



Synthesis of alcotex/3-aminopropanoic acid polymer thin film and its structural and opto-electrical properties



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ABSTRACT

We report that alcotex/3-aminopropanoic acid (PVA- β -alanine) polymer thin film was synthesized by taking different concentrations of PVA- β -alanine by the solution casting process, and their structural, opto-electrical and ionic conductivity were examined for the first time. In the X-ray diffraction (XRD) study, the crystallite structure of the semi-crystalline film can be clearly seen with an increase in β -alanine and a decrease in the PVA concentrations. The presence of functional groups and optical response was analyzed for the prepared material using the Fourier Transform Infrared (FT-IR) and optical absorption tests. The wider optical band gap values are calculated to be 4.89 to 5.07 eV using the Tauc plots for polymer thin film materials at various PVA- β -alanine concentrations. The effects of various PVA/ β -alanine wt% concentrations on the ionic conductivity, electrochemical impedance spectroscopy (EIS) parameters, power-law exponent (n) and hopping frequency of the prepared polymer films have been elucidated.

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1. Introduction

In recent years, developments in the preparation of thin film using precursor-based polymers have led to significant improvements in the field of optical and electronic devices, supercapacitors, energy storage and biomedical applications etc. [1–15]. This was due to its low electrical conductivity, large optical band gap and excellent chemical stability. Over the past few years, thin film based polymers have been synthesized using various chemical synthesis methods [1–14]. Polymers of Polyvinyl alcohol (PVA) are highly preferable polymers due to their excellent thermal and physico-chemical properties [1–4,10–15]. In addition, they are semi-crystalline and synthetic hydrophilic polymers commonly used in various fields, such as food packing, resins and cosmetics. There are a few literature reports concerning polymer/amino acid materials [1,10–13]. Amino acids contain the carboxylic acid ($-\text{COOH}$) donor proton and the acceptor proton ($-\text{NH}_2$) group has an effect on the function of organs, glands, tendons and arteries. When amino acid is combined with polymeric materials, ionic conductivity can be improved [1,10]. In addition, the present solution

casting process [1,10–12] has some advantages such as low temperature synthesis reactions, short time reactions, non toxicity, low cost etc.

In the present work, PVA- β -alanine polymer thin film, was synthesized using different concentrations of PVA- β -alanine via a solution casting route. The impact of PVA- β -alanine concentrations on the structural, optical and electrical properties is explored for the first time.

2. Experimental

Comprehensive information on the preparation of alcotex /3-aminopropanoic acid polymer electrode thin film and its structural, optical and electrical conductivity characterization can be found in the Supporting Information.

3. Results and discussion

The XRD patterns of (a) pure β -alanine, (b) 95Mwt%PVA:05Mwt% β -alanine (PBA1), (c) 90Mwt%PVA:10Mwt% β -alanine (PBA2) and (d) 85Mwt%PVA:15Mwt% β -alanine (PBA3) samples are demonstrated in Fig. 1. The pure β -alanine sample observed sharp diffraction peaks in the XRD pattern (Fig. 1a). Further, the diffraction peaks located at $2\theta = 12.7^\circ, 18.3^\circ, 21.3^\circ, 25.7^\circ, 37.3^\circ$ and 38.7° ,

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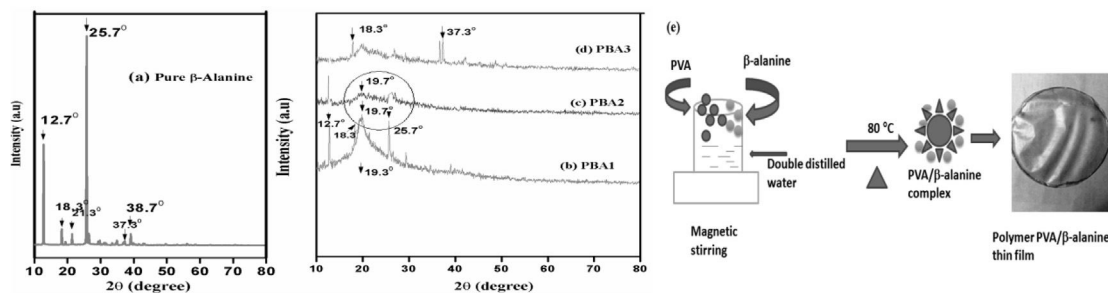


Fig. 1. XRD pattern of (a) pure β -alanine, (b) PBA1, (c) PBA2, (d) PBA3 samples and (e) Schematic formation of the PVA/ β -alanine thin film.

respectively, are well correlated with the previous analysis of pure β -alanine. The broad peak (crystalline nature) has changed to the sharp diffraction peak (semi-crystalline nature) due to the increased β -alanine and decreased PVA concentration (Fig. 1(b-d)). In addition, it can be clearly seen in Fig. 1(b-d) that the mixed phase of β -alanine and PVA in the XRD pattern demonstrated the formation of polyvinyl alcohol complexes with the β -alanine polymer. The crystallite size (D) is determined from the detection of high-intensity diffraction peaks at $\sim 19.7^\circ$ for PBA1, PBA2 and PBA3 samples by applying the Debye Scherrer's equation [10] and are given in Table 1 (Supporting Information). We found that the PBA2 polymer sample had a smaller crystallite size of 1.6 nm compared to the other samples. The schematic formation of the PVA/ β -alanine thin film is shown in Fig. 1(e). The FT-IR spectra of pure β -alanine and PVA complexes with β -alanine and their outcome and discussion are given in the Supporting Information. Based on the FT-IR studies, the prepared polymer thin film samples have confirmed the formation of PVA- β -alanine [1,10].

The optical absorption analysis provided details on the optical band gap of the polymer thin film. Fig. 2a displays the optical absorption spectra observed for PVA complexes with varying concentrations of β -alanine in the 200–500 nm range. The optical absorption spectrum of PVA- β -alanine samples (Fig. 2a) is observed in the ultraviolet (UV) region. We noticed that strong absorption of the PBA2 sample, which suggest the high surface-to-volume ratio of the polymer particles interacting with light. The optical band gap can be estimated using the Tauc plot. Fig. 2(b) shows the variation of $h\nu$ vs $(\alpha h\nu)^2$. The optical band gap (E_g) was determined to be 5.07, 4.89 and 5.01 eV for the PBA1, PBA2 and PBA3 samples, respectively. In addition, the prepared polymer samples have a wider band gap material and may therefore be used for insulating devices.

The complex impedance plots of the samples PBA1, PBA2 and PBA3 at room temperature are displayed in Fig. 3(a). The depressed arc shows the bulk resistive behavior of the sample due to ion diffusion [10]. This depressed arc was noticed in the high frequency range represented by the bulk capacitor (C_p) parallel to the bulk resistor (R_b), and a large capacitive spike was observed in the

low-frequency range due to the space charge polarization [10]. The bulk resistance (R_b) was measured from the low frequency intercept of the depressed arc and the high frequency end of the straight line on the real axis (Z') as shown in the inset of Fig. 3a. The ionic conductivity of the PVA- β -alanine polymer was calculated using the Cole-Cole plot data with the ionic conductivity formula ($\sigma = l/AR_b$, Where, l -thickness, A -area of the polymer thin film, and R_b -bulk resistance) [10].

The ionic conductivity values for three different compositions of PVA- β -alanine complexes are shown in Table 3(a) (Supporting Information). As the temperature rises, the ionic conductivity of all PVA- β -alanine complexes increases, as shown in Table 3(b) (Supporting Information). The maximum ionic conductivity for PBA2 at room temperature (303 K), 323 and 343 K is shown in Table 3(a) as compared to the PBA1 and PBA2 samples. This was attributed to an increase in the movement of a number of charge carriers in the PBA2 sample, leading to an increase in ion transport [1]. Electrochemical impedance spectroscopy (EIS) parameters values from the Cole-Cole plot data are shown in Table 3(b). Table 3(b) shows that the PBA2 sample found higher values of constant phase element (CPE) and n relative to the other samples.

Frequency-dependent AC conductivity spectra for the prepared polymer thin film at room temperature and for the PBA2 sample at different temperatures are represented in Fig. 3(b & c). The electrical conductivity of the PBA2 sample is significantly improved compared to that of the other samples, as shown clearly in Fig. 3(b). In addition, the electrical conductivity of the PBA2 sample increased when the temperature increased from 303 to 343 K, as shown in Fig. 3(c).

This plot consists of three distinct regions: (i) the high frequency region due to electrical relaxation associated with short-range ion migrations; (ii) the intermediate-frequency region, where the relaxation is associated with long-range ion migration and (iii) low-frequency regions where electrical relaxation can be due to the build-up of the space charge and the transfer of charge to the blocking electrodes. The value of the power exponent (n) was determined using this formula $n = \text{backward hopping rate/site relaxation time}$ by fitting the conductivity spectra to the Jonscher

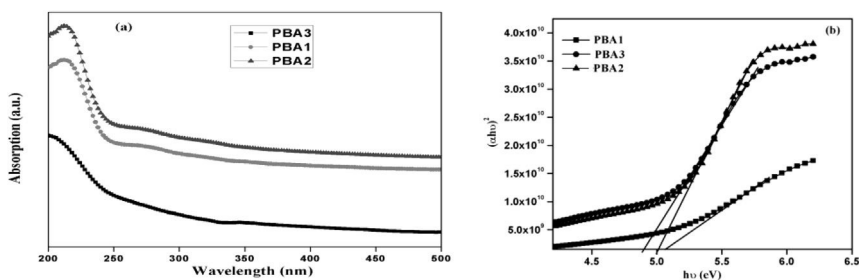


Fig. 2. (a) Optical absorption spectra and (b) Tauc plot of the PBA1, PBA2 and PBA3 samples.

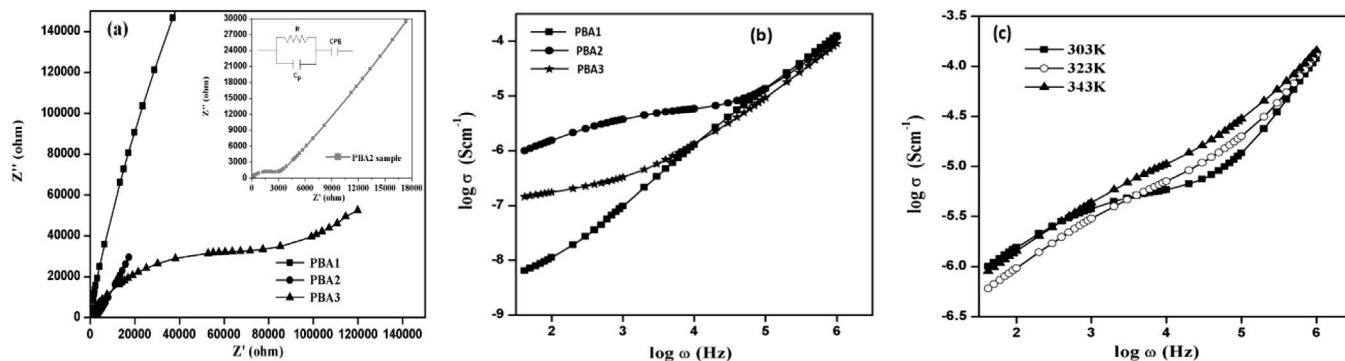


Fig. 3. (a) Complex impedance plots of the PBA1, PBA2 and PBA3 samples. (b) Conductance spectra for all compositions of PVA/ β -alanine polymer thin film at 303 K, and (c) Conductance spectra for PBA2 polymer thin film at various temperatures.

power law equation using a non-linear square fitting and the values are shown in Table 4 (Supporting Information). If $n < 1$, i.e. backward hopping, is slower than site relaxation, whereas $n > 1$, backward hopping is faster than site relaxation [12]. The n values are less than one for all the compositions. Among these values, the PBA2 value is low. This lower n value is clearly shown to have the highest ionic conductivity due to the number of free ion hopping sites available over the other PBA1 and PBA3 samples. In addition, the temperature-dependent conductivity and compositional dependence of the synthesized polymer thin film interpretation are set out in the Supporting Information. Based on the above-mentioned temperature-dependent conductivity studies, it could be noted that conductivity increases linearly with increase in temperature. The activation energy (E_a) and ionic hopping rates (ω_p) of the PBA2 sample can be determined using the DC conductivity formula ($\sigma_{dc} = \sigma_0 \exp(-E_a/KT)$) [12] with the aid of the temperature dependence conductivity data. Furthermore, it could be noticed that the ω_p values of the PBA2 sample are higher than those of the other samples. Based on the compositional dependence spectra, it can be observed that PBA2 has the maximum electrical conductivity compared to the PBA1 and PBA3 samples.

4. Conclusions

In summary, we have reported on the preparation of PVA/ β -alanine polymer thin film with a solution casting technique. The XRD analysis confirmed that the crystalline nature was changed to semi-crystalline with an increase in β -alanine/decreasing concentrations of PVA. The FT-IR studies evidence the formation of PVA and β -alanine complex material. The prepared polymer thin film has found a larger band gap that suggests good insulating properties and can be used for insulating devices. The maximum ionic conductivity was observed for PBA2 relative to PBA1 and PBA3 using the conductance spectra.

CRediT authorship contribution statement

R. Bhuvaneshwari: Methodology, Writing - original draft, Writing - review & editing. **J. Gajendiran:** Investigation, Writing - orig-

inal draft, Writing - review & editing, Conceptualization. **S. Karthikeyan:** Formal analysis. **S. Selvasekarapandian:** Formal analysis. **S. Gnanam:** Writing - review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.128690>.

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