

DBAR investigation on films of polypyrrole incorporated polyvinylalcohol doped with ferric chloride

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Abstract. Flexible films of pyrrole (Py) sorbed, ferric chloride (FeCl₃) doped polyvinylalcohol (PVA) were prepared by solution casting. The films were characterized by XRD, UV-Visible spectrometry, Thermal Analysis (DSC, DTA/TGA), FTIR and electrical measurements. In this paper, the results of Doppler Broadening of Annihilation Radiation (DBAR) spectra in the doping range, from 4 wt% up to 18 wt%, are discussed. The XRD and DSC scans complement the DBAR results. The computed S- parameter and W -parameter reflect changes in the degree of crystallinity and the average crystallite size, respectively, of polypyrrole (PPy) incorporated PVA samples doped with ferric chloride.

1. Introduction

Polyvinylalcohol (PVA) is a polymeric material, with many versatile applications. It has been doped with different reduction/oxidation (redox) agents like iodine, ferric chloride and other salts, and these doped polymeric materials show significant modifications in their micro-structural features, as well as their thermal, optical and electrical properties [1]. The blend of PVA with other polymers has been extensively studied [2]. Flexible films of pyrrole (Py) sorbed, ferric chloride (FeCl₃) doped PVA were prepared by solution casting, after in-situ polymerization in aqueous solution [3]. Ferric chloride acts both as a dopant (redox agent) as well as an initiator for the polymerization of pyrrole, resulting in the formation of a conducting polymeric blend [4]. The films were characterized using optical spectrometry, powder X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and the Doppler Broadening of Annihilation Radiation (DBAR) technique of Positron Annihilation Spectroscopy (PAS). The DBAR spectrum was analysed using line-shape parameters, namely, S-parameter and W- parameter. The two important portions of the Doppler broadened 511 kilo- electron Volt (keV) line are the area under the curve immediately around the peak, and the area under the tails of the curve, on both sides [5]. The S parameter can be defined as the ratio of area around the 511 keV peak normalised over the total area, and the W parameter is defined as the normalised area under the tails [6]. The energy of the electron – positron pair undergoing two gamma annihilation is not equally shared by them, in the laboratory frame of reference. The energy of one of these annihilation photons is increased (Doppler shifted upwards) and the other annihilation photon is decreased (Doppler shifted downwards) by an amount given by $\Delta E = (c \times P_L)/2$, where ' P_L ' is the longitudinal component of momentum of the electron-positron pair in the direction of gamma ray emission and ' c ' is the velocity



of light in vacuum. In terms of P_L , every S and W parameter was obtained by the fraction of counts which appeared at $0 \sim 4 \times 10^{-3} m_0 c$ and $15 \sim 30 \times 10^{-3} m_0 c$ from the centre to the total counts for the annihilation peak. Here, ' m_0 ' refers to the rest mass of the electron (or positron).

2. Experimental

The incorporation of PPy in PVA matrix is achieved by in-situ polymerization of pyrrole (Py). Aqueous solutions of PVA doped with different concentrations (from 4 wt% up to 18 wt %) of ferric chloride (FeCl_3) were exposed to Py vapour for sixteen hours. The resulting mixture was dried in an air cooled, temperature controlled furnace, maintained at 40°C , to obtain the FeCl_3 doped, PPy incorporated PVA films. These films were characterized using XRD, DSC, Attenuated Total Reflectance- Fourier Transform Infra-red Spectrometry (ATR-FTIR) and Ultraviolet (UV)-Visible Spectrometry. Fig. 1 shows the variation of average crystallite size of the samples (extracted from the XRD data) for different doping levels of FeCl_3 in PPy- PVA blend. The XRD curves were analysed using the PowderX software [7]. The ATR-FTIR scans reveals that an absorption peak appears at 1640 cm^{-1} (attributed to amine vibrations within the pyrrole ring) [8], which increases in intensity on increasing the doping level (Fig. 2). In addition, the NH absorption peak is observed at 3400 cm^{-1} , thereby confirming the formation of PPy in the PVA matrix. For DBAR studies, a high resolution High Purity Germanium (HPGe) detector was used to record the energy spectrum of annihilation gamma rays from the sample. The energy resolution was measured to be 1.4 keV at 662 keV photo-peak of Cesium-137 source. A 300 kilo-becquerel (kBq) sodium -22 (Na^{22}) source, deposited on a thin kapton foil of thickness 7 micro-metres (μm), was used as a source of positrons. This source was sandwiched on either side by the FeCl_3 doped PPy-PVA films (stacked to 1 mm thickness, on either side of the source). The source-sample sandwich assembly was kept at a distance of 10 cm from the beryllium window of the HPGe detector. Each spectrum was analysed using a programme developed by us to extract the line-shape parameters, namely, the S- parameter (Fig. 3) and the W- parameter (Fig. 4).

3. Results and discussion

The modifications in the micro-structure of FeCl_3 doped PVA caused by incorporation of PPy are discussed in this paper. It is noted from Fig. 1 that the average size of crystallites (obtained from XRD scans) increases at low and moderate doping levels (from 0.5 wt% up to 5.7 wt% of FeCl_3 in PPy incorporated PVA), beyond which it decreases. Note that the W- parameter of DBAR (see Fig. 4) also shows a similar trend (increase from 4 wt% up to 10.7 wt%, followed by a decrease). The S- parameter (Fig. 3) shows an increase at higher dopant levels (from 5.7 wt% up to 18 wt %) indicating enhanced annihilation of positrons with low momentum electrons (at higher dopant concentrations), which is expected when the material becomes more amorphous, as indicated by the XRD results (Fig. 5). The DSC curves (Fig. 6) for these samples supports this line of reasoning. At low levels of doping, there is molecular level distribution of the dopant (FeCl_3) in the blend, and the chlorine ions will interact with the PVA chains, thereby aligning these chains, and increasing the average crystallite size of the sample. As the dopant concentration increases, the polymerization process of pyrrole (in-situ polymerization in aqueous solution before casting) increases, and the polypyrrole regions start accumulating in the sample, thereby drastically reducing the average crystallite size and the degree of crystallinity of the sample. This explanation can account for the fact that, as the doping concentration is increased from 4 wt% up to 10.7 wt%, there is increase in W- parameter, followed by a decrease (reversal in trend) at higher doping concentrations. Note that (see Fig. 1 and Fig. 4) there is a correlation between the W- parameter (DBAR) and the average crystallite size (XRD). Also, note the inverse relationship between the S- parameter (DBAR) and the degree of crystallinity (XRD) of these samples (Fig. 3 and Fig. 5). The XRD results are supported by the DSC curves (Fig. 6).

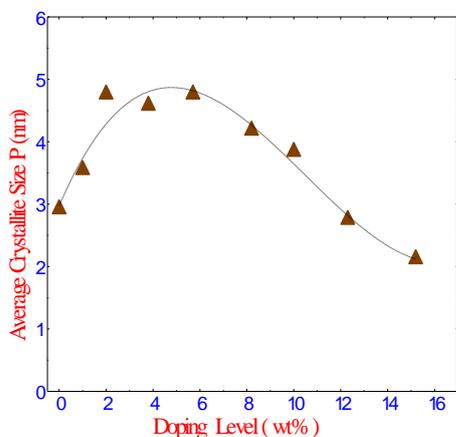


Figure 1. Average crystallite size of the FeCl₃ doped, PPy incorporated PVA ,

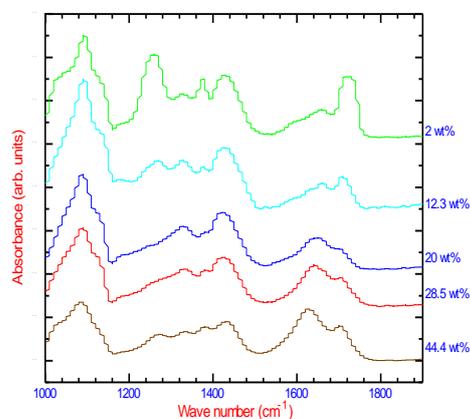


Figure 2. FTIR Scans of the FeCl₃ doped, PPy incorporated PVA films in the finger print region.

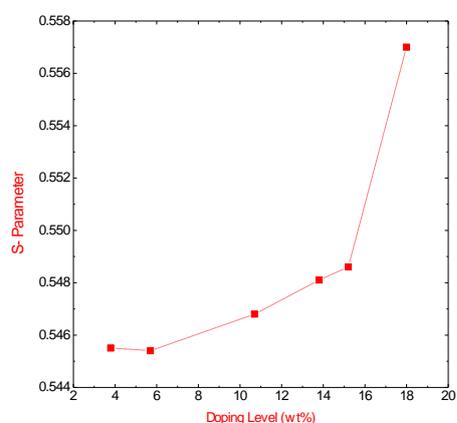


Figure 3. Variation of S-parameter of DBS relative to FeCl₃ doping level in PPy incorporated PVA

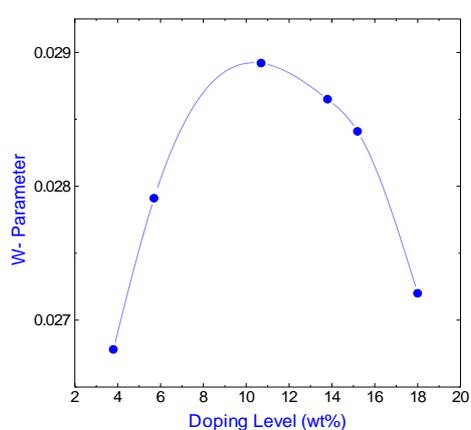


Figure 4. Variation of W-parameter of DBS relative to FeCl₃ doping level in PPy incorporated PVA

4. Conclusion

The variation of line-shape parameters of DBAR spectra of PPy incorporated PVA films with variation in FeCl₃ doping level is discussed. The S- parameter shows an increase at higher dopant levels (from 5.7 wt% up to 18 wt %) indicating enhanced annihilation of positrons with low momentum electrons (at higher dopant concentrations), which is expected when the material becomes more amorphous, as indicated by the inverse trend shown by degree of crystallinity of the PPy-PVA blend, extracted from the XRD data. This conclusion is supported by the DSC curves. The W-parameter of DBAR shows a trend similar to the average crystallite size, extracted from the XRD data.

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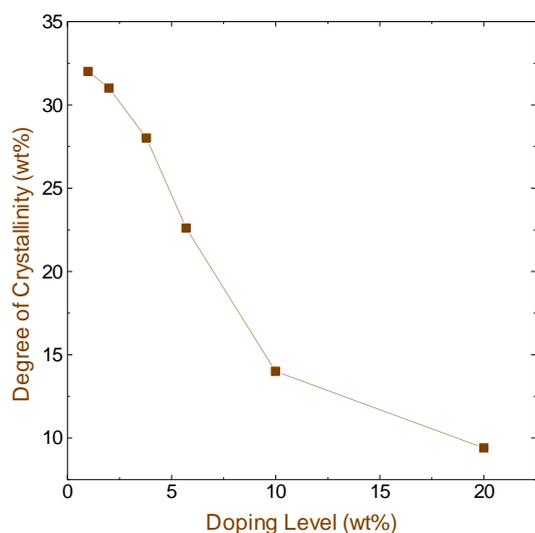


Figure 5. Variation of the degree of crystallinity of FeCl_3 doped PPy incorporated PVA films, for different concentrations (in wt %) of the dopant

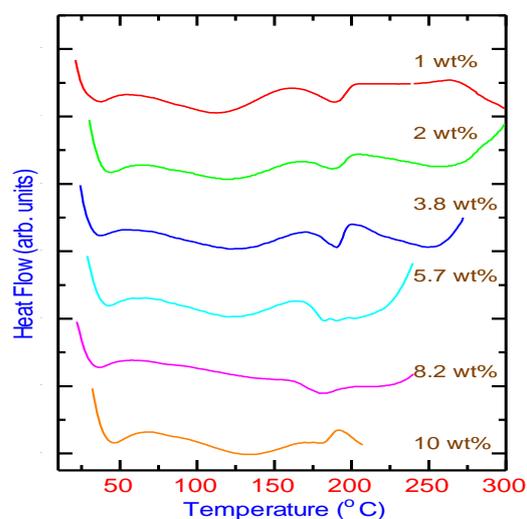


Figure 6. DSC scans of FeCl_3 doped PPy incorporated PVA films, for different concentrations (in wt %) of the dopant

References

- [1] Lobo. B, Ranganath. M. R, Ravi Chandran T. S. G, Rao. G. V, Ravindrachary.V , and Gopal. S 1999 *Phys. Rev. B* **59** 13693.
Tawansi. A, El-Khodary. A, and Abdelnaby. M. M 2005 *Current Applied Physics* **5** 572.
Bhajantri R F, Ravindrachary V, Harisha A, Ismayil and Ranganathaiah C 2009 *Physica Status Solidi C* **6** 2429.
- [2] Patil.R.V, Ranganath. M. R and Lobo. B 2014 *AIP Conf. Proc.* **1591** 183.
Patil.R.V, Ranganath. M. R and Lobo. B 2013 *AIP Conf. Proc.* **1512** 578.
Ravindrachary. V, Bhajantri. R. F, Harisha. A, Ismayil and Ranganathaiah. C 2009 *Physica Status Solidi C* **6** 2438.
- [3] Ranganath. M. R and Lobo. B 2009 *Solid State Physics (India)* **54** 535.
- [4] Benseddik. E, Bonnet. A and Lefrant.S 1998 *J. Appl. Polym. Sc.* **68** 709.
Dhawan. S. K and Trivedi. D. C 1993 *Bulletin of Materials Science* **16** 371.
- [5] Choudalakis. G, Gotsis. A. D, Schut. H and Picken S. J 2011 *European Polymer Journal* **47** 264.
- [6] Mohammed. H. F. M and Abd El-Aziz . N. S 2001 *Polymer* **42** 8013.
- [7] Dong. C 1999 *J. Appl. Cryst.* **32** 838.
- [8] Cruz. G. J, Morales . J and Olayo. R 1999 *Thin Solid Films* **342** 119.