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Characterization of Chitosan-starch Blend Based Biopolymer Electrolyte Doped with Ammonium Nitrate

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Abstract: Polymer electrolyte is an ionic conductor formed by dissolving salt in polymer host. In this work, starch/chitosan blend based polymer electrolyte was prepared with different weight percentage of Ammonium Nitrate (NH_4NO_3) via solution casting technique. The film was characterized by impedance spectroscopy HIOKI 3531- 01 LCR Hi-Tester to measure its ionic conductivity over a wide range of frequency between 50Hz-5MHz and at ambient temperature. Sample with 35 wt% of NH_4NO_3 shows the highest conductivity of $(6.34 \pm 1.52) \times 10^{-7}$ Scm^{-1}. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to correlate the ionic conductivity results.

INTRODUCTION

Polymer electrolytes (PE) from biodegradable sources were aggressively studied. Biopolymer such as Cellulose, Chitosan, Starch and Pectin possess some has unique properties including being abundant in nature, biodegradable, and is low in cost have attracted attention many researchers for the development of biopolymer electrolytes (BPE) [1-3]. Chitosan, derived from chitin which is extracted from the hard outer skeleton of shellfish, including crab, lobster, and shrimp have wide range of application either in its original or modified forms. Chitosan have been widely investigated in biomedical area [4], formation of biodegradable films [5], photography, food processing, cosmetic [6] and others. It is biocompatible and enzymatically biodegradable making it ecologically safe with non-toxic properties [7] and also known to be inexpensive material because of its natural abundances.

Chitosan possess lone pair electrons both nitrogen and hydrogen atoms in its amine and hydroxyl functional groups. The lone pair electrons are essential in a polymer electrolyte system as they will create dative or coordination interactions with the charge carriers. The continuous interactions of the charge carriers with the available functional group will then generate motion of the polymer chain segments and thus makes the polymer conductive [8]. Chitosan is soluble in weakly acidic solutions resulting in the formation of a cationic polymer with a high charge density and can form polyelectrolyte complexes with wide range of anionic polymers [9]. Due to several properties like good complexity with ionic salts, high ionic conductivity, nontoxicity and biodegradable, chitosan has been frequently used as polymer electrolyte main host in various study such as for supercapacitor application [10], electrochemical devices [2], biodegradable thermoplastic [11] and batteries [5].

Starch on the other hand has been used to produce biodegradable films to partially or entirely replace plastic polymers because of its low cost renewability and mechanical properties [10]. Starch, however has hydrophilicity properties that led to poor film strength. The usage of acetic acid in starch helps to counter this problem by enhancing the hydrophobicity and mechanically strength of the starch film [12]. Ochubiojo & Rodrigues (2012) reported that when starch reacts with an acid, the water solubility of the starch granules is enhanced. Ammonium

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salt such as ammonium bromide, ammonium chloride and ammonium nitrate which is proton (H^+) species are frequently used in proton conducting electrolyte system [13]. This type of salt can be classified as good proton donor and could enhance the ionic conductivity of PE [14-16].

In this work, starch was used to blend with chitosan and have been doped with different percentages of ammonium nitrate (NH_4NO_3). Polymer blending becomes the most favourable among scientists as it may involve easy way of preparations, having good properties and lower cost. Polymer blends often show better properties than the single polymers [17]. The objective of this work is to investigate the conductivity of the BPE of starch/chitosan blend with addition of NH_4NO_3 at room temperature. Apart from that, the amorphousness of the blends were verified using XRD and while FTIR will be used to verify the complexation of the materials.

MATERIAL AND METHODS

Sample preparation

Tapioca starch powder, chitosan powder, acetic acid, ammonium nitrate (NH_4NO_3) 99.0% purity laboratory grade were purchased from Sigma-Aldrich. 0.5g of chitosan was dissolved in 50ml diluted acetic acid (1%v/v) and then gently stirred overnight at room temperature until a homogenous and viscous solution was formed. 0.5g of starch was dissolved in 50ml distilled water on the hotplate with a controlled temperature of 80°C for 30 min. The starch solution was cooled to room temperature prior mixing with the dissolved chitosan. Different weight percentage of NH_4NO_3 was then added into the mixture. The blend was stirred continuously with a magnetic stirrer overnight to obtain homogenous solution before casting into different petri dishes and left to dry completely in air. The composition of the sample and variation of salt are tabulated in Table 1.

TABLE 1: Composition of Chitosan-starch-NH_4NO_3 BPEs.

Designation	**Chitosan(g)**	**Starch(g)**	**NH_4NO_3(wt.%)**
BPE0	0.5	0.5	0
BPE5	0.5	0.5	5
BPE10	0.5	0.5	10
BPE15	0.5	0.5	15
BPE20	0.5	0.5	20
BPE25	0.5	0.5	25
BPE30	0.5	0.5	30
BPE35	0.5	0.5	35
BPE40	0.5	0.5	40
BPE45	0.5	0.5	45
BPE50	0.5	0.5	50

Electrochemical Impedance Spectroscopy (EIS)

EIS was used to determine the impedance of the sample at room temperature over a frequency range (50 Hz to1MHz) using HIOKI 3532 LCR Hi Tester bridges interfaced to a computer. The bulk resistance, R_b was obtained from the plot of negative imaginary impedance, Z_i versus real impedance, Z_r with the horizontal and vertical axes having the same scale. The room temperature conductivity of the sample can then be calculated using

$$\sigma = t / R_b A \tag{1}$$

where R_b is bulk resistance, t is the thickness of the thin film and A is the surface area of contact.

X-ray Diffraction (XRD)

Rigaku MiniFlex II was used to get XRD pattern with CuKα radiation scanned at room temperature from $2\theta = 5°$ to 60° with scan rate of 2°/min powered of 30kV/15mA.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was done to determine the functional group present in the BPE film. The BPEs were tested by Attenuated Total Reflection (ATR) measurement using Thermo Nicolet 380 FTIR spectrometer in the frequency ranging between 650 cm^{-1} to 4000 cm^{-1} with resolution of 4 cm^{-1}.

RESULT AND DISCUSSION

The conductivity of the BPE film at different composition of salt is shown at room temperature plotted in Fig. 1. The conductivity gradually increases with addition of NH_4NO_3 until 35 wt.% where the highest conductivity was achieved at $(6.34 \pm 1.52) \times 10^{-7}$ Scm^{-1}. The value is comparable to that recorded in previous study [18]. The increase in conductivity can be inferred to the increase in salt content which can dissociate to provide more mobile ions as more salt is added, which contribute to the increase in conductivity similarly found by most polymer-salt systems [2,16,19,20]. The cation (NH_4^+) were expected to participate in the ion conduction where it interacts with polar group of blended polymer host. The blending of chitosan/starch has influenced the increase in conductivity value with increasing of amorphous nature of the sample to promote ions transport [21]. However, conductivity decreases after 35 wt% can be explained as ion cluster aggregated leads to the overcrowded traffic of ions in the BPE system [22].

Several factors which influence the ionic conductivity includes; the number of charge carrier and the charge carrier's mobility, cationic or anionic type charge carriers, temperature and the conduction pathway [18,23]. In this work, the increase of the conductivity could be related to the increment of charge carrier and free mobile ions, while the decrease in the conductivity can be explain due to the re-association of ions that reduces the number of free ions and the ions mobility [23].

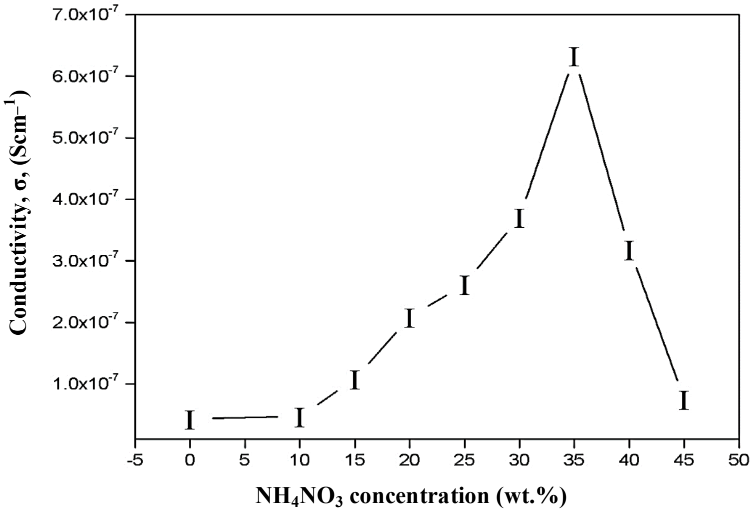

FIGURE 1. The ionic conductivity versus NH_4NO_3 concentration of BPEs obtained at ambient temperature.

The X-ray diffractogram of the samples shows that upon addition of NH_4NO_3, the peak becomes broader and shift to higher 2θ angle from 20° to 22° (Fig. 2). This phenomena proves that the effect of NH_4NO_3 composition has help to increase the amorphousness of the BPE [16,23,24]. An amorphous structure of blend is needed to help the ion migration between the polymer backbones thus improve the conductivity. A continuous ion hopping occur subsequently increases the ionic conductivity. The new peak form at 2θ angle of 13° is correlated to the incomplete dissolution of NH_4NO_3 doping in the chitosan-starch polymer matrix [25].

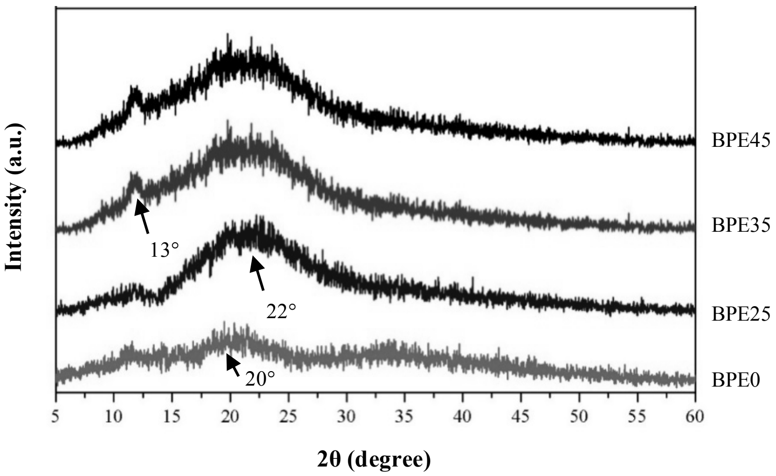

FIGURE 2. XRD patterns of BPEs.

The spectrogram for pure salt NH_4NO_3 and BPE composition are shown in Fig. 3 in the region of 500-2000 cm^{-1}. For pure NH_4NO_3, N-O and N-H asymmetric stretching vibrations are located at 1412 and 1311 cm^{-1} [26]. The band at 1039 and 821 cm^{-1} was assigned to the symmetrical stretching and bending vibration of N-O of the nitrate anion [27]. In the BPE0 spectra, at 1150 to 994 cm^{-1}, a C-O stretching on polysaccharide skeleton was detected [28]. In the salt complexes, the carbonyl band appears at the 1629 cm^{-1} and the amine band at 1524 cm^{-1} indicates that the salt has form interaction between the cation group and the nitrogen atom complexed with amine group. A very sharp peaks at 1311 cm^{-1} which refers to N-H stretching is observed due to the complexation with addition of NH_4NO_3 between the NH_4^+ ions from salt in the BPEs system. The intensity increased with increasing composition of salt proved that interaction happened between chitosan-starch and salt. The bending vibration frequency of N-O from nitrate salt shifted to higher wavenumber from 821 to 827 cm^{-1} shows interaction in the polymer blend.

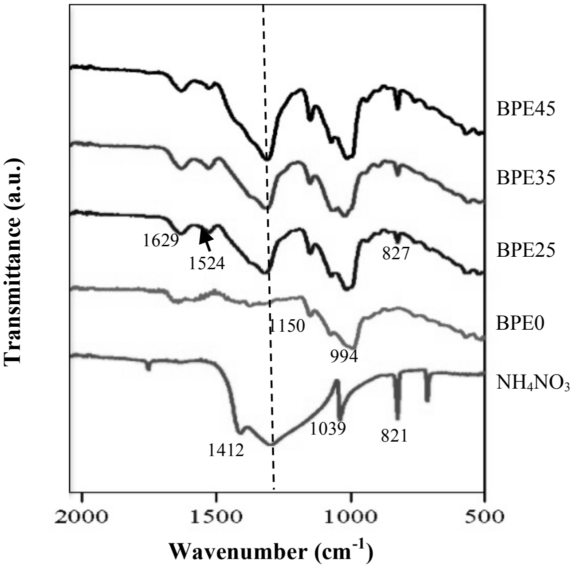

FIGURE 3. FTIR spectra of BPEs.

CONCLUSION

In this work, biopolymer electrolyte was manufactured and experiments were prepared using solution casting technique in order to study the optimum effect of NH_4NO_3 on the ionic conductivity. It was found that samples with 35 wt% of NH_4NO_3 gave highest ionic conductivity at room temperature of $(6.34 \pm 1.52) \times 10^{-7}$ Scm^{-1}. The conductivity is still poor but the study is just to identify the potential of blended chitosan-starch and NH_4NO_3 as biopolymer electrolyte. Conversely, the result obtained through this work confirmed that the blended biopolymer and additional of NH_4NO_3 has improved the conductivity of BPEs via enhanced the amorphousness of the samples and promote more ion dissociate and mobility.

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