Characterization of Proton Conducting Carboxymethyl cellulose/Chitosan Dual-blend Based Biopolymer Electrolytes

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Abstract. This article presents the discovery on biopolymer electrolytes comprising of ammonium nitrate, NH\textsubscript{4}NO\textsubscript{3} with dual-blend biopolymer materials, carboxymethyl cellulose/chitosan which were prepared via solution-casting technique. The biopolymer blend based electrolyte films were characterized by Fourier Transform Infrared spectroscopy to investigate the formation of the dual-blend biopolymer based complexes. X-Ray Diffraction result showed that all dual-blend samples were predominantly amorphous. Electrochemical impedance spectroscopy was conducted to obtain their ionic conductivities. The highest conductivity at ambient temperature of 1.03 \times 10^{-5} \text{ S cm}^{-1} was obtained for the electrolyte film containing 40 wt\% of NH\textsubscript{4}NO\textsubscript{3}. These results indicated that the dual-blend biopolymer based electrolyte has potential for application of electrochemical devices.

Introduction

Solid polymer electrolytes (SPEs) are of immense interest as potential components in storage devices such as batteries and smart windows [1] due to their low cost of production, remarkable properties of free from volatile as well as their potential flexibility and moladability. SPEs also possess the advantage of their unique properties such as ease of fabrication into thin film with large surface area to give high energy density, ability to accommodate a wide range of ionic salts doping compositions, good electrode-electrolyte contact and high ionic conductivity [2]. Furthermore, the use of all solid polymer electrolytes would overcome the limitations of liquid electrolytes, negate the need of separator and be processed easily [3]. Polymer blends have received great interest in recent years as it is an economical technique to develop new polymeric materials with superior properties. It is the cheapest and easiest to obtain new polymeric materials compared to developing new polymers. However, the properties of materials produced by this technique depend on the degree of miscibility of the polymers [4]. No phase separation between the two polymers indicates that the blends are miscible [5]. Besides that, it has been reported that the polymer blend electrolytes exhibited high conductivity [6,7] and good mechanical strength [8-10].

Currently, most of host polymer investigated are petroleum based polymers which are non-biodegradable and harmful to our environment. Natural polymers such as cellulose, chitin, starch and chitosan for example act as alternative materials to commercially available petroleum based polymers. Carboxymethyl cellulose (CMC) and chitosan (CS) are abundantly available polymers which have good film forming property, can form transparent films and possess good mechanical strength [11]. Both polymers are non-toxic, renewable, biocompatible and biodegradable [12]. CMC contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, and hence shows amphiphilic characteristic. In general, cellulose is made up of glucose rings connected by \(-\text{C(1)}-\text{O}-\text{C(4)}\) ether bonds known as \(\beta-1,4\) glycosidic linkages with extensive intramolecular hydrogen [13,14]. Meanwhile, CS is one of the polymer that has a high degree of N-deacetylated form of chitin; a naturally abundant mucopolysaccharide that serves as supporting material of
crustaceans, insects and others [15]. Chitosan is an odourless, flabby powder or flake whose color varies from yellow to white, that can be easily dissolved in some inorganic and organic acids. It has numerous unique properties include polyoxysalt formation, ability to form films, chelate many metal ions, contain reactive amino and hydroxyl groups and possess novel optical and structural characteristics [16] that make chitosan a good host polymer for solid state electrolyte. Besides that, it is insoluble in either water or organic solvents and can be dissolved in hydrochloric acid and aqueous organic acids such as formic, acetic, oxalic, and lactic acids. The solubility of chitosan depends on the concentration and type of acid.

In this work, the structural, amorphousity, and electrical properties of biopolymer dual-blend, CMC/CS impregnated with ammonium nitrate have been investigated. These biopolymer blend electrolytes are hoped can replace commercial polymer to sustain green world in the future.

**Experimental**

**Sample preparation**

CMC (Acros Organic Co.) and CS (W.A. Hammond Drierite Company Ltd.) were dissolved in 1% of acetic acid solution. Solution casting technique was employed to obtain films with varied amount of ammonium nitrate concentration (10-50 wt. %). Pure dual-blend film without dopant was also prepared as a control. In a clean beaker, weighted amounts of CMC and CS powder with 2:1 ratio with NH₄NO₃ crystals (purity 99%) were dissolved in 100 ml of 1% acetic acid at room temperature. Complete dissolution was achieved after 24 hours stirring at room temperature using magnetic stirrer. The final light yellowish solution was then poured into separate Petri dishes and left to dry in an oven to form yellowish transparent thin films. Dual-blend biopolymer electrolyte films were transferred to a desiccator for further drying prior to characterization. Fig. 1 shows the photograph of yellowish-transparent film of CMC/CS-NH₄NO₃ biopolymer electrolyte.

![Photograph of yellowish-transparent film of CMC/CS-NH₄NO₃ biopolymer electrolyte.](image)

**FTIR spectroscopy.** The FTIR measurement was performed by using Thermo Nicolet 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory and a germanium crystal. The samples were placed onto germanium crystal and infrared light will be passed through the sample in the range of 700 cm⁻¹ to 4000 cm⁻¹ with spectra resolution of 4 cm⁻¹ at room temperature. The FTIR data were recorded in the transmittance mode.

**X-ray diffractometer analysis.** XRD patterns were recorded on a Rigaku MiniFlex II Diffractometer. Samples were cut into a suitable size and then adhered onto a glass sample holder. The glass sample holder was then attached to the diffractometer and the samples were directly scanned at 2θ angles between 5° and 80° at room temperature. XRD was performed to determine the nature of the biopolymer electrolytes whether crystalline, amorphous or both.
Impedance spectroscopic study. The impedance study was performed by using Hioki 3532-50 LCR Hi-Tester. Impedance data were collected for the frequency ranging from 50 to 1 MHz. Impedance spectroscopic measurement was performed to determine the ionic conductivity of biopolymer electrolyte films over a temperature range from 30 to 100 °C. The biopolymer electrolyte sample were sandwiched between stainless steel electrodes which have a surface contact area of 2.0 cm² and the samples were mounted onto the sample holder under spring pressure.

Results and discussion

FTIR spectroscopy. The FTIR spectra of the dual-blend biopolymer system change according to their composition and may be able to show the occurrence of complexation and interaction between the various constituent. Fig. 2 reveals that IR-spectrum of dual-blend film, CMC/CS doped with NH₄NO₃ (10-40 wt%) in the spectral range from 700 cm⁻¹ to 2000 cm⁻¹. Upon addition of NH₄NO₃ concentration, the intensity of CMC/CS peak becomes less obvious. The NH₄NO₃ molecules which are relatively small compared to polymer molecules penetrate into CMC/CS matrix and establish attractive forces between NH₄NO₃ molecules and chain segment. These attractive forces reduce the cohesive force between the polymer chains and increase the segmental mobility [1].

The band at 1553 cm⁻¹ confirmed the presence of COO⁻ and assigned to stretching of the carboxyl group. The assignment of the 1553 cm⁻¹ to the asymmetrical COO⁻ stretching indicates that chitosan and acetic acid have formed a chitosan–acetic acid salt. Upon addition of NH₄NO₃ salt, the gap between the carbonyl and amine bands is observed to increase up to 97 cm⁻¹. According to Rinaudo et al. [17], the cation of the acetic acid interacts with the nitrogen atom of the amine group. This leads to a shift of the amine and other bands as well. The bands observed at 1425 and 1370 cm⁻¹ were assigned to –CH₂ scissoring and –OH bending vibration of CMC [14]. The bands at 1114 and 1040 were characteristics of the C-O stretching on polysaccharide skeleton [18]. A new peak is observed at 779 cm⁻¹. This peak is corresponds to the symmetric bending mode of NO₃⁻ and is observed to grow with increase in NH₄NO₃.
X-ray diffraction analysis. Fig. 3 presents the XRD patterns of dual-blend films of CMC/CS containing 0 to 50 wt% of NH$_4$NO$_3$. The XRD analysis reveals that the complex formation in the polymer matrices and shows that all samples are mostly amorphous. Upon addition of the NH$_4$NO$_3$ salt, the diffraction peak centered at ~21° becomes broaden and shifted to the higher Bragg’s diffraction angle. These changes can be caused by the increase of interaction of the ionic dopant with the polymer that results in the increase of amorphpoussness in the CMC/CS-NH$_4$NO$_3$ biopolymer blend system [19, 20]. This proves that the addition of NH$_4$NO$_3$ helps to generate more amorphous region and disrupted the semi-crystalline region in the dual-blend CMC/CS systems.

Impedance Spectroscopy Study. Fig. 4 presents the graph for conductivity against concentration of NH$_4$NO$_3$ at ambient temperature (303 K). The conductivity was calculated using:

$$\sigma = \frac{\epsilon}{R_b A}$$

where $A$ is the area of electrode–electrolyte contact in cm$^2$, $\epsilon$ is the thickness of the sample in cm and $R_b$ is bulk resistance which can be obtained by plotting the negative imaginary impedance, $-Z'$, versus real part, $Z'$, of impedance.

![Fig. 3 XRD patterns of CMC/CS containing (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 40 wt% and (f) 50 wt% of NH$_4$NO$_3$.](image)

![Fig. 4 Ambient temperature ionic conductivity of CMC/CS-NH$_4$NO$_3$.](image)
From Fig. 4, pure polymer blend (NH$_4$NO$_3$-0 sample) indicates the ionic conductivity of $1.79 \times 10^{-8}$ S cm$^{-1}$. The conductivity increases from the addition of 10 until 40 wt% of NH$_4$NO$_3$. As the salt composition increases, more protons (H$^+$) are supplied due to the dissociation of the ionic dopant. The maximum ionic conductivity achieved is $1.03 \times 10^{-5}$ S cm$^{-1}$. The increase of ionic conductivity with addition of NH$_4$NO$_3$ concentration is due to the increase of the number of charge carrier and mobility of ions/conducting species [21]. However, the conductivity dramatically declines after addition of 40 wt% NH$_4$NO$_3$. Ng and Mohamad [22] reported that as NH$_4$NO$_3$ concentration increases, the host matrix (polymer blend) becomes more crowded with the dopant ions. Hence, reduces the transportation of charge carriers due to limitation of ionic mobility [23].

Summary
Biopolymer dual-blend based CMC and CS incorporated with NH$_4$NO$_3$ were prepared and characterized. The obtained results revealed that the NH$_4$NO$_3$ influence the ionic conductivity of the biopolymer blend electrolytes and the best value of $5.77 \times 10^{-5}$ S cm$^{-1}$ was obtained for the system containing 40 wt% of NH$_4$NO$_3$ at ambient temperature. This is attributable to the increase in the number of ions in the system. IR spectra provides insight into the possible interaction occur upon the addition of NH$_4$NO$_3$ with CMC. XRD studies reveal that the increase in the amorphosity of all samples upon the incorporation of NH$_4$NO$_3$, consequently attributed to the increase in conductivity.

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References


