

Synthesis and Characterization of Partial Blended Green Polymer Electrolytes

H.Aswathaman¹&Chitrakara Hegde²

^{1&2} Alliance College of Engineering and Design, Alliance University, Bangalore 562106, Karnataka, India.

ABSTRACT:- This work reports the ionic conductivity of polymer films of tapioca / 1,4-polyphenylene ether ether sulfone (PPEES), with lithium based salt and multiwall carbon nanotubes (MWCNT) as fillers which were prepared by solvent casting technique. The ionic conductivity of the films is studied at room temperature using ac impedance spectroscopic technique. X-ray diffraction (XRD), FTIR and SEM studies have been made to investigate the structural, complexation and variation in film morphology of the polymer electrolyte. The thermal of the films have been studied by TG/DTA.

Keywords:- Ionic conductivity, Impedance spectroscopy, Solid polymer electrolytes

I. INTRODUCTION

Polymer electrolytes have received considerable attention because of their potential applications in solid-state batteries, chemical sensors and electrochemical devices[1]. These polymer electrolytes have to satisfy several requirements, including high ionic conductivity, good mechanical properties and excellent electrochemical stability. The search for green ion containing polymer electrolytes can be interesting not only for understanding conductivity mechanism in the polymer, but also due to their lower cost, and ease of handling and fabrication as thin film membranes and environmental considerations. Several methods are available to prepare polymer and modulate conductivity of the polymer electrolytes. Among the above, blending of polymers is a useful tool to develop new polymeric materials with improved mechanical stability. The advantages of the blend system are simplicity of preparation and very ease to control the physical properties by compositional change [2].

As well known, synthetic polymer materials have been widely used in every field during last decades. These artificial macromolecular are non-degradable and use of non-biodegradable polymers has caused serious environmental problems. This reminds us to focus on natural polymers, which are inherently biodegradable [3]. Among the natural polymers, tapioca is of interest, owing to its complete biodegradability, low cost and renewability, tapioca is considered as a promising candidate for developing sustainable materials. Less effort has been exerted to develop tapioca-based polymers electrolyte. In this paper, the status of preparation and applications of tapioca-based polymers is reviewed and presented.

II. STRUCTURE AND PROPERTIES OF TAPIOCA AND PPEES

Tapioca is a common plant that can be found in almost every in tropical country. It has biodegradable starch which is an important source of carbohydrates[4]. In general, the starch of tapioca is made up of two major macromolecular components, which are amylose and amylopectin [5]. Amylose is a linear component polymer that is primarily composed of (1 fi 4)-linked α -glucan (Fig. 1). The degree of polymerization of amylose can up to 600. In tapioca starch, the amylose content can vary from 17% to 20%. Alternatively, amylopectin is the major component of tapioca starch (Fig. 2). This polymer is made up of a (1 fi 4)-linked α -glucan with an α -(1 fi 6) branch point. Amylopectin is significantly different than amylose because amylopectin contains approximately 5% branch points[6]. When tapioca starch is heated in excess water, an irreversible structure transition takes place, which is known as starch gelatinization or pasting. The granules of tapioca starch lose their birefringence and crystallinity as more water is absorbed. Upon cooling, tapioca starch experiences an increase in viscosity, and some loss of clarity can be seen before a weak gel or film is formed. The re-association of the amylose molecules in the aqueous system is attributed to these changes. This gel-forming process is known as retrogradation. Poly (1,4-phenylene ether ether-sulfone) is in the form of semitransparent beads. The structure of PPEES is shown in the figure 3

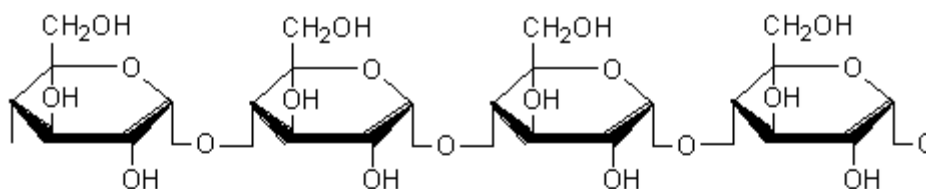


Figure 2 Amylose

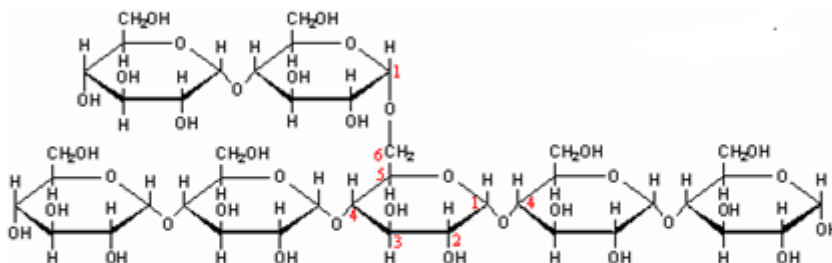


Figure 1 amylopectin

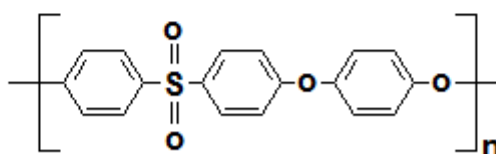


figure 3

1,4 poly phenylene ether ether sulfone

III. EXPERIMENTAL PART

Preparation of polymer films of tapioca / 1,4.polyphenylene ether ether sulfone (ppes)

Poly (1,4-phenylene ether-sulfone), PPEES were obtained from Sigma Aldrich in the form of semitransparent beads. Reagent grade anhydrous lithium perchlorate(LiClO₄) was used after drying in vacuum at 110°C for 24 hours. Dimethyl sulfoxide (DMSO) which was obtained from Merck-India was used without any further purification. Polymer electrolytes were prepared by dissolving appropriate amounts of the corresponding constituents by weight percentage in anhydrous dimethyl sulfoxide(DMSO). The electrolytes were prepared by the solvent casting technique. The cast films were maintained at 110 temperatures in the hot air oven to allow slow evaporation of DMSO. Residue of remaining DMSO was removed by further drying vacuum at 24 hrs at 100°C.

CHARACTERIZATION OF TAPIOCA / PPEES FILMS

IR spectra were recorded using Nicolet Avatar 330 FT-IR (Thermo Corporation) spectrometer. The XRD equipment used in this study was JEOL, JDX 8030 X-ray diffractometer. The electrical conductivity of polymer complexes were measured from AC impedance plots at different temperatures using Keithley 3330 LCZ meter. Scanning Electron Microscope (JEOL, JXA-840 Japan) was used for micro structural studies.

IV. RESULTS AND DISCUSSION

Spectral Studies

In order to obtain detailed information about the formation of the blend membranes, FT-IR spectra of the membrane were recorded. IR spectroscopy has several advantages for membrane studies. Firstly, variations in frequency, line width, and intensity are sensitive to structural transitions of membrane components. The Fig. 4 shows the FTIR spectrum of pure tapioca and PPEES. Fig. 5 shows IR spectrum of the Tapioca-PPEES membrane (50:50 Weight percentage). Following observed stretching frequencies confirms formation of blend membrane, 3600 - 3200 cm⁻¹ for O-H stretching vibrations, 2980-2880 cm⁻¹ for asymmetric and symmetric C-H. 1407 cm⁻¹ for asymmetric C-H bending deformation of methyl group, 1325 cm⁻¹ for symmetric C-H bending deformation [7], 1325-1298 cm⁻¹ for doublet resulting from asymmetric O=S=O stretching of sulfone group,

1242 cm^{-1} for symmetric C-O-C stretching of aryl ether group, 1148 cm^{-1} for asymmetric O=S=O stretching of sulfonate, 1010 cm^{-1} for symmetric O=S=O stretching of sulfonate group.

The vibrational peaks of tapioca are (1016,1641,2931 and 3417 cm^{-1}), and LiClO_4 (1366, 1378 and 2924 cm^{-1}) are shifted in the polymer electrolyte. Shifting of new peaks suggest the polymer-salt interaction in PEMA based gel polymer electrolytes.

X-RAY DIFFRACTION

Fig 6, shows the X- ray diffraction patterns of pure tapioca, PPEES and LiClO_4 . Fig 7 shows XRD pattern of [(X-50) tapioca - x PPEES] and - LiClO_4 with x =10 complexes respectively. The diffraction peak of pure

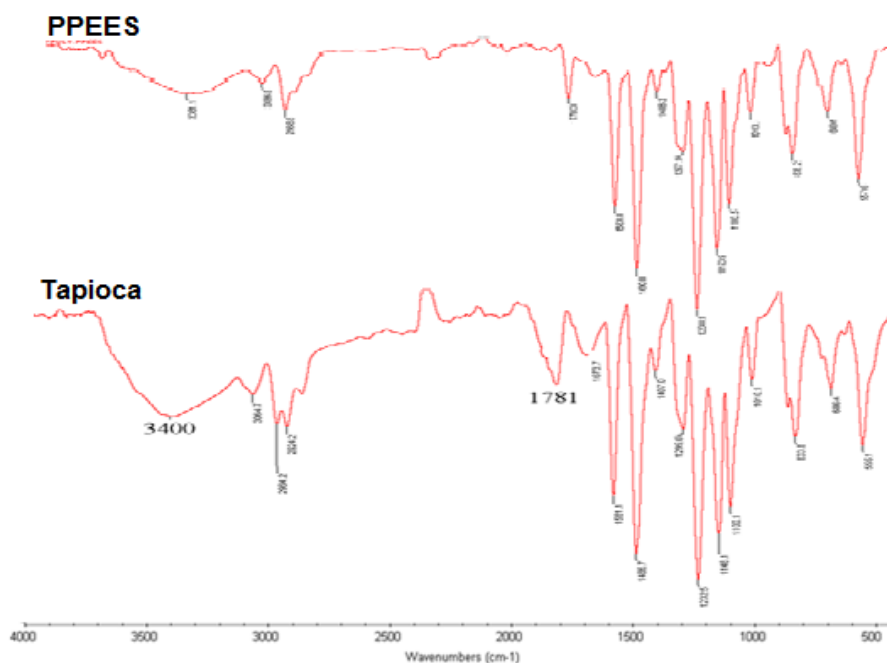


Fig 4 FTIR spectrum of PPEES and Tapioca

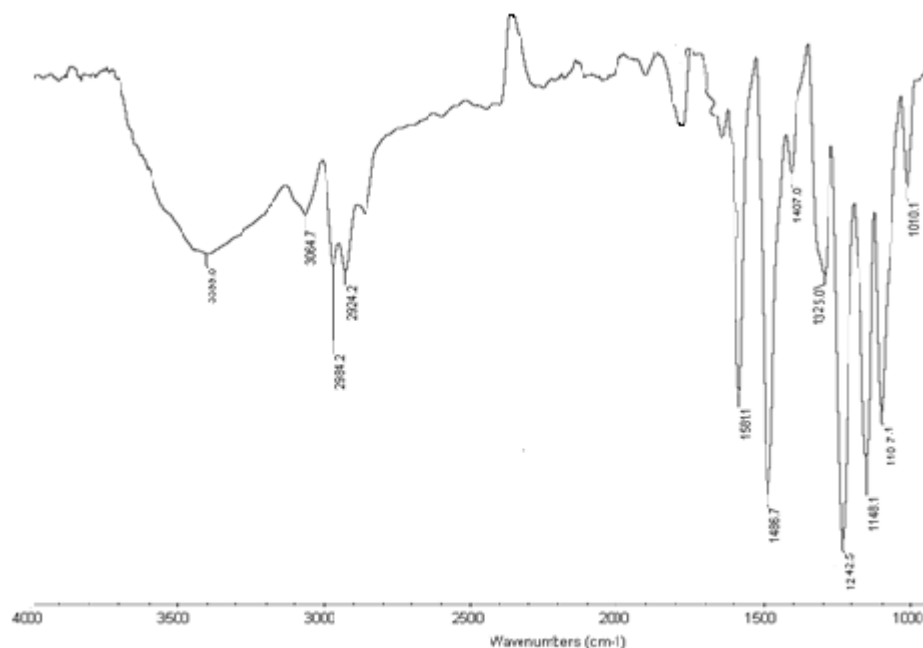


Fig 5 FTIR Spectrum of PPEES(50) and Tapioca (50)

tapioca was observed at $2\theta=17.1^\circ$ and that of PPEES at $2\theta=13^\circ$. In polymer complexes, these pure peaks of tapioca and PPEES appeared as one broad peak with less intensity. It may be due to the incorporation of LiClO_4 and, which would have disturbed the crystalline region and increased the amorphous phase. Diffraction pattern of the complexes reveal the amorphous nature, which is responsible for small increase in conductivity. These observations apparently reveal that the polymer undergoes significant structural reorganization while adding salt. No peaks corresponding to pure LiClO_4 were observed in the polymer complexes, revealing absence of excess salt in the polymer complexes.

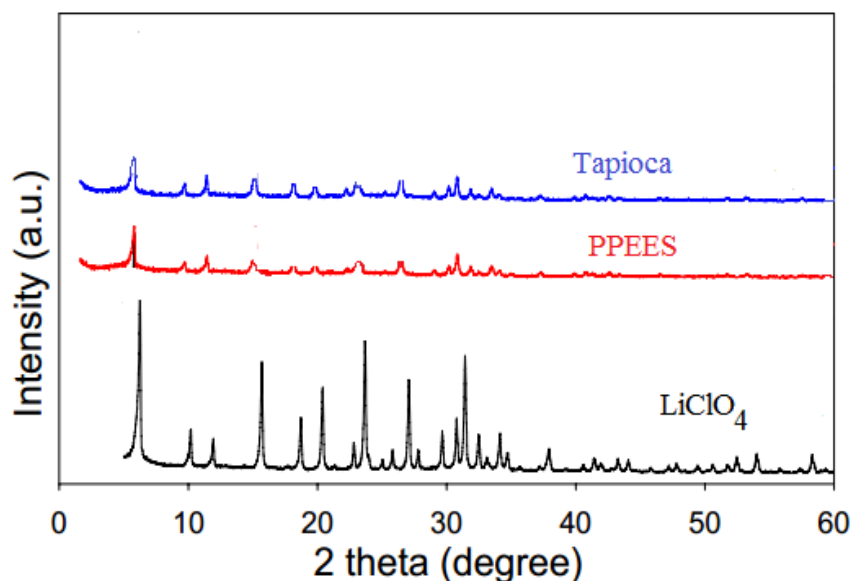


Figure: 6

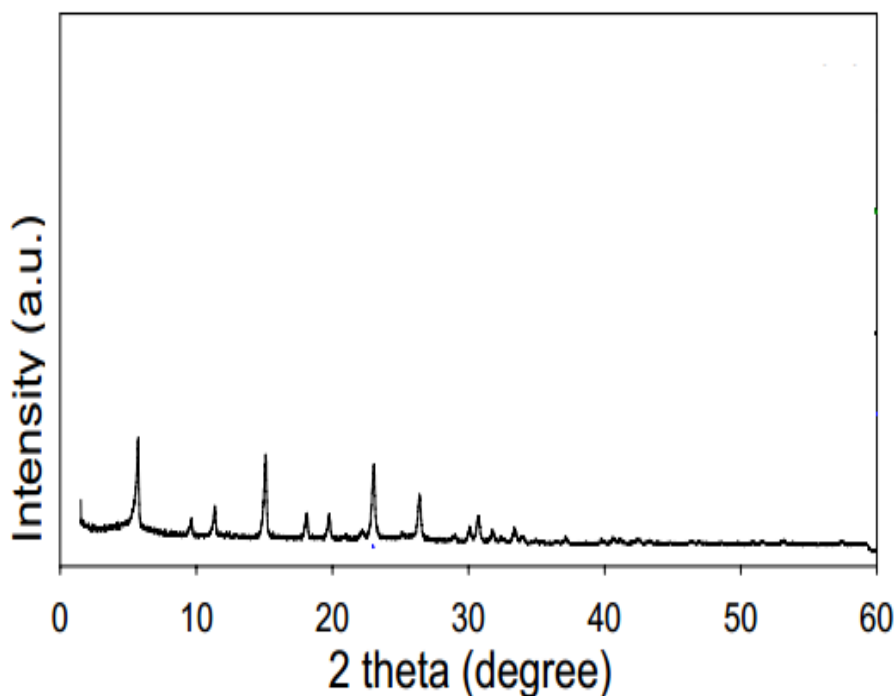


Figure: 7

V. SEM ANALYSIS

Fig 8, shows the SEM images of PPEES film and PPEES/Tapioca polymer electrolyte. The pores in the micrographs indicate the occurrence of phase-separation in the polymer electrolytes. The several pores or craters, which have formed on the surface, are due to the slow evaporation of the solvent (DMSO). The difference in the pore size is related with the difference in the driving force for phase separation [8].

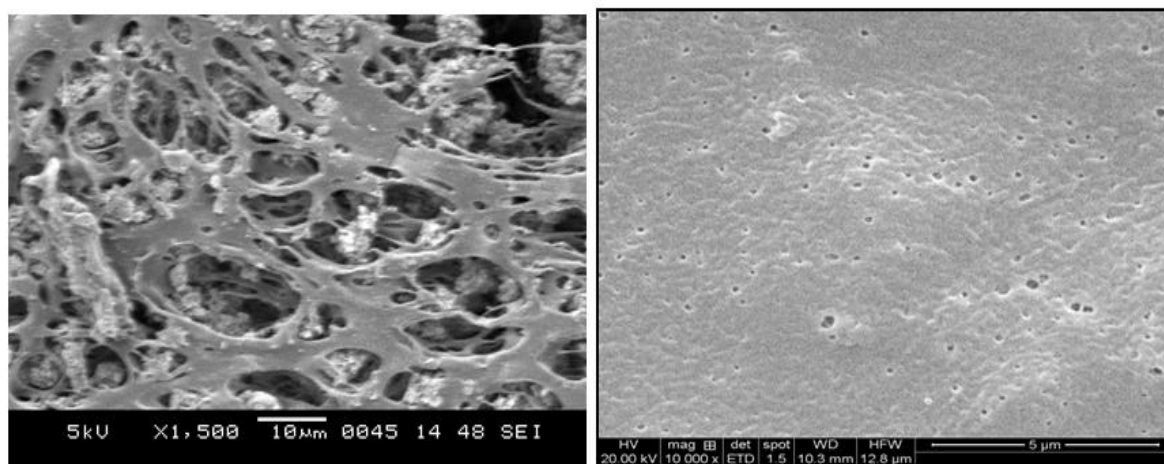
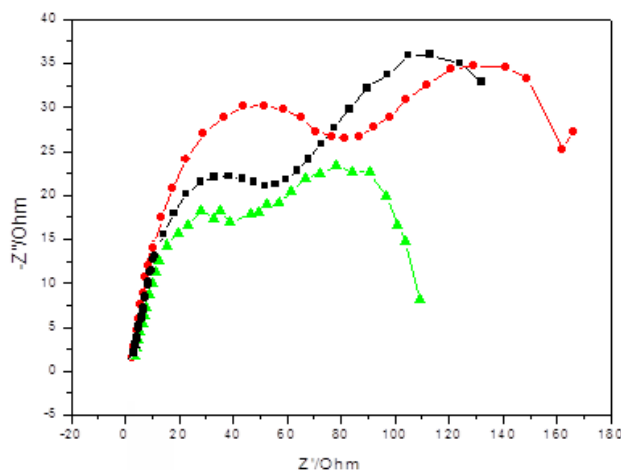


Figure: 8

V. CONDUCTIVITY MEASUREMENTS

The ionic conductivity of polymer electrolytes is calculated from $\sigma = l/RbA$, where 'l' the thickness of the film, 'A' the area of the film and R_b the bulk resistance of the material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance. Figure 9 indicates typical impedance plot of polymer electrolyte at room temperature. The existence of semicircular portion in the high frequency region of complex impedance plot indicates that the conduction due to the ions is very less [9]. The conductivity of Tapioca and PPEES are measured as 2.15×10^{-6} S/cm and 7.0×10^{-5} S/cm. The conductivity of Tapioca/PPEES/ LiClO_4 The conductivity increased to 9.0×10^{-5} S/cm. The conductivity of the polymer is increased.

Figure :9



VI. CONCLUSIONS

Tapioca based polymer electrolytes were prepared by solvent casting technique. The complex formation in Tapioca-PPEES- LiClO_4 system has been confirmed from XRD and FTIR studies. For the given composition electrolyte does not show appreciable conductivity at room temperature. The conductivity is in the order of 10^{-5} S/cm. For a good electrolyte the conductivity should be in the range of 10^{-3} S/cm at room temperature. The conductivity of the polymer electrolyte shows increment than the PPEES and Tapioca so by adding fillers and varying the composition the conductivity can be increased.

REFERENCE

- [1]. Polu A R and Ranveer Kumar Bull. Mater. Sci., Vol. 34, No. 5, August 2011, pp. 1063–1067.
- [2]. Rocco A M, Pereira R P and Felisberti M I 2001 Polymer 42 5199
- [3]. Chiellini E, Solaro R.: Biodegradable polymeric materials. Advanced Materials, 4, 305–313 (1996)
- [4]. Blagbrough IS, Bayoumi, S a L, Rowan, M.G., Beeching, J R, 2010. aPhytochemistry 71, 1940–1951.
- [5]. Chung, H.-J., Liu, Q., 2009. Carbohydrate Polymers 77, 807–815.
- [6]. Azlan AL, Isa MIN (2011 Solid State Sci. Technol. Lett. 18:124-129.

- [7]. T.Fahmy, M.T. Ahmed, Polymer testing 20 (2001)477.
- [8]. H.J. Rhoo, H.T. Kim, J.K. Park, T.S. Hwang, Electrochim. Acta 42(1997)15
- [9]. M.Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohbaki, J.Appl.phys. 57(1) (1985) 123.

