Preparation and characterization of Biopolymer based on Dextran and Poly (Vinyl alcohol)

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Abstract

Biodegradable bio polymer electrolyte based on different concentration of Dextran and PVA was prepared by using solution casting technique. The Thermal, Structural, Vibrational, Electrical properties of polymer electrolyte were investigated by using XRD, FTIR, DSC, and AC Impedance. The amorphous nature of the polymer electrolyte has been confirmed by X- ray diffraction. FTIR study confirms the complex formation between the two biopolymers Dextran: PVA. T<sub>g</sub> of different concentration of Dextran: PVA polymer membranes were measured by using differential scanning calorimetry. From AC Impedance study the maximum ionic conductivity of 1.07 x 10<sup>-7</sup> S/cm has been observed in DEX 4 (700mg Dex: 300mg PVA) at room temperature.

Keywords:-AC Impedance, Biopolymer electrolyte, Dextran, DSC, FTIR, XRD.

Introduction

Electrochemical devices such as batteries and fuel cells play an important role in the modern day today life. An electrolyte is a main part of the electrochemical devices for the ion transportation. In recent days most of the researchers have concentrated the growth of new solid state polymer electrolyte to replace liquid electrolyte because of its disadvantages such as leakage, poor compatibility with electrolyte, poor stability, corrosion and etc [1]. The solid polymer electrolyte has high stability, flexibility, safe and long life. Especially the proton conducting polymer electrolyte has great attention in electrochemical devices, fuel cell, and supercapacitor [2-5]. Compare to synthetic polymer, bio polymer have extraordinary properties such as biodegradability, non-toxicity, inexpensiveness, echo friendly [6]. Bio polymers are extracted from natural bio derivatives. Biopolymers such as starch [7], Chitosan [8], Agar-Agar [9], Carrageenan [10], Pectin [11], Dextrin [12] have been successfully used in electrochemical devices.
Among different types of biopolymer, Dextran is a natural polysaccharide derived from sucrose. The native chain of dextran which consist of alpha-1, 6 glycosidic linkages between glucose molecules while branches begin from alpha-1, 4 linkage (alpha-1,2 and alpha-1,3) [13]: Dextran is natural and water soluble, easily filtered, biocompatible, biodegradable, more stable. Dextran widely used in food industries and medicine [14]. Pure dextran has low film forming capacity. To improve this PVA added with dextran because of poly vinyl alcohol has good film forming capacity [15,16] and also non-toxic, biodegradable, high chemical and thermal stability [17]. In the present work we have developed membrane X gram Dextran : Y gram PVA (Where X= 700mg, 750mg, 800mg, 850mg : Y= 300mg, 250mg, 200mg, 150mg) by solution casting technique. The developed membranes have been characterised by different techniques such as XRD, FTIR, DSC, AC Impedance. The results are presented and discussed.

Materials and methods

In the present work Dextran with an average molecular weight (Mw =15000-25000 Sigma Aldrich) and PVA (Mw= 850000-1,240000 Sd fine ) used as a raw materials for the preparation of the polymer electrolyte. Dextran: PVA based electrolytes of different compositions have been prepared by solution casting technique with double distilled water as a solvent. Initially Dextran was added to the solvent and stirred continuously till complete dissolution in the solvent. The suitable concentration of PVA added to the solution and stirred continuously for several hours until the clear solution obtained. Then the solution poured into polypropylene petridish and dried at 600 C in hot air oven for two days. The free standing transparent films were obtained. The complex formation between the host polymers Dextran: PVA have been confirmed by FTIR using Thermo Fisher (Model-Nicolet is 10), USA with resolution of 1cm-1 in the range 400-4000cm-1. Crystalline/ amorphous nature of developed membrane have been studied at room temperature by XRD using Rigaku Ultima IV Japan with in the range of 2θ=100 to 900. The ionic conductivity of the polymer blend has been measured from Impedance analysis at room temperature by using HIOKI 3532-50 LCR Hi-Tester in the frequency range between 42 Hz and 1 Hz meter. The glass transition temperature of the prepared polymer electrolyte has been found out by using Model DSC (Q20) V4, USA at the heating rate of 100 C/min under nitrogen atmosphere in room temperature.

Nomenclature of prepared membrane

- 850mg Dex: 150mg PVA - DEX1
- 800mg Dex: 200mg PVA - DEX2
- 750mg Dex: 250mg PVA - DEX3
- 700mg Dex: 300mg PVA - DEX4

Result and discussion

X-ray diffraction analysis (XRD)

X-ray diffraction has been carried out to study amorphous /crystalline nature of the developed membrane. Figure.1 show that the XRD pattern for pure powder Dextran, XRD pattern and XRD deconvolution pattern of different compositions of Dextran: PVA (DEX1, DEX2, DEX3, and DEX4) polymer electrolytes. The Peaks observed at 15.290, 17.40, 19.10, 20.70 and 29.330 agree well with the earlier reported values for pure Dextran [18, 19, 20]. Previously reported values of diffraction peaks at 19.60 and 400 for pure PVA [21].The XRD pattern of DEX1 consists of two peaks at 19.100 with the intensity of 4650 a.u. and 40.600 with the intensity of 1078 a.u. The peaks deconvoluted and its consist of four peaks 19.340, 19.590, 19.700 and 38.410. The peaks at 19.340 and 19.590 correspond to pure Dextran , 19.700 and 38.410 correspond to pure PVA respectively. The XRD peaks of DEX2...
consist of three peaks at 19.10°, 28.64° and 40.44° with the intensity of 2486 a.u,786 a.u and 717 a.u respectively. The above peaks are deconvoluted and it has four peaks observed at 19.2°,19.2°,19.9° and , 38.9°.The peaks observed 19.2°,19.2° for pure Dextran and 19.9°, 38.9° for pure PVA respectively. The peaks observed at 14.08°, 19.10° and 28.96° for DEX3 with the intensity of 1085 a.u,1270 a.u and 809 a.u respectively. The deconvoluted peaks of DEX3 have two peaks observed at 20.8° and 28.9°.The peak 28.9° corresponds to pure Dextran and 20.8° correspond to pure PVA respectively. The DEX4 exhibits the peaks values at 14.86°,17.16°,18.44°,19.90° and 29.12° with the intensity of 560 a.u,614 a.u, 644 a.u, 686 a.u and 336 a.u respectively. The XRD deconvoluted peaks of DEX4 consists of 14.6°,14.6°,19.1°,20.8°,29.04° and 40.90°.The peaks 14.6°,14.6°,19.1°,20.8°,29.04° corresponds to pure Dextran and 40.90° for pure PVA respectively. Due to the addition of PVA with Dextran with different wt % (150mg, 200mg, 250mg, 300mg) the intensity of peak decreases and the broadness increases so the amorphous nature of the polymer blend also increases. A correlation between the height of the peak and the degree of crystallinity can be interpreted in terms of Hodge et.al [22]. The flexibility and segmental motion of ions increases with amorphous nature of the polymer matrix. The XRD pattern reveals DEX4 has lowest intensity compare to DEX1, DEX2 and DEX3.The maximum amorphous nature observed for DEX4 polymer membrane, which enhances the movement of ions in the polymer matrix and increases its ionic conductivity [23].

Fig.1 XRD spectra for pure powder Dextran,XRD spectra and XRD deconvolution spectra of different composition of Dextran : PVA (DEX1,DEX2,DEX3,DEX4)
Fouriertransforms infrared (FTIR) spectroscopy analysis

FTIR spectroscopy is important for the investigation of polymer structure. It has been used to identify the interaction between the polymers in the polymeric mixture which changes the vibrational modes of the atoms or molecules in the material. Figure 2 shows that the FTIR spectra of Dextran:PVA polymer blend with different compositions recorded at room temperature in the wave number region of 400-4000 cm$^{-1}$ with resolution of 1cm$^{-1}$. The vibrational peaks at 3421 cm$^{-1}$, 2923 cm$^{-1}$, 1653 cm$^{-1}$, 1458 cm$^{-1}$ and 765 cm$^{-1}$ corresponding to O-H stretching, C-H stretching, C=C stretching, C-H bending, C-H out of plane bending for pure Dextran respectively [24]. The vibrational band at 3475 cm$^{-1}$, 2933 cm$^{-1}$, 1458 cm$^{-1}$ corresponds to O-H stretching, C-H stretching, CH$_2$ bending for pure PVA respectively [25]. The vibrational peaks observed at 3421 cm$^{-1}$, 3475 cm$^{-1}$ for pure Dextran and PVA respectively assigned to O-H stretching, now appears at 3433 cm$^{-1}$, 3446 cm$^{-1}$, 3437 cm$^{-1}$, 3565 cm$^{-1}$ for DEX1, DEX2, DEX3, DEX4 respectively. Bands observed at 2923 cm$^{-1}$, 2933 cm$^{-1}$ ascribed to C-H stretching for pure Dextran and PVA respectively have shifted to 2921 cm$^{-1}$, 2924 cm$^{-1}$, 2919 cm$^{-1}$ and 2919 cm$^{-1}$ for DEX1, DEX2, DEX3, DEX4 respectively. C=C stretching band observed at 1653 cm$^{-1}$, 1664 cm$^{-1}$ of pure Dextran and PVA respectively, appears at 1650 cm$^{-1}$, 1640 cm$^{-1}$, 1651 cm$^{-1}$ and 1650 cm$^{-1}$ for DEX1, DEX2, DEX3, DEX4 respectively. C-H bending observed at 1458 cm$^{-1}$ and 1456 cm$^{-1}$ for pure Dextran and PVA have been shifted to 1456 cm$^{-1}$, 1459 cm$^{-1}$ and 1456 cm$^{-1}$ for DEX1, DEX3, DEX4 respectively. The vibrational bands at 765 cm$^{-1}$, 734 cm$^{-1}$ assigned to C-H out of plane bending for pure Dextran and PVA respectively have been observed at 765 cm$^{-1}$, 762 cm$^{-1}$ and 755 cm$^{-1}$ for DEX1, DEX3, and DEX4 respectively.

<table>
<thead>
<tr>
<th>DEXTRAN</th>
<th>PVA</th>
<th>DEX 1</th>
<th>DEX 2</th>
<th>DEX 3</th>
<th>DEX 4</th>
<th>ASSIGNMENT</th>
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<tr>
<td>3421</td>
<td>3475</td>
<td>3433</td>
<td>3446</td>
<td>3437</td>
<td>3565</td>
<td>O-H Stretching</td>
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<td>2933</td>
<td>2921</td>
<td>2924</td>
<td>2919</td>
<td>2919</td>
<td>C-H stretching</td>
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<tr>
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<td>1664</td>
<td>1650</td>
<td>1640</td>
<td>1651</td>
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<tr>
<td>1458</td>
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<td>1456</td>
<td>-</td>
<td>1459</td>
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<td>C-H bending</td>
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<td>765</td>
<td>734</td>
<td>765</td>
<td>-</td>
<td>762</td>
<td>755</td>
<td>C-H out of plane bending</td>
</tr>
</tbody>
</table>

Fig.2 FTIR spectrum of pure Dextran and different composition of Dextran : PVA(DEX1, DEX2, DEX3, DEX4)
Differential scanning calorimetry (DSC)

DSC has been used to measure glass transition temperature of polymer blend. The DSC curve of DEX1, DEX4 are shown in Figure 3 and the values of glass transition temperatures have been shown in Table 2. Glass transition temperature of pure PVA is 90°C [26] and the pure Dextran is 220°C [27]. The glass transition of pure Dextran is decreased with increasing of PVA. The glass transition temperature decrease due to softening and flexibility of the complexation by the addition of PVA. The glass transition temperature values exist between 90°C to 220°C for DEX1, DEX4. This has been indicating the interaction between the polymers. The presence of a single glass transition temperature has been widely accepted as the demonstration of the miscibility of polymers [28]. The glass transition temperature of DEX4 has been observed at 176.34°C. At low glass transition temperature segmental ions motion has been increased in polymer electrolyte which enhance its ionic conductivity. So the maximum conductivity has been observed for DEX4 compare to other concentrations.

**Fig.3 DSC thermograms of (a) DEX1 (b) DEX4**

<table>
<thead>
<tr>
<th>DEXTRAN: PVA compositions (mg)</th>
<th>Glass transition temperature ($T_g$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEX1</td>
<td>195.02</td>
</tr>
<tr>
<td>DEX4</td>
<td>176.34</td>
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</table>
AC impedance analysis

Cole – Cole

The electrical properties of polymer electrolytes have been analyzed by using AC impedance technique. The impedance spectra of different composition of Dextran: PVA are shown in Figure. 4 The Cole-Cole plot consist of two regions, a depressed semicircle at high frequency representing the parallel combination of bulk resistance and capacitance which is due to the bulk effect of the electrolytes and the linear region which in the low frequency range is attributed to the effect of the blocking electrodes [29, 30]. The bulk resistance $R_b$ of polymer electrolyte has been measured using EQ software program developed by Boukamp[31]. Electrical conductivity of polymer electrolyte has been calculated by

$$\sigma = \frac{L}{R_bA}$$

where $\sigma$ - Ionic conductivity, $R_b$ -bulk resistance, $L$, $A$ - thickness and area of the sample. The calculated conductivity values for DEX1, DEX2, DEX3 and DEX4 are provided in Table.3. The two regions such as high frequency semicircle and low frequency spike have been observed in DEX4 which has the maximum ionic conductivity in the order of $1.07 \times 10^{-7}$ S cm$^{-1}$. 

Fig. 4(a) Cole-Cole plot for DEX1(850mg DEX: 150mg PVA)        Fig. 4(b) Cole-Cole plot for DEX2(800mg DEX: 200mg PVA)
Conductance spectra analysis

The conductance spectrum of Dextran: PVA based biopolymer with different compositions are shown in the Figure 5. In general the conductance spectrum consists of three different regions such as low frequency dispersion region, frequency independent plateau region and high frequency region [32]. In the present work the two regions low frequency and mid frequency regions have been observed from the different compositions of Dextran: PVA polymer electrolyte spectrum. The low frequency dispersion region observed can be ascribed to the space charge polarization at the blocking electrodes. The mid frequency region corresponds to the frequency independent plateau region and the extrapolation of the plateau to zero frequency gives the value of dc ionic conductivity [33]. The highest DC conductivity value has been obtained for DEX4 biopolymer. The conductivity values from conductance spectra have good agreement with values from Cole-Cole plot.

Fig.5 Conductance spectra for different composition of Dextran: PVA
Table. 3 Conductivity of Dextran with PVA polymer electrolyte

<table>
<thead>
<tr>
<th>S.No</th>
<th>Composition of electrolyte (mg)</th>
<th>Ionic conductivity (Scm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DEX1</td>
<td>7.05x10⁻⁹</td>
</tr>
<tr>
<td>2</td>
<td>DEX2</td>
<td>7.31x10⁻⁹</td>
</tr>
<tr>
<td>3</td>
<td>DEX3</td>
<td>7.91x10⁻⁹</td>
</tr>
<tr>
<td>4</td>
<td>DEX4</td>
<td>1.07x10⁻⁷</td>
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</tbody>
</table>

Conclusion

The biodegradable polymer electrolyte based on Dextran with PVA has been prepared by using solution casting technique. The prepared films were characterized by using XRD, FTIR, DSC, AC impedance. The amorphous nature of the polymer electrolyte has been confirmed by XRD. The interaction between the two host polymers Dextran: PVA was examined by using FTIR. The glass transition temperature of DEX4 has been found 176˚ by using DSC. The maximum ionic conductivity of DEX4 is 1.07x10⁻⁷ S/cm has been confirmed by AC impedance analysis.

References

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