Journal of Non-Crystalline Solids 453 (2016) 131–140

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Review

Investigations on proton conducting biopolymer membranes based on tamarind seed polysaccharide incorporated with ammonium thiocyanate

M. Premalatha [a,b], T. Mathavan [a,*], S. Selvasekarapandian [b,*], S. Monisha [a,b], D. Vinoth Pandi [c], S. Selvalakshmi [b,d]

[a] Research Department of Physics, N.M.S.S. Vellaichamy Nadar College, Madurai, Tamilnadu 625 019, India
[b] Materials Research Center, Coimbatore, Tamilnadu 641 045, India
[c] Department of Physics, Coimbatore Institute of Technology, Coimbatore, Tamilnadu 641 014, India
[d] The Standard Fireworks Rajaratnam College for Women, Sivakasi, Tamilnadu 626 123, India

ARTICLE INFO

Article history:
Received 5 July 2016
Received in revised form 23 August 2016
Accepted 6 October 2016
Available online xxxx

Keywords:
Biopolymer
Proton conducting membranes
Ionic conductivity
TNM measurement
Electrochemical device applications

ABSTRACT

Naturally available materials such as biopolymers and polysaccharides have gained much attention in the development of polymer electrolytes due to its biodegradability, film forming nature and non-toxicity. The proton conducting biopolymer membranes have been prepared by polysaccharides, tamarind seed polysaccharide (TSP) with different concentrations of ammonium thiocyanate (NH_4SCN) as dopant. Distilled water has been used as a solvent and solution casting technique has been employed to prepare the biopolymer membranes. The prepared biopolymer membranes have been characterized by different techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), AC-impedance spectroscopy and transference number measurement (TNM). From XRD results, the crystalline or amorphous nature of the biopolymer membranes with increasing salt concentration (NH_4SCN) has been studied. The complex formation between the biopolymer-TSP and NH_4SCN has been investigated by FTIR analysis. The glass transition temperature of the prepared biopolymer membranes has been found using DSC technique. The highest conductivity is 2.85×10^{-4} S cm^{-1} for the composition of 1 g TSP: 0.4 g NH_4SCN at ambient temperature, which has been obtained by AC-impedance spectroscopic studies. The conduction of ions within the biopolymer membrane has been confirmed by TNM. The primary proton battery has been constructed with the highest conducting membrane 1 g TSP: 0.4 g NH_4SCN. Its open circuit voltage is 1.51 V. The discharge characteristics of the battery for a load 1 MΩ has been explained. The present investigation confirms that the NH_4SCN doped TSP biopolymer membrane has got the essential properties required for the electrochemical device applications.

Contents

* Corresponding authors.
E-mail addresses: tjmathavan@gmail.com (T. Mathavan), sekarapandian@rediffmail.com (S. Selvasekarapandian).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.10.008
0022-3093/

1. Introduction

In the modern society, the producibility of smart energy storage devices such as batteries, fuel cells and portable electrochemical devices from the renewable energy sources is most vital one. Solid polymer electrolyte (SPE) plays a central role in electrochemical devices and the development of SPEs becomes a thrust area, which offers simple sample preparation in different form, no leakage of electrolytes, higher conductivity, high mechanical stability and good adhesive properties than the liquid electrolytes. There has been plethora of research focusing on the development of polymer electrolytes using synthetic polymers as host. High cost and not "environmentally green" are the main two factors hindered the applications of synthetic polymer electrolytes. In that aspect, biopolymers have gained enormous attention as a result of white pollution, which overcomes the shortcomings of synthetic polymers. The three major classes of biopolymers are proteins, polyesters and polysaccharides. Polysaccharides are polymers composed of many monosaccharide units linked by glycosidic bonds. There are different sources for polysaccharides, which include plant seeds, plant cell wall, seaweed extracts, bacterial cell wall, plant roots tubers etc. Already few attempts have been done in the development of polymer electrolytes (PE's) using polysaccharides such as starch, cellulose, pectin, agarose, chitosan, carboxy methyl cellulose and carrageenan [1–8].

Tamarind seed polysaccharide (TSP) is one of the polysaccharide, which act as a cell wall storage unit in seed and can be obtained from the seeds of tamarind tree. TSP contains monomers of glucose, galactose and xylose sugars in the molar ratio of 3:1:2, which constitutes about 65% of the seed components [9–12]. In the TSP, main chain glucose is linked by β-D-1,4 glycosidic bond, side chains xylose are linked by α-D-1,6 glycosidic bond and galactose is linked by β-D-1,2 glycosidic bond. TSP is a tasteless, non-ionic, neutral, hydrophilic and highly branched polysaccharide in the form of white and light yellow freely flowable powder, which is soluble in hot water around 80 °C. Due to its excellent properties such as gelatinization, water-keeping, film forming etc., TSP used extensively as food gums. In food industries, TSP is used as an emulsifier and a stabilizer. The good thickening property of TSP makes is an excellent thickening agent for textile industries. Due to its soil stabilizing property, TSP is extensively used in mining industries. TSP also used as a dissolution improvement in pharmaceutical applications and in manufacture of bioadhesive tablets.

Literature survey reveals that in the electro chemical device applications, there has been no work using TSP as host polymer. Hence, the present work aims to develop a new type of proton-conducting biopolymer membranes using TSP as a host polymer with the different concentrations of ammonium thiocyanate (NH_4SCN) as an ionic dopant, since ammonium salts are reported as a good proton donor to the polymer matrix [13–16], as one of four proton attached to Nitrogen atom is loosely bound. The loosely bound proton by hopping mechanism moves in the polymer network. Daniel et al., has studied Poly (Ethylene Oxide) or Poly (Acrylic Acid) with NH_4HSO_4 electrolytes. Srinivas Reddy et al., has developed poly (ethylene oxide) complexed with tetra-methyl-ammonium bromide. Arof et al., has studied Phthaloyl chitosan (PhCh) doped with NH_4SCN. They all reported that proton conduction in their samples is due to the loosely bound proton of attached ammonium ion [17–19]. The prepared TSP based biopolymer membranes have been characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), AC-impedance spectroscopy and transference number measurement (TNM).

2. Experimental

TSP was purchased from Tokyo Chemical Industry, Japan. NH_4SCN was purchased from Thermo Scientific, Mumbai. The biopolymer membranes were prepared by solution casting technique using distilled water as a solvent. 1 g of TSP was dissolved in hot water around 80 °C. After the dissolution of TSP, various concentrations of NH_4SCN (0.35, 0.375, 0.4, 0.425 and 0.45 g) were added to it. The mixtures were stirred using magnetic stirrer. After several minutes, highly viscous and homogeneous solution was obtained. Then the homogenous solution was poured into polypropylene petri dishes and kept in oven at 60 °C to evaporate the solvent. After 24 h a transparent thin films of thickness ranging from 0.10–0.12 mm were obtained. Fig. 1 illustrates the photograph of the transparent thin film of pure TSP.

The XRD diffractograms of the prepared biopolymeric membranes were recorded using XPERT-PRO diffractometer at 2θ angles between 10°–80° with Cu Kα radiation at 40 kV and 30 mA. SHIMAZDU IR Affinity-1 spectrometer has been used for FTIR measurement in the wavenumber region of 4000–400 cm^{-1} with the resolution of 1 cm^{-1}. The DSC thermograms of the prepared biopolymer membranes were recorded by DSC Q20 V24.10 Build 122 at a heating rate of 10 °C/min

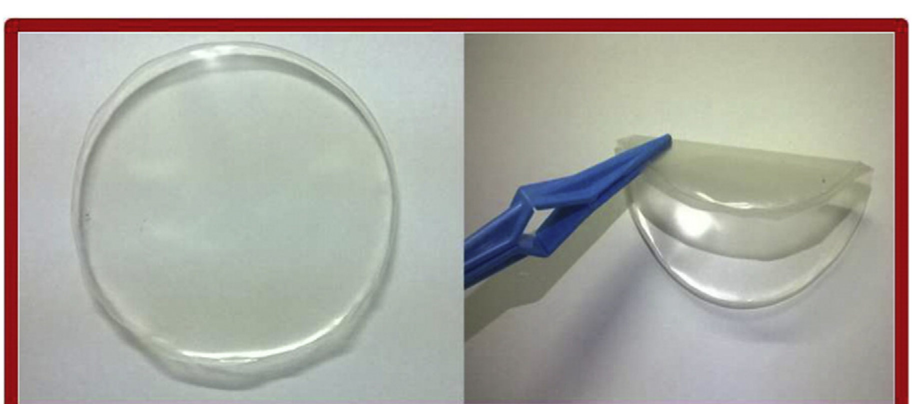

Fig. 1. Photograph of the transparent thin film pure TSP biopolymer membrane.