

Study of Polyaniline Polyacrylamide Composites by Positron Annihilation Technique

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ABSTRACT: Polyaniline doped with nonoxidizing Bronsted acids is recognized as a conducting material, as its electrical conductivity changes with percentage of doping. In the present work, different percentages of doped polyaniline were blended with polyacrylamide and their electrical conductivities as well as the positron annihilation lifetimes were measured. Analysis of data yielded three lifetime components. It was observed that the value of the short lifetime

component remained constant for doping concentration, whereas that of the intermediate component τ_2 decreased. The relative intensity pertaining to τ_2 , however, increased with the increase in doped PANI concentration. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 930–933, 2003

Key words: conducting polymer; polyaniline; composites

INTRODUCTION

Polyaniline attracts considerable interest as a conducting material in its doped state (protonated PANI) due to the inexpensiveness of aniline and because protonated PANI can be easily synthesized. The wide range of associated electrical, electrochemical, and optical properties, coupled with excellent environmental stability of its emeraldine base and emeraldine salt form, make PANI potentially attractive for a variety of applications despite its brittleness and lack of processibility.^{1–4}

To render this material useful, it is desirable to remove these drawbacks and make PANI processible. The present work is aimed at preparing a protonated composite PANI-based composite blend with another insulating polymer, polyacrylamide (PAM).

Positron annihilation lifetime (PAL) in a solid is determined not only by the electron density in its bulk and lattice structure but also by the existing defects such as cation vacancies that can trap positron and give rise to a longer lifetime component.^{5,6} Peng et al.⁷ correlated positron annihilation data with the conductivity obtained for different protonation levels in PANI. The present work is aimed at investigating the positron lifetimes as a function of doping concentration of protonated PANI in the blend.

EXPERIMENTAL

Materials

For synthesis of protonated PANI on the PAM base, we used PAM (BDH, MW 5,000,000), aniline (E. Merck), ammonium peroxydisulphate (E. Merck, Bombay, India), and hydrochloric acid (International Chemicals, Calcutta, India).

PAM (2 g) was dissolved in 200 ml water; ammonium peroxydisulphate (aniline : oxidant = 1 : 1.5) was added and thoroughly mixed. PAM films were cast on previously weighed glass plates and dried under vacuum at 50°C for 48 h until they attained constant weight. These films were exposed to HCl and then to aniline vapor and finally dried at 75°C under vacuum to remove excess aniline. The time of exposure over aniline varied to vary the polyaniline content of the composite. The films having low percentage of polyaniline were translucent but their opacity was seen to increase with an increase in the percentage of aniline.

Positron annihilation setup

The PAL measurements at room temperature were carried out with a 4 μCi ²²Na positron source, sandwiched between two identical pellets of blended PANI. The sandwich was then placed in between two ultrafast BaF₂ scintillators (2.5 cm diameter and 2.5 cm thick) coupled to two XP2020Q photomultiplier tubes. These scintillation counters grafted into a slow–fast coincidence assembly constituted the PAL coincidence spectrometer. A time resolution of 190 ps was

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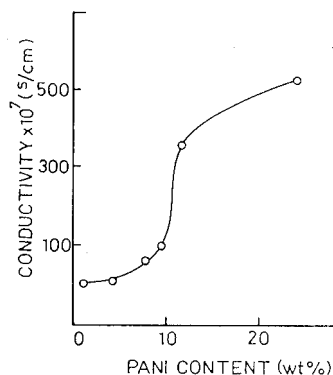


Figure 1 Variation of conductivity as a function of doped PANI in different blend systems.

achieved in this setup. Not less than 0.5 million total coincidence counts were recorded in each of the spectra. The lifetime data were analyzed by using the computer program PATFIT-88.⁸

RESULTS AND DISCUSSION

Five different sets of samples having various percentages (viz., 1.3, 4.5, 8, 11.8, and 24) of protonated PANI blended with PAM were subjected to PAL studies. The resistivity of these samples were measured by employing the standard four-probe method. Figure 1 shows dependence of the results of conductivity on different blend compositions and Figure 2 shows the log of conductivity versus blend composition. It was seen that the conductivity increased from 1.6×10^{-8} to 3.6×10^{-5} mho up to 11.8% of protonated PANI, but attained a nearly constant value for higher percentages. The classical percolation theory^{9,10} predicts a percolation threshold of 16% for spherical conducting particles dispersed in an insulating matrix. The value of percolation threshold ($\approx 12\%$) obtained in the present work was somewhat lower but was still large enough, indicating poor dispersion of PANI in the PAM matrix. Similar high values of percolation

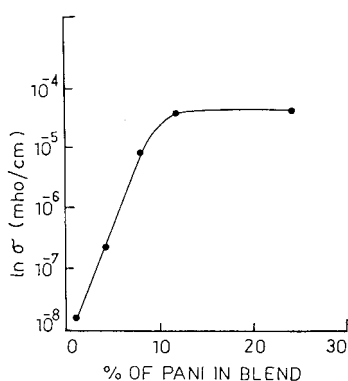


Figure 2 Variation of conductivity plotted on a log-scale as a function of doped PANI in different blend systems.

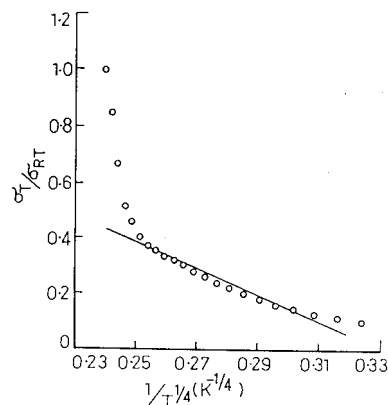


Figure 3 Variation of conductivity as a function of temperature for the sample having 11.8% PANI in the blend.

threshold were not uncommon and were reported, for example, by Hotta et al.¹¹ for polythiophenes/polystyrene composites.

That the degree of dispersion had an important influence on the percolation threshold is quite well known. Wang et al.^{12,13} reported percolation threshold lower than 15% for polypyrrole (PPy)/polyvinyl methyl ketone (PVMK) and PPy/PC systems and attributed this to better dispersion of PPy in the matrix polymer. The increased homogeneity observed for the PPy/PC system is due to H bonding between the carbonyl group of polycarbonate and the —NH group of polypyrrole. Similar results were observed for poly(*N*-methyl pyrrole)/polycarbonates and PPy/poly (*n*-vinyl carbazole).^{14,15} Lefrant and coworkers¹⁶ obtained a low-percolation threshold for PPy/PVA composites and reported this to be due to good dispersion.

Many blend systems show a sharp percolation threshold. For comparison, we reproduced a figure (Fig. 4) from Machado et al.¹⁷ along with our experimental results (curve F, Fig. 4). As can be seen, curve A for PA/low-density polyethylene (LDPE) blend shows a sharp percolation threshold at a very low volume fraction, which has been attributed to the fact that polyacetylene is incorporated only in the amorphous regions of the LDPE matrix. Curve C (Fig. 4) and curve E (Fig. 4) show broadened percolation at higher loadings. Machado et al. ascribed this behavior to the development of a nonequilibrium morphology. Curves B and D (Fig. 4) are for poly(methyl methacrylate) (PMMA)/graphite systems with PMMA matrices of different molecular weights. The percolation threshold observed for the present system (curve F, Fig. 4) is rather high and is due to poor dispersion of PANI in PAM, resulting in larger domains. This is consistent with the observations of Wang et al.,¹³ who attributed lower percolation threshold to better dispersion of the conducting component in the matrix. The concentration dependence of PANI-PAM com-

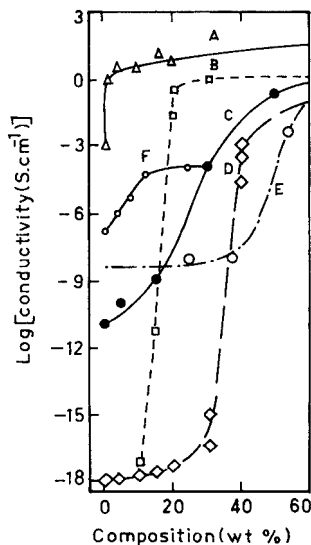


Figure 4 Conductivity as a function of composition for some composite systems: (A) PA/LDPE, (B) Graphite/PMMA, (C) Polyparaphynylene vinyl/Acrylamide, (D) Graphite/PMMA, (E) Phthalocyanine/Kevlar, (F) Present system.

posites observed conforms to the model of phase-segregated metallic domains (PANI) in an insulating matrix (PAM) proposed recently.¹⁸

The temperature dependence of PANI–PAM blends are shown in Figure 3 and follows the relation¹⁹

$$\sigma(T) = \sigma_0 \exp[(T_0/T)^\gamma] \quad (1)$$

with $\gamma = 1/4$ and corresponds to variable range-hopping mode of transport among exponentially localized states. This is in agreement with the report of Salaneck et al.²⁰ showing that the conduction mechanism of PANI conforms to variable range-hopping mode.

Each PAL spectra of the PANI–PAM blends was resolved into three components; the short component, τ_1 , is due to the free annihilation of the positron^{21,22} and the intermediate component, τ_2 , is due to the partial trapping of positrons at the vacancy defects. The longer third component, τ_3 , having values lying between 1.3 and 2 ns, is ascribed to the pick-off component of the ortho-positronium triplet.⁶

In the present experiment, τ_1 is found to remain constant (145 ps) but τ_2 decreases from 400 to 370 ps for an increase in doping of protonated PANI in the blend. The longest third component is ascribed to positronium formation and subsequent ortho- to para-conversion in the large voids in the blend system. The relative intensity of the τ_3 component is rather large (10–13%).

The intensity of the intermediate lifetime component I_2 needs be given special attention here because the values of I_2 are related to the level of protonation in PANI⁷ that controls the conductivity in this poly-

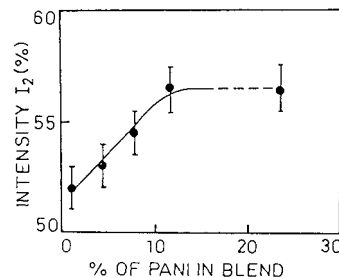


Figure 5 Variation of intensity I_2 as a function of doped PANI in different blend systems.

mer. We optimally doped PANI and increased its percentage as a whole in the blend. This doped PANI has a constant amount of dislocations,⁷ and hence, τ_1 remains constant. The τ_2 component originates from annihilation of positrons in the dislocation sites. However, as we increase the doped PANI in the blend, the dislocation density in the blend increases, and as a result, I_2 increases. Figure 5 shows the variation of I_2 and Figure 6 shows the variation of $(I_2 + I_3)$ with the increase of doped PANI in the blend. From both figures, we see the I_2 or $(I_2 + I_3)$ attains saturation at about 12% of doped PANI in the blend. In Figure 2 we observe that the conductivity also attains saturation at the percolation percentage (11.8% of doped PANI in PAM). The doped PANI enters into the PAM structure up to 11.8% to form the conducting chain, and the remaining part does not contribute very much to conductivity. From the positron annihilation parameter, it is also seen that a small contribution has come from this excess portion of doped PANI in PAM.

From the experimental lifetime data, the bulk lifetime, τ_B , using the simple two-state trapping model,²³ is calculated,

$$\tau_B = \frac{(I_1 + I_2)}{\left[\left(\frac{I_1}{\tau_1} \right) + \left(\frac{I_2}{\tau_2} \right) \right]} \quad (2)$$

Figure 7 shows the variation of τ_B with the percentage of protonated PANI in PAM where τ_B is seen to decrease as the percentage of protonated PANI in

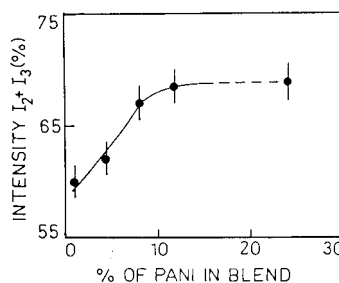


Figure 6 Variation of intensity $(I_2 + I_3)$ as a function of doped PANI in different blend systems.

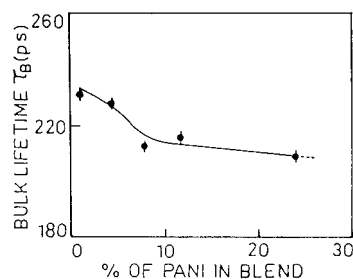


Figure 7 Variation of bulk lifetime τ_B as a function of doped PANI in different blend systems.

PAM increases up to the percolation percentage, above which τ_B becomes nearly constant.

CONCLUSION

In conclusion, the present article attempts to correlate the positron annihilation lifetime spectra with the composition of the PANI–PAM blend. It is observed that the conductivity reaches the maximum value for 11.8% percolation percentage of doped PANI in PAM and attains saturation for the higher percentage. Our main objective was to understand this effect by analyzing the positron annihilation parameters. While doing so, we found that the intensity of the intermediate positron lifetime component I_2 and the bulk lifetime, τ_B , also attained nearly constant value above the percolation percentage.

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