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Ionic Conductivity of Biopolymer Electrolyte Based on Pva/Cs Polymer Blend with Ionic Crosslinking

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Abstract
Biopolymer electrolytes are currently attracting a great deal of attention as substitute for synthetic polymers, or mixing of biopolymer and synthetic polymers in electrochemical devices, as they are cost effective and eco-friendly. In this research the Chitosan/PVA blend polymer electrolyte film was doped in KNO_3 by solution casting method, we aimed to enhance the electrical conductivity of chitosan(CS)-Polyvinyl Alcohol(PVA) blend crosslinking with Potassium nitrate (KNO_3) as ionic crosslinker. The blending of CS-PVA along with calcium chloride as crosslinking agent was confirmed by X-ray Diffractometer (XRD). The ionic conductivity of the films was increased with the increase in frequency for all synthesized samples which showed an increase in the number of effective charge carriers. The dielectric constant and dielectric loss are exponentially decreases with increase of frequency for chitosan (CS)-Polyvinyl Alcohol (PVA) blend doped with potassium nitrate as crosslinker.

Keywords: *Chitosan-Polyvinyl Alcohol blend, Poatssium nitrate and Ionic crosslinking of films.*

I.INTRODUCTION

Chitosan (Cs) is derived from chitin found in the exoskeleton of insects, shells of crustaceans or various fungi. Chitin and chitosan have tremendous applications in the biomedical field due to their good biocompatibility, biodegradability, and capacity to form membranes, beads, fibers, scaffold and gels [1–6]. Chitosan inhibits the growth of a wide variety of fungi, yeasts, and bacteria. Chitosan also represents interesting properties such as excellent film forming capacity and gas and aroma barrier properties at dry conditions, which makes it a suitable material for designing food coatings and packaging structures [7].

Polymer electrolytes (PE) have been extensively studied because of their potential application in electrochemical devices. PE is defined as a solvent-free system whereby the ionically conducting pathway is generated by dissolving the low lattice energy metal salts in a high molecular weight polar polymer matrix with aprotic solvent [8]. A lot of polymers have been used as a host in solid polymer electrolyte such as polyethylene oxide (PEO), polyvinyl pyrolidone (PVP), polyvinyl alcohol (PVA) and polyvinylidene fluoride (PVDF). Scientists are currently actively looking for alternative polymer host with improved conductivity and mechanical properties as well as being cost effective and environmentally friendly. Starch is a polysaccharide composed of amylose and amylopectin. It is a natural polymer that is non-toxic, available in abundance, biodegradable and renewable, When comparing the solid polymer electrolyte to gel and liquid type, solid polymer electrolyte possess some advantages such as leakage-free and also has a simple preparation[9-10]. But it main drawback such as low in conductivity value gives an obstaclefor researchers to produce high quality polymer electrolyte with good ionic conductivity[11], which then give a space forresearchers to study and search on the best solution. There are many attempts has been made to enhance the conductivity of PE system, such as copolymerization[12-13], plasticization, blending, reduction of crystallinity, addition of unusual or inorganic salts, varying the salts concentration and addition of ceramic filler/additives[13.]

Blending technique was proposed in this work and it is believed could enhance the conductivity and improved structural stability of the electrolyte films[14]. From the polymerist point of view. polymer blend is a mixture or combination of at least two macromolecular substances, polymers and copolymers[15-18].

From the literatures, there is no report so far suggesting CMC and CS blend as natural polymer electrolyte film. In facts, organic polymer is usually known as insulator based in electronic component which gives the lowest ionic conductivity value (10^{-12}-10^{-18})[19]. With the blending technique applied to the system, it can enhance the conductivity value to the range of 10^{-8} Scm^{-1} though it is still cannot satisfy the conductivity requiredfor electrolyte in battery system. However, with the incorporation of dopant it is believed could further increase the conductivity value. Most of the previous reports show that the conductivity increase after the addition of salts into the polymer host, for example, 10^{-6} Scm^{-1} for PVC/ PEO-KBr salt[20], 10^{-7} Scm^{-1} for PEO/PVP-NaBr salt[21] and $10^{-6}Scm^{-1}$ for CS/PVANH4I salt[22].

II.MATERIALS AND METHODS

Shrimp source Chitosan in a form of white flaks with a degree of deacetylation of 88.1% defined by UV method [23] was obtained from commercial source. Polyvinyl alcohol was purchased from Sigma Chemicals Co. (UK).). Potassium nitrate was purchased from Merck (Germany). Cs was prepared by dissolving 5 g of chitosan in 500 mL of acetic acid (0.1 M) followed by stirring and heating at 60ºC for 14 to 16h and PVA powder was dissolved in preheated ultra pure water followed by stirring at a temperature of 90ºC for about 2 hours until clear solutions were obtained.The prepared CS-PVA (50-50)blend, were ionically crosslinked using the method described by Huang et al. [24]. The dried of CS-PVA (50-50) films were immersed in a different weight percentages of Potassium nitrate in aqueous Methanol solution, as shown in Table 1.

Table 1 - CHITOSAN-PVA blended films with different composition of ionic crosslinker,

Sl.no	Films designation	Potassium Nitrate (grams)	Methanol (ml)
01	CHITOSAN/PVA(50/50) blend	0.1	20
02	CS/PVA(50/50)	0.2	40
03	CS/PVA(50/50)	0.3	60
04	CS/PVA(50/50)	0.4	80
05	CS/PVA(50/50)	0.5	100

III.EXPERIMENTAL RESULTS:

3.1: XRD STUDIES:

X-ray diffraction patterns were analyzed for the films dried naturally in room temperature by Rigaku X-ray diffractometer. The X-ray source was Ni-filtered Cu K_ radiation (40 kV, 30 mA). The film sampleswere scanned from10◦ to 60◦ 2θ at a scanning rate of 3◦ min−1.X-ray patterns of chitosan and chitosan–PVA blend are shown in Fig. 1. The diffraction peak of chitosan is at around 10◦ and 20◦ of 2θ Chitosan exhibited the major crystalline peak at 2θ= 20º in agreement with the literature values [25]. Additional diffraction peaks are seen at the regions 2theta= 37º, 43º, 64º and 77º indicative of a clear structural change in chitosan as a result of blending with polyvinyl alcohol. On hydrolysis to alcohol, the intensity of all the peaks was enhanced, this may be due to the comparatively high crystalline nature of the chitosan-poly(vinyl alcohol) blend. This confirms that blending has been done .similarly the CS-PVA blend is crosslinked with 0.1,0.2,0.3,0.4 and 0.5g of Potassium nitrate(KNO_3) which is shown below. These figures shows one broad and one small peaks at around 20º and 41º,indicating that crosslinkimg has been done successfully.from the number of peaks observed, it was concluded that, the CS-PVA blend has higher crystalline nature whereas the CS-PVA blend with potassium nitrate as crosslinking agent has amorphous nature and its crystallanity is decreases with increasing the crosslinker ratio to the CS-PVA blend[26].

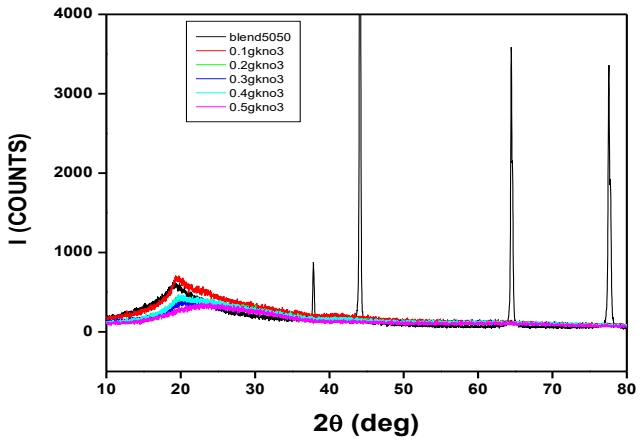
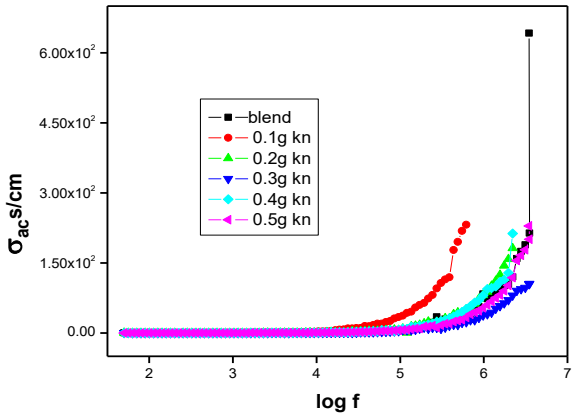


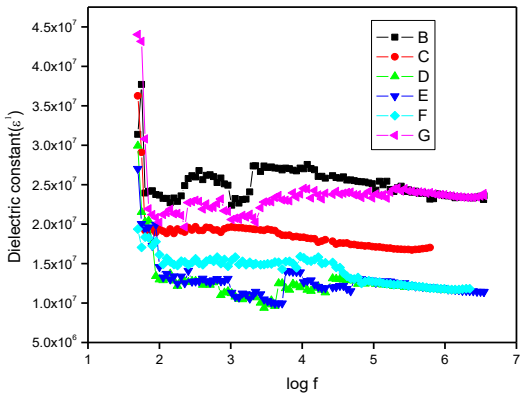
Fig. 1 -XRD graph of CS-PVA blend(50-50) and its corresponding crosslinked film with varying ratios of ionic crosslinker.

3.2: IONIC CONDUCTIVITY STUDIES:

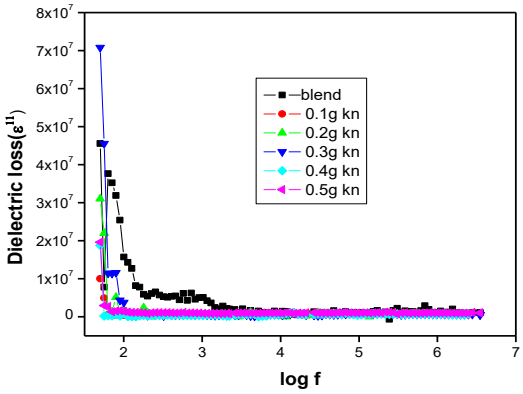
Figure 2(a) illustrates the ionic conductivity of the prepared CS-PVA blends with various amount of KNO_3 against the frequency. From this Figure it can be clearly seen that the polymer electrolytes exhibit Arrhenius behavior, this linear relationship shows that the ionic conductivity is thermally activated. Figure 2(b) and (c) represents the variation of εr and εi with frequency for CS-PVA blend systems with various percentages from 0.1g to 0.5g KNO_3 dopants, which clearly show both dielectric constant and dielectric loss values rise sharply towards lower frequency side indicating the presence of electrode polarization and space charge polarization of charges by the accumulation of charges at electrode-electrolyte interface and confirming non-Debye behaviour of the polymer electrolytes[27]. Whereas, εr and εi decrease with increasing frequency as the periodic reversal of the electric field occurs so fast that there is no time for accumulation of charge at the interface.The ionic conductivity of the films was increased with the increase in frequency for all synthesized samples which showed an increase in the number of effective charge carriers. The dielectric constant and dielectric loss are exponentially decreases with increase of frequency for chitosan (CS)-Polyvinyl Alcohol (PVA) blend doped with potassium nitrate as crosslinker.



(a)



(b)



(c)

Figure 2: (a) conductivity of CS-PVA blend along wwith different percentages of ionic salts, (b) dielectric contant of CS-PVA blend along wwith different percentages of ionic salts, (C) Dieletric loss E of CS-PVA blend along wwith different percentages of ionic salt.

IV.Conclusions

XRD,studies were performed for CS/PVA blend and CS/PVA/KNO3 crosslinked polymer in order to examine the structural and behavior of the films. The prepared new ductile materials with the addition of crosslinker Potassium nitrate has increased in conductivity [27] shown in Fig (3) .The ionic conductivity of the films was increased with the increase in frequency for all synthesized samples which showed an increase in the number of effective charge carriers. The dielectric constant and dielectric loss are exponentially decreases with increase of frequency for chitosan (CS)-Polyvinyl Alcohol (PVA) blend doped with potassium nitrate as crosslinker, hence chitosan based film by blending and crosslinking with polyvinyl alcohol and Potassium nitrate in order enhance the conductivity of mechanical chitosan biopolymer. This modified chitosan film may be a promising material Biomedical and electro chemical device applications.

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