $\tau_5$ and the positron lifetime $\tau_2$ correspond to Ps and positron trapping in different regions of the polymeric material. The lifetime $\tau_5$ corresponds to pick-off annihilation of Ps trapped in the constraint free amorphous regions of the polymeric material. However, the lifetime $\tau_2$ comprises of contributions from positrons trapped in micro-voids of the crystalline region as well as a constrained region of the amorphous zone (constrained by the crystalline areas) [4, 14]. The XRD patterns of MPDMAPP doped PVA/PVP blend films are shown in Fig. 4. It is observed from the figure that the XRD patterns of the films reveals a dominant amorphous nature at low dopant concentration, and manifests the semicrystalline nature at moderate and high concentration of the dopant. There is a sudden drop in $o$-Ps lifetime $\tau_5$ and intensity $I_3$ at 1 wt% doping level, due to aggregation of dopant in the amorphous regions. This results in increase in crystallinity of the sample.

4. Conclusions
The PLT results of the prepared MPDMAPP doped PVA/PVP blend films shows that the intermediate lifetime component $\tau_2$, with intensity $I_2$ are considered to be associated with the annihilation of positrons trapped by defects present in the crystalline regions or trapped at the crystalline-amorphous interface regions. At low dopant concentrations, there is molecular level homogeneous distribution of dopant. The $o$-Ps intensity $I_3$ varies in a manner similar to the $S$-parameter of DBS spectrum. Positron trapping rates of the MPDMAPP doped blend were calculated. Distortions induced by aggregation of dopant (at higher doping) results in increase in trapping rate up to 0.5 wt% dopant concentration.

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