X-Ray Diffraction and Infrared Spectroscopic Analysis of Solid Biopolymer Electrolytes Based on Dual Blend Carboxymethyl Cellulose-Chitosan Doped with Ammonium Bromide

A. A. Mejenom[1], M. N. Hafiza[1] and M. I. N. Isa[1*]

[1]*Advanced Nano Materials (ANoMa) Research Group,*
School of Fundamental Science, Universiti Malaysia Terengganu,
21030 Kuala Nerus, Terengganu, Malaysia.

The present work discusses the structural studies of dual blended solid biopolymer electrolytes (SBEs) based carboxymethyl cellulose (CMC)/chitosan (CS) doped with various ammonium bromide (AB) composition using solution casting technique. X-ray Diffraction (XRD) result reveal that all samples are completely amorphous except for sample Ab-30. FTIR analysis shows interaction has occurred between CMC/CS and NH_4Br. Analysis of transport properties has shown that the dependency of ionic conductivity was on the ionic mobility, μ and diffusion coefficient, D of mobile ion.

Keywords: Structural studies, carboxymethyl cellulose, chitosan, polymer blend, FTIR deconvolution, ammonium bromide, solid biopolymer electrolyte

I. INTRODUCTION

Electrolyte is one of the main components in battery which has been used as a medium for ion transportation between anode and cathode during charging-discharging process [1]. Conventional batteries contain aqueous acid and hazardous chemical such as nickel cadmium, cadmium sulfate, titanium and lead acid [2]. Nowadays, the use of battery has created many environmental problems such as toxic metal pollution which also brings negative effect to human health [3]. Additionally, it can also damage the equipment and contributes to electronic waste [4]. In order to solve the arising problems, solid polymer electrolyte (SPE) has been considered.

SPEs have attracted attention worldwide due to their potential to replace hazardous liquid or aqueous electrolyte today. This is due to several advantages of SPE such as a good surface contact between electrode and electrolyte, easy to prepare, leak-proof electrolyte and dramatically improved in safety hazard [4],[5]-[6]. SPE involves the dissolution of ionic salt in the polymer matrix. To improve the properties of SPEs, polymer blending has been introduced due to the easy preparation and physical properties of the electrolyte can be controlled [7].

In this work, carboxymethyl cellulose (CMC) and chitosan (CS) are chosen as the host polymer for this dual blend solid biopolymer elec-

*corresponding author:ikmar$_i$sa@umt.edu.my

trolyte (SBE) system. Both biopolymers were grouped in the most popular biodegradable and inexpensive materials due to their abundance in nature. CMC is a natural polymer that contains amphiphilic characteristics [4]. It consist a lot of hydrophilic carboxyl group and hydrophobic polysaccharide backbone [8]. Chitosan is second most abundance natural polymer on earth [9]-[10]. In chitosan, complexation occur because the present of hydroxyl and amine functional group which possess lone pair electrons for nitrogen and oxygen [10]-[11]. Previous study has reported the value of ionic conductivity for this SBE [6]. So in this work, the investigation is focusses primarily on the structural of SBE using FTIR and XRD, and their transport properties was calculated using FTIR deconvolution method.

II. MATERIALS AND METHODS

A. Sample Preparation

Carboxylmethyl cellulose (CMC) and chitosan (CS) were purchased from Arcos Organic Co. and W.A. Hammond Drierite Company LTD., respectively. Those two polymers were mixed in 1% of acetic acid solution and stirred until completely dissolved. Different amount of ammonium bromide (AB) as stated in Table 1 were added into the solutions and stirred until homogenous solution was achieved. The solutions then were casted into Petri dishes and were

put in the oven for films forming. The films were kept in desiccator to avoid the presence of water prior to sample characterization.

Table 1. The designation and composition of CMC/CS-AB dual blend SBE.

Sample	CMC/CS	NH$_4$Br wt.%
AB-0		0
AB-5		5
AB-10		10
AB-15	2:1	15
AB-20		20
AB-25		25
AB-30		30

B. X-ray Diffractometer (XRD)

This study was carry out to identify the nature of SBE films whether they are amorphous, crystalline or both. XRD were carried out at room temperature using Rigaku Mini-Flex II diffractometer with CuKα radiation in the range of 10° to 80°. The samples were cut and adhered onto glass slides before measurement.

C. Fourier Transform Infrared (FTIR) spectroscopy

FTIR test was done to confirm the interaction between CMC/CS and AB involved in the system. It was performed using Thermo Nicolet 380 FTIR spectroscopy provide with a germanium crystal with an Attenuated Total Reflec-

tion (ATR) accessory. The films were cut into appropriate sizes and put on the sample holder. Within the frequency range of 650 cm^{-1} to 4000 cm^{-1} with spectra resolution of 4 cm^{-1} at room temperature, the infrared light was passed through the sample.

FTIR deconvolution technique, where the Gaussian-Lorentz function is adapted to the Origin Lab software was used by (Chai and Isa, 2016) in their work [12]. The selected FTIR spectra were deconvoluted and the transport parameter were analyzed using data analysis program (Origin Software version 8).

The area under the peaks was figured and by using the equation below the free ions percentage was determined [12]:

Percentages free ions (%)

$$= \frac{A_f}{A_f + A_c} \times 100\% \qquad (1)$$

$$n = \frac{M \times N_A}{V_{total}} \times freeions(\%) \qquad (2)$$

$$\mu = \frac{\sigma}{ne} \qquad (3)$$

$$D = (\frac{kT\mu}{e}) \qquad (4)$$

Where;

A$_f$ - Area under the peak for free ions

A$_f$ - Area under the peak for contact ion

n - Number density

M - Number of moles of dopant used

N$_A$ - Avogadros number (6.02 x 1023 mol$_{-1}$)

V$_{total}$ - Total volume of SBEs

μ - Ionic mobility

σ - SBEs Conductivity

e - Electric charge (1.602 x 10$_{-1}$ C)

D - Diffusion coefficient

k - Boltzmann constant (1.38 x 10-23 J K$_{-1}$)

T - Absolute temperature

III. RESULTS AND DISCUSSIONS

A. XRD analysis

Figure 1 shows XRD patterns of CMC/CS with different AB composition. A broad peak of Figure 1 (a) at angle $2\Theta = 21.24°$ (or known as amorphous hump) has confirmed the amorphous nature of blended polymer, CMC/CS. The relative intensity of broad peak between 15° and 30° tend to decrease with addition of AB composition. The peak broadness indicates the increase in amorphous nature of SBE. This in turn contributes to the increase of the proton transport in amorphous phase, which lead to the increase of ionic conductivity value [13]-[14],[6].

The presence of the intense peak at angle 2Θ = 22.1°, 31.2°, 44.7°, 50.4°, 55.6°, 65.1°, 69.6° and 73.9° in Figure 1 (g) due to the increase in salt composition, which implies the polymer would no longer solvate salt and might be caused of association of ions. Thus, reduces the number of mobility ions and led to the decrease in

conductivity [15]. This was further supported from the work done by [6], where the decrease of ionic conductivity after addition of 20 wt. % AB compositions was due to the formation of ion cluster. Thus lead to decrease of ionic conductivity at higher salt composition.

Table 2. Degree of Crystalliity of each sample

Sampel	Degree of Crystallinity *(nm)*
AB-0	0.92
AB-5	1.005
AB-10	0.941
AB-15	0.924
AB-20	1.264
AB-25	0.967

In order to confirm the amorphousness of SBE, the value of crystallite size was calculated and listed as in Table 2. Based on the result, in the range $0.92nm$ to $1.26nm$, the value does not follow the conductivity trend. Even though the highest conductivity sample has the highest degree of crystalline, it still consider acceptable.

B. FTIR analysis

Figure 2 shows the FTIR spectrum of CMC/CS-NH$_4$Br complexes. From Figure 2, a broad peak at 3350 cm^{-1} corresponds to O-H stretching of CMC/CS film. Peak at 1597 cm^{-1} is assigned to overlapping peak of carboxyl group from CMC and amine band of CS [13],[16]. The peak at 1423 cm^{-1} is ascribed to overlapping
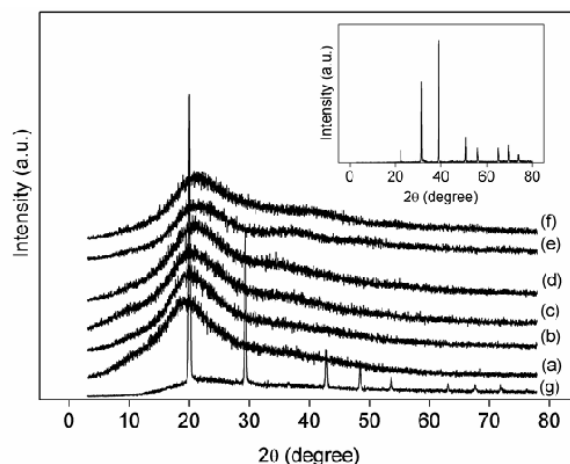

Figure 1. XRD pattern for (a) AB-0, (b) AB-5, (c) AB-10, (d) AB-15, (e) AB-20, (f) AB-25 and (g) AB-30

peak of N-H deformation and O-H stretching of CS and CMC, respectively [13],[16]-[17]. Peak at 1333 cm^{-1} is attributed to the C-H bending of CMC [17]. The sharp peak at 1068 cm^{-1} is expected belongs to C-O stretching of CMC and CS polysaccharide skeleton [2]. All peak observed in Figure 2 confirm the presence of CMC and CS polymer.
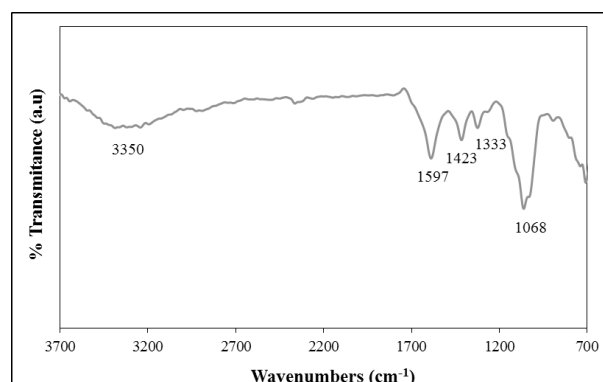

Figure 2. FTIR spectrum of CMC/chitosan polymer blend

The possible interaction between CMC/CS

film and AB are further discussed and the spectrum was depicted as in Figure 3. New peak which corresponds to N-H stretching was observed in the O-H region (Figure 3 c). Two peaks at 1597 cm^{-1} and 1423 cm^{-1} were found to increase in the intensity and peak at 1068 cm^{-1} was shifted to 1072 cm^{-1} with addition of AB [18]. The emergence and presence of the peak shows the interaction between salts and polymer blend were existed. It can be concluded that the complexation between CMC/CS polymer blend and AB was due to the conduction occurs through the substitutions of ions between of H^{+} and coordinating site (oxygen) [11].

Our previous work also found that ionic transference number, t$_{ion}$ for SBE was 0.95 (t$_{ion}$ ~1). From this value obtain, it can be inferred that H^{+} ion of NH$_4$Br is the main conducting species in this SBE which also means that this SBE is a proton conducting [19].

According to (Hema *et al.*, 2008), the shifting of peak in polymer-AB system may be due to the establishment of dative bond between H^{+} from AB and nitrogen or oxygen coordinating position in the CMC/CS dual blend [18]. In ammonium salt, the weakly bound of H^{+} from NH$_4^{+}$ ion can be simply separated under the impact of electric field. The hopping of H^{+} ions allows the conduction to occur via each coordinating site of nitrogen and oxygen atom [18],[20]. Thus, increase the conductivity value as reported in our previous work [21].
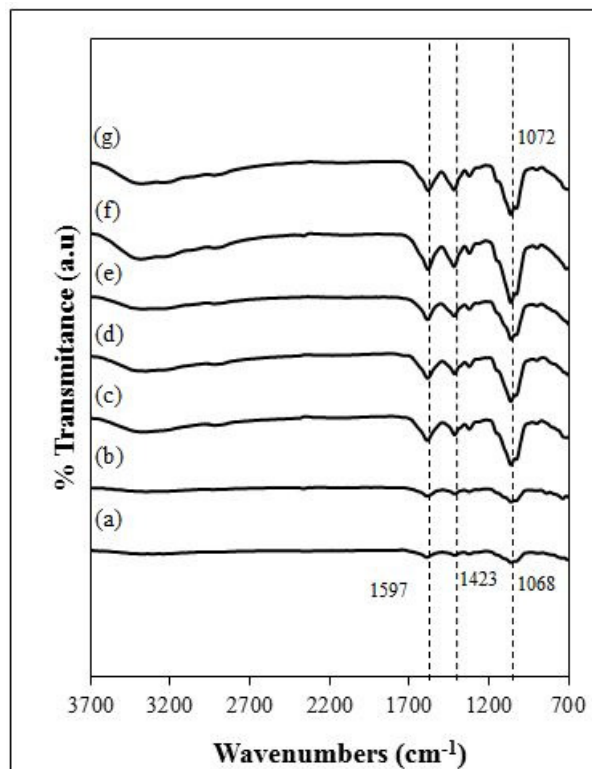

Figure 3. FTIR spectrum for (a) AB-0, (b) AB-5, (c) AB-10, (d) AB-15, (e) AB-20, (f) AB-25 and (g) AB-30

C.   FTIR Deconvolution Study

The area of de-convoluted of FTIR peak can show the transport parameter. In this study, the FTIR spectra range of 1450-1750 cm^{-1} was chosen, where the significant interaction of several peak can be spotted as stated in FTIR analysis. The peak selected was similar to the work done by Sohaimy and Isa, (2017) who also use ammonium salt [22]. Due to the spectra range of AB is not included, we choose NH peak instead of AB peak. The deconvoluted peak of all the sample CMC/CS-AB can be seen in Figure 4. The peak centered around 1589 cm^{-1}

are the peak from carboxylic group of CMC as mentioned before. The peak at $1548cm^{-1}$ represented the amine band from chitosan group [16]. Free ion and contact ions peak within their range was done through comparison with other journals [23]-[24]. The free ion peak is situated between 1603 -$1643cm^{-1}$ meanwhile contact ions peak are between 1644 -$1690cm^{-1}$.

Free ions peak comes from the NH_4^+ which deprotonated into NH_4^+ ions. This peak is the same peak that being reported by Ritthidej *et al.*, 2002 and Fadzallah *et al.*, 2014). The percentage was calculated and listed in Table 3. As shown, the percentage of free ions decreased from 90.28 % (5 wt. %) to 58.9 % (15 wt. %) before start to increase back at 20 wt. % and 25 wt. %. From the work reported previously, the highest ionic conductivity sample is at 20 wt. % of AB composition [6]. The value of free ions may contribute to the conductivity. Although the percentage of free ion does not follow the trend of ionic conductivity, the value is still higher compare to contact ion. As for sample 30 wt. %, the percentage of free ion is lower than contact ion. This might be due to the salt that no longer solvate in this sample, as proven from the XRD analysis before.

The ionic transport parameter (number of mobile ion, n, ionic mobility, μ, and diffusion coefficient,D) were plotted in Figure 5. As can be seen, the graph almost follows the trend plot for ionic conductivity except at the certain point.

From Figure 5, it can be seen that number of

Table 3. Free ions percentage against NH_4Br concetration

Sample (wt. %)	Free ion (%)	Contact ion (%)
AB-5	90.28	9.72
AB-10	74.76	25.24
AB-15	58.90	41.1
AB-20	74.98	25.02
AB-25	85.65	14.35
AB-30	44.77	55.23

ion increased as the salt concentration increase which also explain the increasing in ionic conductivity. This statement was supported by Samsudin *et al.*, (2014) which stated that the highest conductivity should have the highest number of mobile ion [25]. However, the number of mobile ion keep increasing for sample 25 wt. % which has lower conductivity compare to sample 20 wt. % (highest). As stated by Ramlli and Isa, (2016), the optimum value of number of mobile ions was obtained in the highest conductivity sample, and higher composition of salt will result in overcrowding hence decreasing in diffusion of ion and ionic mobility [26]. This statement is further supported in Figure 5 (b) and (c). It can be seen that after sample 20 wt. % which has the highest μ and D, the ionic mobility and diffusion coefficient decreasing parallel to decrease in ionic conductivity.
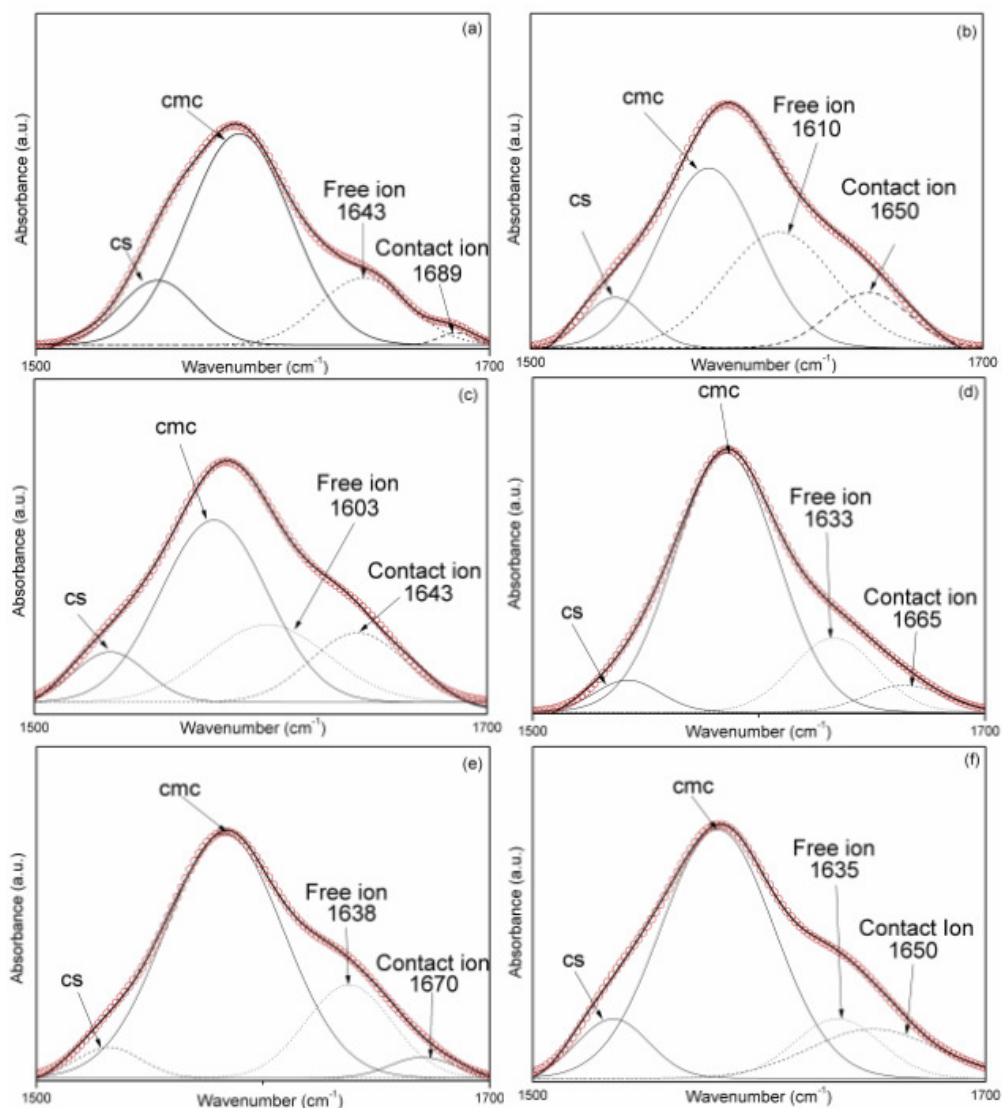
Figure 4. De-convoluted peak of FTIR spectra for CMC-CS-AB SPE (a) AB 5 (b) AB 10 (c) AB 15 (d) AB 20 (e) AB 25 (f) AB 30

IV. SUMMARY

Solid biopolymer electrolytes (based on blended polymer, CMC/CS with varied amount of AB was successfully prepared via solution casting technique. FTIR study revealed the interactions between CMC/CS and AB have been occurred and the ionic species involved in this SBE system were confirmed to be proton conductor (H^+). XRD analysis confirmed that the SBE film were predominantly amorphous in nature. The transport properties of SBEs were identified using deconvolution of FTIR spectrum and it can be concluded that ionic mobility and coefficient diffusion of ion play major part in ionic conductivity of the sample.
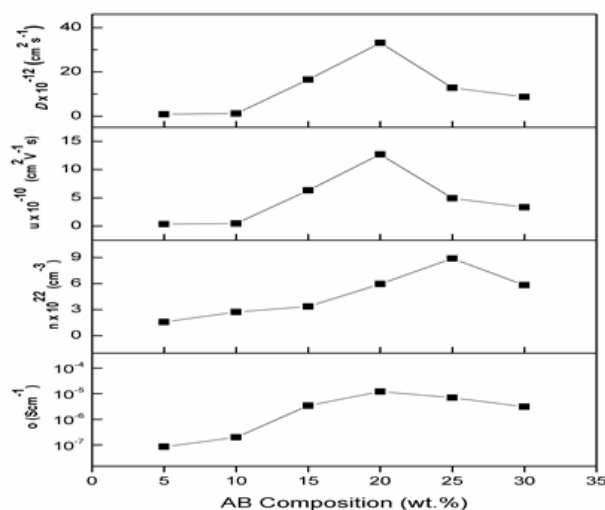
Figure 5. The transport parameter of
CMC-CS-NH$_4$Br SPE system

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