



Study of Aloe Vera as a Natural Plasticizer in PEO based Polymeric Electrolyte

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ABSTRACT

Development of biodegradable natural polymers, open the enormous field of applications in the area of technical as well as medical science. Today, various natural polymers have been utilized in different biomedical applications. Aloe vera is one of them. Synthesis of PEO- Lithium acetate composite polymer electrolyte with organic and natural plasticizers shows the better thermal stability and ionic conductivity. The electrolyte film was synthesized by solution cast technique. Changes in structural morphology have been observed using XRD and FTIR technique. Variation of electrical conductivity with temperature was studied with the aid of impedance spectroscopy.

Key words: Polyethylene oxide (PEO), Polymer salt complexation, Natural Plasticizer, Aloe vera gel, NCPEs

INTRODUCTION

The field of polymer has become a driving force in the advances in different technology with the emergence of the 21st century. This requires the availability of solid polymer electrolyte films with adequate conductivity, good mechanical property, electrochemical stability and ease of processing. The most commonly studied solid polymer electrolyte membranes are complexes of different salts with a high molecular weight polyethylene oxide (PEO). PEO is a double helical chain structure and low conductivity polymer [1-3]. To enhance the conductivity and mechanical thermal strength numerous methods were tried by the researcher [4-5]. Addition of different salts, filler and plasticizers in polymeric host, tries to enhance their conductivity [6]. To enhance the ionic conductivity of PEO based electrolyte an easily dissociable lithium acetate (CH₃COOLi) salt is used for the facilitation of Lithium ion as mobile charge carrier. In the development of solid state polymer electrolyte plasticization is a better approach. The purpose of plasticization is to enhance the thermal, mechanical and electrical conductivity. Mostly studied synthetic plasticizers are of low volatile, low molecular weight substances. Recently, study show that some natural substances could be used as plasticizers for the polymeric materials. [7-8] The use of natural plasticizer with low toxicity and good compatibility in several polymer applications has become more attractive.[9-10] Natural plasticizers have aroused a lot of interest in view of its applications in the industrial and biomedical sectors[11-12]. The primary role of such substances is to improve the flexibility and processability of polymers. Recently various natural, biodegradable polymers are tried. An innovative approach has been made to use Aloe Vera gel as a natural plasticizer, in development of PEO –lithium acetate electrolyte membrane.

Aloe Vera is a member of Liliacea family. It is popular as medicine from long time. The first document record, show aloe was used date back to 1552 BC. In 14AD, the Greek physician Dioscorides's medical log – De Materia Medica –describe aloe as “an effective purgative” but also suggested its ability to heal[13-15].

It is a succulent plant species. The leaves are thick and fleshy, green to grey-green. The margin of the leaf is serrated and has small white teeth. The plant Aloe Vera is used in Ayurvedic, Homeopathic and Allopathic streams of medicine, and not only tribal community but also most of the people use it for food and medicine. The plant leaves contain numerous vitamins, minerals, enzymes ,amino acids, natural sugars and other bioactive compound with emollient, purgative, anti-microbial, anti-oxidant, anti-inflammatory, anti-fungal, anti-septic and cosmetic values for health care. This plant has potential to cure sunburns, burns and minor cuts and even skin cancer. The

external use in cosmetic primarily act as a skin healer and prevents injury of epithelial tissue, cures acne and gives a youth glow to skin, also act as a extremely powerful laxative. Aloe vera in its inner gel contains number of amino acids minerals and vitamins But majority of it contains carbohydrates mainly glucomannas (galactose) and polymannas predominant sugar [16-17].

In this paper we study the effect of Plasticizers on the structural and ionic behavior of the PEO + Lithium acetate electrolyte using the different experimental tools. [Natural Plasticizer (Aloe Vera) and Organic Plasticizer (Ethylene Carbonate or EC + Propylene Carbonate or PC)].

EXPERIMENTAL

Composite polymer electrolyte film 90[60 PEO – 40 AV/(EC+PC)] :10 { Li (CH₃COO)} were prepared using solution cast technique. The Poly (ethylene oxide) PEO (mw-6 x 10⁵ ACROS Organics) and salt Lithium Acetate [(CH₃COO Li) or LiAc] (Rankem India, AR grade) were used to synthesize the composite electrolyte. The extracted Aloe Vera gel was dispersed stoichiometrically in host polymer. To get the AV gel leaves were collected and processed from a single garden plant. The process of gel extraction is similar to others [18].

PEO – Aloe Vera gel (in the stoichiometric ratio) was dissolved in double distilled water (40°C) with CH₃COO Li Salt composition was ball milled for 5hrs (in Agate Vessel with 4 Agate ball). This gelatinous polymeric solution was finally casted in polypropylene dish. This film was dried in BOD incubator for controlled evaporation followed by Vacuum drying to obtain the solvent free standing film.

Structural behavior of these polymeric system were studied by X-ray diffractometer (Phillips X-pert model) in the Bragg's angle (2θ) 15-60° using Cu- α radiation ($\lambda=1.542\text{\AA}$).the SEM Image of different composite electrolyte systems were recorded with JEOL JXA-8100EPMA instrument. Infrared spectrogram (Bruker Alpha Infrared Spectrophotometer, Germany) were used to investigate the complexation behaviour. The electrical characterization of the solid polymer composite electrolyte was carried out using Impedance spectroscopy (HIOKI LCR Hi Tester, model 3522, JAPAN)on the application of small a.c. signal (~20mV)across the sample cell with Pt-blocking electrode. Dielectric relaxation behaviors were carried out by the impedance data.

RESULT AND DISCUSSION

XRD curve of 90[60 PEO – 40 (AV/EC+PC)] :10 {Li (CH₃COO)} is shown in Fig. 1. In inset we present the PEO-AV X-ray structural curve. This curve clearly shows the amorphous nature of the modified polymeric matrix. But with the salt and plasticizer, PEO matrix retains the original nature and both characteristics appear clearly. The other peaks at 15.5°, 26° and 31° are the signature peaks of lithium acetate. Comparative studies of both XRD pattern shows that the polymeric film containing the Aloe Vera plasticizer has relatively small and broader peaks than the synthetic plasticizers. The peak at 19.2° and 23° show sharp singlet and triplet peak with EC/PC combination in composite polymer electrolyte. After the replacement of synthetic plasticizer with natural plasticizer few peaks (18.6°, 22.1° and 22.6°) are reduced drastically, some merges together and their area increases (shown in inset of Fig. 1). This alteration behavior suggests the natural plasticizer based polymer composite system become more amorphous than organic plasticizer modified matrix. The calculated average crystallite size in Aloe vera based composite electrolyte system is 67nm.

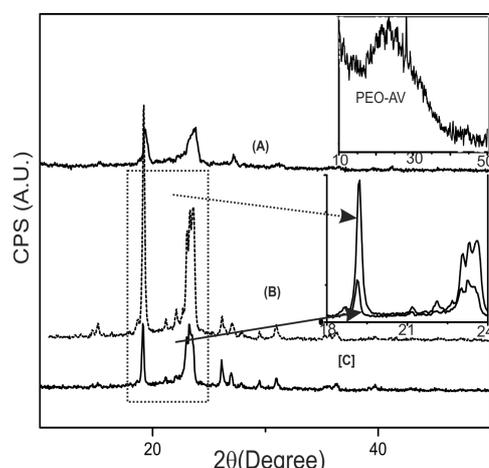


Fig. 1 XRD spectra of natural and organic plasticized polymer electrolyte system. In inset (up) PEO-AV system and (in middle) enlarged view of characteristic peaks of composite film

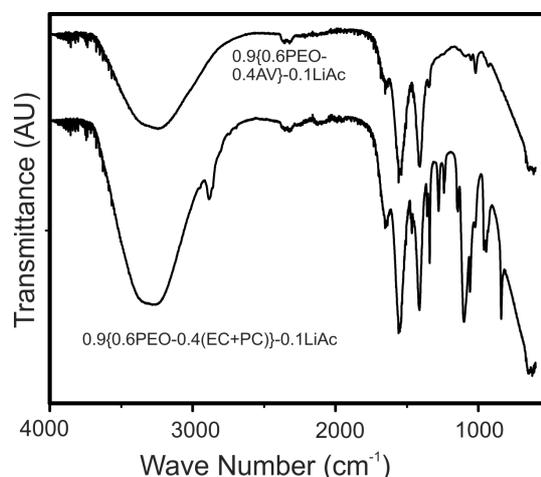


Fig.2 FTIR Spectra of Natural and organic plasticized polymer electrolyte

Infrared spectrum of 90[60 PEO – 40 (AV/EC+PC)] :10 { Li (CH₃COO)} electrolyte films are shown in Fig. 2. Some peaks related to skeleton vibration of salt with deformation and bending vibration are appearing in the lower wavenumber region. In 90[60PEO–40(EC+PC)]:10 (CH₃COO Li) the presence of plasticizer increases the frequency of vibration of polymer chain, which facilitates more flexibility. A comparative study of the FTIR spectra of synthetic and natural plasticizer polymer composite system shows the disappearance of some prominent peaks in AV based systems. These peaks are 841,932 and 962 cm⁻¹ related to the ring breathing modes of the propylene carbonate [19]. Similarly, peaks at 1060cm⁻¹(-C-O band of EC),1340 cm⁻¹ and 1410 cm⁻¹ attributed to the band C=O stretching bond of EC and -C-O- of organic carbonate completely vanished in the natural plasticizer based electrolyte. The polymer salt interaction is evidenced from the shift in 1561cm⁻¹ peak related to O=C band of lithium acetate. Other prominent peaks in 90[60PEO-40AV]:10Li (CH₃COO) electrolyte film, are absorption peaks at 943cm⁻¹ due to C=O deformation. The peaks at 1571cm⁻¹ and 1409 cm⁻¹ related to the C-O asymmetric stretching and C=O / C-O symmetric stretching are recorded respectively. This implies that the role of plasticizer is more helpful in improving the interaction of polymer/salt in composite system. In the aloe vera plasticized polymer system the absence of different functional groups, give the information regarding the better flexibility of the modified polymer chain.

In order to examine the effect of plasticizer on PEO-LiAc electrolyte system, we checked the electrical conductivity of all four electrolyte systems at room temperature. The conductivity (Fig. 3) of PEO-AV system is very low but the conductivity of PEO-LiAc system is significantly high [20]. The room temperature conductivity of 90[60PEO-40(EC+PC)]+10 LiAc and 90[60PEO-40AV]+10 LiAc are 1.56×10^{-6} S/cm and 4×10^{-5} S/cm respectively. The higher conductivity of aloe vera based system is due to interaction of lithium ion (Li⁺) with the oxygen of PEO and H-bonding between saccharides of PEO- AV in the nanocomposite polymeric film (Fig. 4). Here, it can be notified that the increase in the salt leads to the increase of the charge carrier and hence the ionic conductivity of the system increases. The variation of electrical conductivity with temperature of all four systems is shown in Fig. 3. The electrical conductivity of 90[60PEO-40(EC+PC)]+10 LiAc system is higher than pristine at room temperature, but its increase with temperature is slow, after 70°C sudden increase is due to phase transition of PEO. Finally conductivity decreases after 100°C due to melting of polymer matrix.

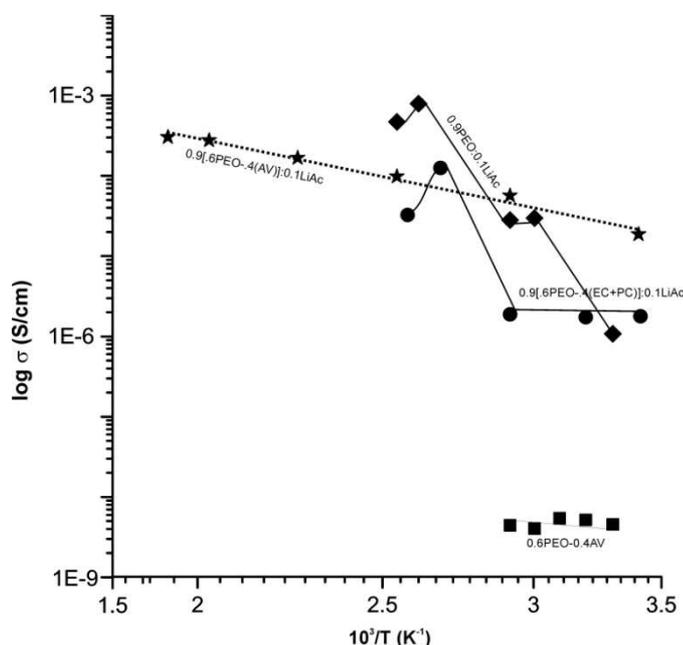


Fig.3 Variation of electrical conductivity with temperature of different electrolyte systems

In the NCPE system 90[60PEO-40AV]+10 LiAc, conductivity is maximum at room temperature among the all four systems. The increase in temperature show the linear behavior upto 230°C and follows the Arrhenius type thermally activated process. In other case, the behavior of increase in conductivity with temperature is explained by VTF type nature as described by the following relation [21].

$$\sigma = \sigma_0 \exp(-B/T-T_0)$$

Where σ_0 is the pre exponential factor, B is constant related to activation energy and T_0 is reference temperature associated with ideal T_g . This is possibly due to the pre melting of the polymer and uneven complexation with host matrix.

The high ionic conductivity of solid polymer electrolytes is mainly governed by two important factors, are ion conducting species concentration and the charge carrier mobility, along with the type of charge carriers (cationic/anoic) and temperature.

Improvement in conductivity could be due to the complexation and the formation of a new polymeric system through H-bonding with in the polymeric lattice (shown in Fig. 4). Lithium ions (Li^+) have enough energy to form chain of polymer until all the segments of the polymer are fully occupied by the complexation process. The other possible reason is the hydration power of Li^+ cation is very high, therefore it can be assumed that the Li^+ cations present in the interlayer of the polymeric membrane would be hydrated, in addition to the weakly bonded water molecules within the layers. The intercalations of Li^+ ions within the interlayer spacing of PEO-LiAc-AV migrate into the membrane and neutralize the layer charge. This may have been due to the fact that some regions within the interlayer spacing have been occupied by hydrated Li^+ cations involved in H-bonding with the polymeric membrane. However, at higher temperatures water get removed. This eliminates the possibility of protonic conductivity due to the presence of water molecules. PEO gets easily intercalated into the interlayer spacing of AV. PEO molecules are bonded to the layers of AV pulp, and Li^+ cations. The overall results thus showed that the conductivity of solid polymer electrolyte membrane is mainly due to the Li^+ cation and not due to water molecule. The modified matrix is thermally stable upto 230°C which means that aloe vera is better plasticizer than combination of EC and PC for polyethylene oxide.

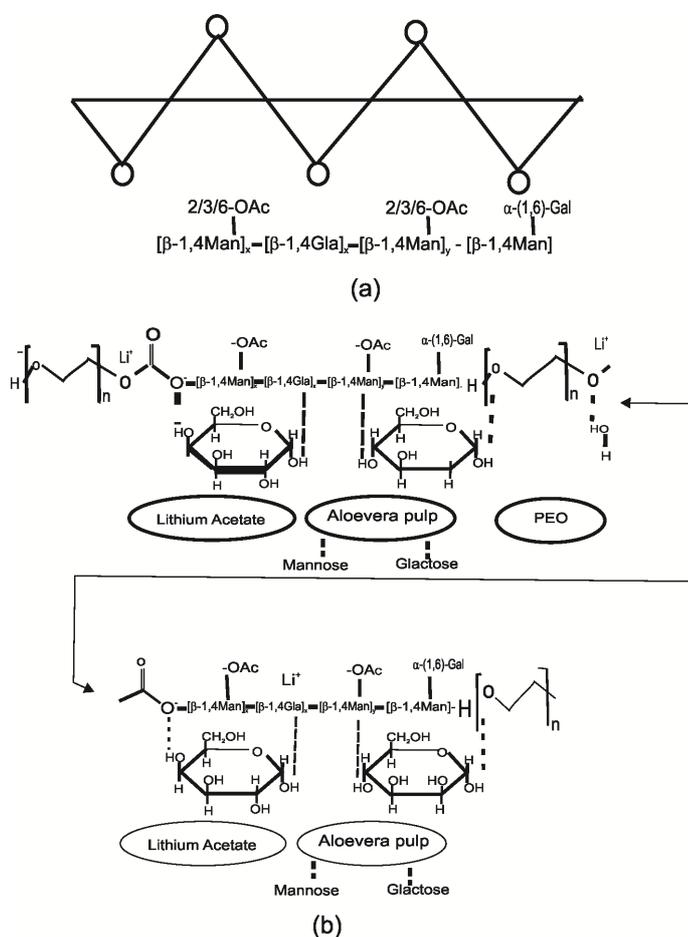


Fig.4 Systematic representation of PEO-AleoVera gel -LiAc interaction in polymeric membrane

CONCLUSIONS

This paper reports the comparative study of structural and ionic behavior of the two plasticizers used in PEO-LiAc electrolyte system. The Aloe vera gel plasticized electrolyte show much better modification in the polymer matrix, which leads to the better polymer salt interaction, more flexibility (or good amorphosity), higher electrical conductivity and thermal stability upto 230°C (usually polyethylene based electrolytes are thermally stable maximum up to $130-150^\circ\text{C}$).

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