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Research Article

Effect of Adipic Acid Composition on Structural and Conductivity Solid Biopolymer Electrolytes Based on Carboxy Methylcellulose Studies

M.L.H. Rozali, N.H. Ahmad, M.I.N. Isa

Advanced Materials Research Group, School of Fundamental Science, Center of Corporate Communication and Image Development, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

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ABSTRACT

Solid biopolymer electrolytes (SBEs) based on carboxy methylcellulose (CMC) has been prepared by doping different concentration of Adipic acid (AA) via solution casting technique. Fourier Transform Infrared spectroscopy was used to study the interaction between the host and ionic dopant. New peaks were observed at at 1714 and 1261 cm^{-1} at AA-5. It also can observe that 5 peaks intensity have become decrease. XRD analysis was shown the CMC-AA was the amorphous solution. The highest ionic conductivity achieved at room temperature is $6.12 \times 10^{-7} \text{ S cm}^{-1}$ for CMC incorporated with 5 wt. % AA. In addition, the temperature dependence of the SBEs exhibit Arrhenius behavior. That the activation energy of relaxation is lower than the activation energy of conduction implies that the charge carrier has to overcome the higher energy barrier during conducting.

Keywords: Solid biopolymer electrolyte, carboxy methylcellulose, adipic acid, conductivity.

INTRODUCTION

One of the main issues of concern in studies of polymer electrolytes is the question of what types of polymers might be useful. A distinctive structural feature of cellulose materials is heterogeneity owing to its fiber structure [1]. Several researches done on this very famous cellulose were largely investigated by various scientists around the world due to its mysterious and unexplored properties. The solubility behavior of cellulose was the main concern of the previous researches. Nevertheless, this behavior was extensively studied and several solutions were proposed to increase the solubility. Work done by [2] and some other researches concentrate on the application of cellulose as coatings of food product. The cellulose was found to act as sacrificing agents

retarding moisture loss from food products.

The CMC contains of hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups and hence shows amphiphilic characteristic. In addition, CMC is an ionic polymer that in general, cellulose is made up of glucose rings that connected by $-C(1)-O-C(4)$ ether bonds known as β -1, 4 glycoside linkages with extensive intermolecular hydrogen bonding. In this paper, carboxy methylcellulose (CMC) would be explored in term of its electrical conductivity as well as to improve previous researches in understanding the potential of this material as an ionic conductive polymer. The introduction of ionic dopant into the CMC would expect to increase the cellulose film electrical properties for further usage of the SBE in today's electrochemical application.

Corresponding Author: M.I.N. Isa, Advanced Materials Research Group, School of Fundamental Science, Center of Corporate Communication and Image Development, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

2. Objectives:

Formulate carboxyl methylcellulose (CMC) as the host and dope with adipic acid (AA) as the donor material to obtain solid biopolymer electrolytes. To characterize the CMC bio-polymer electrolytes of the complexation of the biopolymer host and the ionic dopant and the phase structure and crystalline of the solid bio-polymer electrolytes

Materials and Methods

In this research, CMC was obtained from Acros Organic Co. ($M_w = 90000$ g/mol and viscosity = 400 cp) and employed as host polymer. AA ($M_w = 146.14$ g/mol) was used as ionic dopant. The proton conducting solid biopolymer electrolytes consist of

CMC complexed with various compositions of AA had been prepared by solution casting technique.

3.1 Sample preparation:

For this solvent method CMC was dissolved in ethanol and the different composition of AA (2-7wt %) was dissolved in distilled water separately. The AA solution was added slowly into the CMC solution and continuously stirred until homogenous solution was obtained. The mixture solution was then casted into several petri dishes and left today in oven at 333 K until the film was form. For further drying, the SBE samples were kept in a desiccator. The composition of the samples and their designations are tabulated in Table 1.

Table 1: Designation and composition of SBE samples.

Designation	CMC (g)	AA (g)	AA (wt. %)
AA-2	2.000	0.041	2
AA-3		0.062	3
AA-4		0.083	4
AA-5		0.105	5
AA-6		0.128	6
AA-7		0.151	7

3.2 Sample characterization:

Thermo Nicolet 380 Fourier Transform Infrared (FTIR) spectrometer was used to confirm the occurrences of complexation in the SBEs system. The spectrometer was equipped with an attenuated total reflection (ATR) accessory with a germanium crystal. The sample was put on a germanium crystal and infrared light was passed through the sample with a frequency ranging from 4000 to 700 cm^{-1} with spectra resolution of 4 cm^{-1} . By interpreting the infrared transmitted spectrum, the chemical bonds in a molecule can be determined. The FTIR spectrum provides the band properties, frequency and intensities that can be used to predict the chemical process, identify a species, and determine the increase in the number of certain entities from increase in the area of the band [3].

X-ray diffraction (XRD) measurement were performed on Rigaku Mini Flex II diffractometer equipped with an X'celerator using CuK_α radiation in the range of $2\theta = 5^\circ$ to 80° . The X-ray diffraction (XRD) was performed to study the nature of the SBEs system. The samples were cut into a suitable size (2 cm x 2 cm) and then adhered onto glass slide for XRD measurement.

Impedance measurement of the CMC-SA biopolymer electrolytes were carried out using Electrical Impedance Spectroscopy (HIOKI 3532-50 LCR Hi-Tester) that was interfaced to a computer in the frequency range of 50 Hz to 1 MHz at 303K-393K. The conductivity of SBE films was calculated from the equation:

$$\sigma = t / R_b A. \quad (1)$$

Here A (cm^2) is the electrode-electrolyte contact area of the SBE film and t its thickness. R_b is bulk

resistance obtained from the complex impedance plot (Cole-Cole plot) at the intersection of the real impedance axis.

Results and Discussions

4.1 FTIR Analysis:

4.1.1 Pure CMC:

Figure 1 shows the FTIR spectrum of CMC from 700 to 4000 cm^{-1} . The characteristic transmission band at 3202 cm^{-1} shows the hydrogen bonding OH stretching region [4]. The small hump at 2922 cm^{-1} and 2872 cm^{-1} shows the attributable to C-H stretching vibration. The sharp peak observed at 1587 cm^{-1} confirms the presence of COO^- is assigned to stretching of the carboxyl group [5]. This band was important in determining the complexation between polymer and salt and this is expected to shift or otherwise if complexes occur. The band around 1410 cm^{-1} and 1319 cm^{-1} are assigned to OH stretching in-plane and C-H stretching in symmetric of CMC. [6]. The IR spectrum of CMC polymer showed the bands at 1107 cm^{-1} and 1039 cm^{-1} were characteristic of the C-O stretching on polysaccharide skeleton [7].

4.1.2 Pure AA:

Adipic acid belongs to the monoclinic crystal structure. The space-symmetry group is P21/n. there are two molecules in a unit cell ($Z = 2$). The adipic acid molecules are linked together by O-H...O hydrogen bonds grouped in $(\text{COOH})_2$ cycles forming infinitely long chains, which become elongated along the c-axis [8]. Figure 2 shows the FTIR spectrum of pure AA salt. It can be observed that a strong band appears at 1689 cm^{-1} belongs to C=O stretching of

carboxylic acid group for AA. The same groups shows a medium peak at 1280 cm^{-1} corresponding to in plane deformation of C-O-H and at 1196 cm^{-1} due to $-(\text{C}-\text{O})\text{H}$ stretching. The hydrogen bonded cyclic

dimers display a very broad, intense peak in the region of $2500\text{--}3500\text{ cm}^{-1}$ due to the strong hydrogen bonding ($\text{C}-\text{OH}\dots\text{O}=\text{C}$) [9].

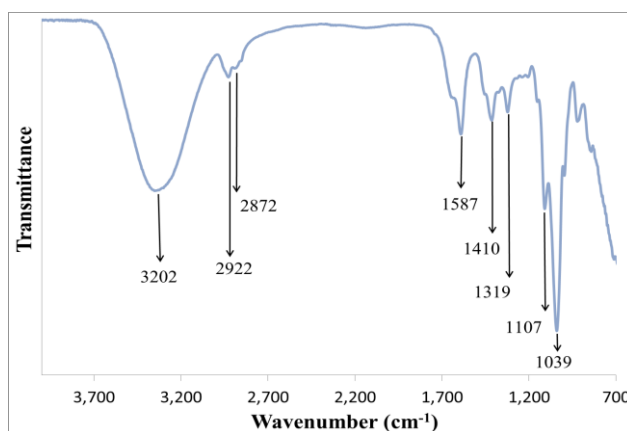


Fig. 1: FTIR spectra of pure CMC.

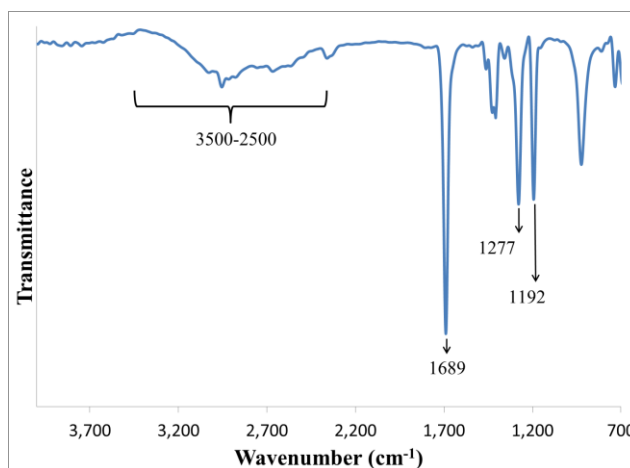


Fig. 2: FTIR spectra of pure AA.

4.2 FTIR of CMC-AA biopolymer electrolytes:

Figure 3 shows the infrared spectrum of CMC-AA biopolymer electrolytes films for samples AA-2 and AA-5 concentration in the region from (a) 1600 to 1800 cm^{-1} and (b) 1200 to 1300 cm^{-1} . From the graph (a) it can be observed that subsequent to blending of CMC with AA, a new broad peak appears at 1714 cm^{-1} . Upon addition of AA from AA-2 to AA-5, the peak C=O group of AA at peak 1689 shifted to this new broad peak. Then upon addition of AA from AA-2 to AA-5 also the new peak emerged at 1261 cm^{-1} from Figure 3 (b). The C-O-H group from AA was 1280 cm^{-1} decrease to the new lower wavenumber at 1261 cm^{-1} . From this new peak was indicated that the deprotonation of the AA increases showed from the intensity of the peak increase. In addition, the increase of peak showed the interaction between CMC and AA have been completed mixed and the dissociation of free protons (H^+) came from the carboxyl group ($-\text{C}-\text{O}-\text{H}$) of AA.

Figure 4 it can be observed that had three peak had shifted and decrease by addition of AA from AA-2 to AA-5. For Figure 5 (a) the of COO^- group from 1589 cm^{-1} was decreased to the lower peak at 1587 cm^{-1} . Then, the peak has decrease the density at peak 1412 cm^{-1} was belonging to vibrations of OH bonds that showed at Figure 4 (b). Another group that belong C-H group also decrease the density at peak 1319 cm^{-1} .

Besides that, by increasing concentration of AA, it also can observe that 2 peaks intensity have become decrease at Figure 5. The peak was 1099 cm^{-1} and 1053 cm^{-1} that belong to C-O group.

4.3 X-Ray Diffraction (XRD) analysis:

The X-ray diffraction patterns of pure CMC and samples AA-2 until AA-7 at room temperature from $2\theta = 5^\circ$ to 80° were shown in Figure 6. From this XRD analysis was shown the CMC-AA was the amorphous solution. When the amorphous increase,

the conductivity must increase. But from this research that had shown the conductivity increase but will be decrease at when the AA wt. % was more added. When more AA was added more ion proton will be increase in the sample. Besides, it can be clearly seen that AA-5 had the highest intensity at the

peak of 21° due to H^+ occurred in the present samples and accommodated to the values of the conductivity obtained.

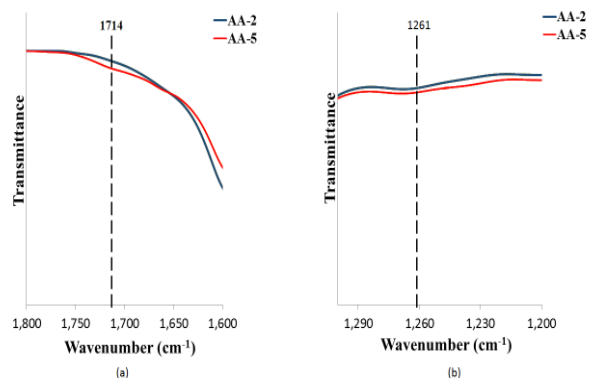


Fig. 3: CMC-AA IR spectrum in the region between (a) 1800 cm^{-1} to 1600 cm^{-1} and (b) 1300 cm^{-1} to 1200 cm^{-1} for AA-2 and AA-5.

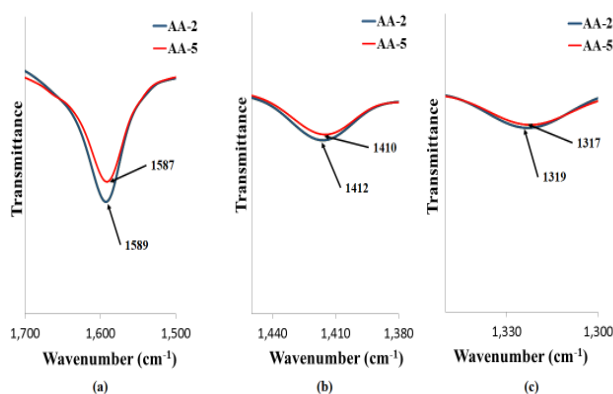


Fig. 4: CMC-AA IR spectrum in the region between (a) 1700 cm^{-1} to 1500 cm^{-1} and (b) 1450 cm^{-1} to 1380 cm^{-1} (c) 1350 cm^{-1} to 1300 cm^{-1} for AA-2 and AA-5.

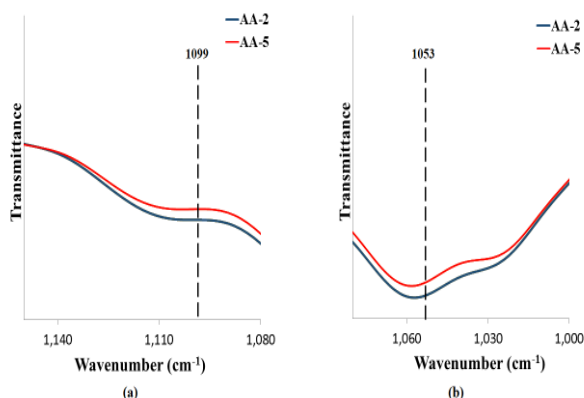


Fig. 5: CMC-AA IR spectrum in the region between (a) 1140 cm^{-1} to 1080 cm^{-1} and (b) 1060 cm^{-1} to 1000 cm^{-1} for AA-2 and AA-5.

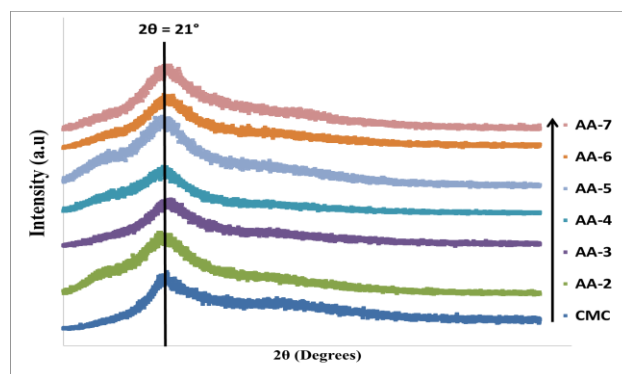


Fig. 6: XRD pattern for different samples of CMC-AA.

4.4 Conductivity study:

The ionic conductivity depends on numerous factors, such as types of charge carrier (cation/anion),

salt composition and temperature [10]. Figure 7 depicts the ionic conductivity, σ of CMC-AA SBEs at ambient temperature, 303K.

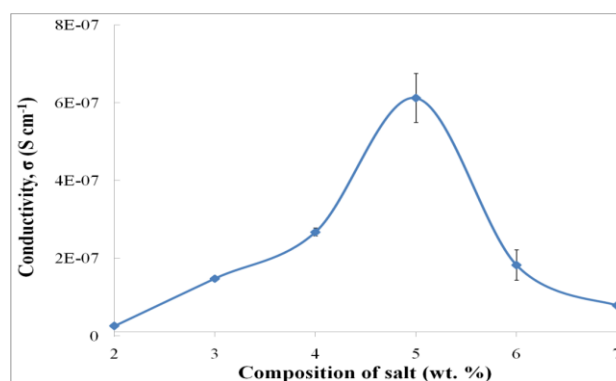


Fig. 7: Ionic Conductivity of SBE sample at 303K.

It can be seen that the ionic conductivity increases with the addition of AA which can be attributed to the increase in the number of mobile charge carriers [11]. The ionic conductivity achieved the maximum value of $6.12 \times 10^{-7} \text{ S cm}^{-1}$ (AA-5) for 5wt% AA. Above this composition, ionic conductivity was observed to decline. According to [12], the dependence of ionic conductivity on the dopant concentration provides information on the specific interaction between ionic dopant and the polymer matrix. The decrement of ionic conductivity at higher AA concentration is attributed to the overcrowded of the ions, hence reduces the number of charge carriers and limits their mobility [11].

The temperature-dependent ionic conductivity was performed to analyze the ionic conduction mechanism of polymer electrolytes [13]. Figure 8 depicts the plots of $\ln \sigma$ versus $1000/T$ for the SBEs system and it was found to be a straight line with regression values almost unity ($R^2 \sim 1$) with the increasing of temperature which implies that SBE system follow Arrhenius behavior. The Arrhenius behaviour can be expressed by the relation of,

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (2)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k is the Boltzmann constant and T is the absolute temperature (K).

The E_a (in eV) can be retrieved from $\ln \sigma$ versus $1000/T$ for all SBE samples and was plotted in Figure 9. E_a is the sum of the energy of defect formation and the energy for migration. According to [10], the decrease of E_a with addition of ionic dopant was due to the fact that the increase amount of ions in the polymer electrolytes with concentration leads to the decrease in the energy barrier for the ion transport. However for this SBEs system the E_a value was highest at the highest conductivity. The calculated E_a value for sample AA-5 is 0.64 eV. In this instance, the conducting ions were more easily excited to free ion-like state, which effect in the increase of the CMC-AA SBE conductivity. Nevertheless, it can be due to the increase in number of mobile ions, diffusion coefficient of mobile ions and ionic mobility of mobile ions [10; 13]. The conductivity behavior of SBEs can be further explored from the dielectric studies.

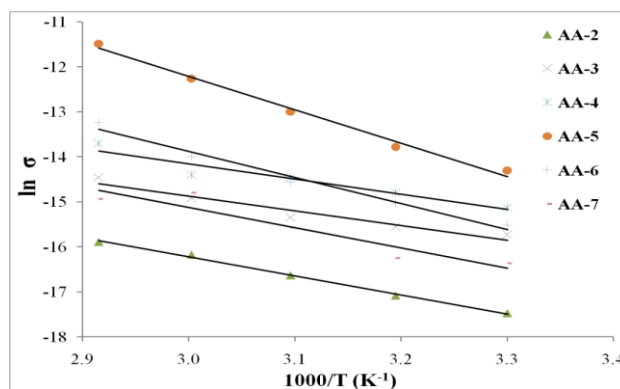


Fig. 8: Temperature-dependent ionic conductivity of SBE samples at 303K-343K.

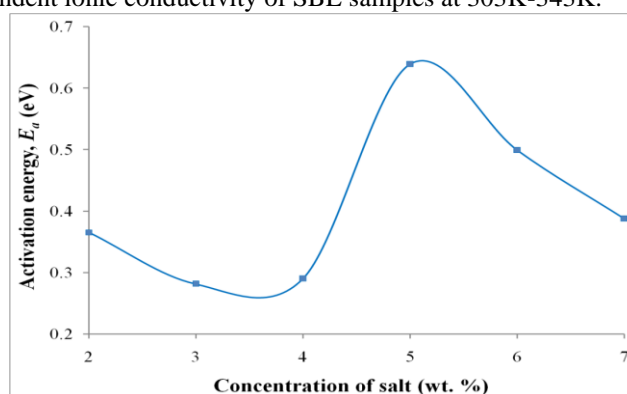


Fig. 9: Activation Energy versus Salt Content.

5. Conclusion:

Carboxy methylcellulose (CMC) based solid biopolymer electrolyte (SBE) was prepared by solution casting technique, with doping of different composition of adipic acid (AA). FTIR studies was carried out to determine the dissociation of free protons (H^+) from the carboxyl group ($-C-O-H$) of AA. XRD measurements confirmed that the SPE system predominantly amorphous in nature. The amount of AA has been found to influence the proton conduction and the high ambient temperature ionic conduction value of $6.12 \times 10^{-7} S cm^{-1}$ has been obtained for CMC with 5 wt. % AA compositions. The temperature dependence of ionic conductivity of these electrolytes exhibited Arrhenius behavior. That the activation energy of relaxation is lower than the activation energy of conduction implies that the charge carrier has to overcome the higher energy barrier during conducting.

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