

See discussions, stats, and author profiles for this publication at: <http://www.researchgate.net/publication/275208618>

Interaction Between Carboxy Methylcellulose And Salicylic Acid Solid Biopolymer Electrolytes

ARTICLE *in* ADVANCED MATERIALS RESEARCH · JUNE 2015

DOI: 10.4028/www.scientific.net/AMR.1107.223

READS

19

3 AUTHORS, INCLUDING:



[Mohd Ikmar Nizam Mohamad Isa](#)

Universiti Malaysia Terengganu

96 PUBLICATIONS 313 CITATIONS

SEE PROFILE

Interaction Between Carboxy Methylcellulose And Salicylic Acid Solid Biopolymer Electrolytes

M.L.H Rozali¹, Z. Ahmad², M.I.N. Isa^{3*}

Advanced Materials Research Group; Renewable Energy Research Interest Group
Department of Physical Sciences, Faculty of Science & Technology,
Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
*ikmar_isa@umt.edu.my.

Keywords: Solid biopolymer electrolyte, carboxy methylcellulose, FTIR, conductivity.

Abstract

In this research, solid biopolymer electrolytes (SBEs) based on carboxy methylcellulose (CMC) has been prepared by doping different concentration of salicylic acid (SA) 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 1700, 2890, 2920 cm^{-1} . The highest ionic conductivity achieved at room temperature is $9.50 \times 10^{-8} \text{ S cm}^{-1}$ for CMC incorporated with 7 wt. % SA. In addition, the temperature dependence of the SBEs exhibit Arrhenius behavior.

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 by [Nigmatullin et al., 2004 \[1\]](#). 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 Miller et al., 1997[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. 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.

Form the open source literature, there were no study done incorporating CMC as the host in an ionic conducting polymer electrolytes. Therefore, it is a very urging to come up with a very abundant known polymer as the main composition for an ionic conductor. The potential of CMC as SBE will be studied extensively by means of conductivity, electrical, optical and ionic transport study. There are two stage of this research, the first is the preparation stage and second is characterization stage. The preparation stage focused on feasibility of producing a CMC-SA thin film biopolymer using solution cast technique. The second, the characterization is focused on determining the characteristics of biopolymer produced by using FTIR spectroscopy.

Methodology

Sample preparation, CMC used in the present research was obtained from Acros Organic Co. Solid biopolymer electrolytes were prepared via solution casting technique. 1g of CMC was dissolved in distilled water. The solution was stirred until the CMC completely dissolved. After that, the salicylic acid (SA) was added to the dissolved CMC by different wt%. The composition of the samples and their designation are tabulated in Table 1. After complete dissolution of the CMC and

SA, the solution were cast in the petri dishes and left dry at the room temperature to form films. The films were then kept in desiccators (with silica gel) for further drying.

Table 1: Designation and composition CMC and SA.

Designation	CMC (g)	SA (wt. %)
SA-0		0
SA-1		1
SA-3	1.000	3
SA-5		5
SA-7		7
SA-9		9

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].

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

Figure 1 shows the FTIR spectrum of CMC. The characteristic transmission band at 3040 cm^{-1} shows the hydrogen bonding OH stretching region. The small hump at 2977 cm^{-1} and 2897 cm^{-1} shows the attributable to C-H stretching vibration. The sharp peak observed at 1602 cm^{-1} confirms the presence of COO^- is assigned to stretching of the carboxyl group [4]. 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 1427 cm^{-1} and 1340 cm^{-1} are assigned to $-\text{CH}_2$ scissoring and $-\text{OH}$ bending vibration respectively. The band at 1060 cm^{-1} is due to CH-O-CH_2 stretching [5].

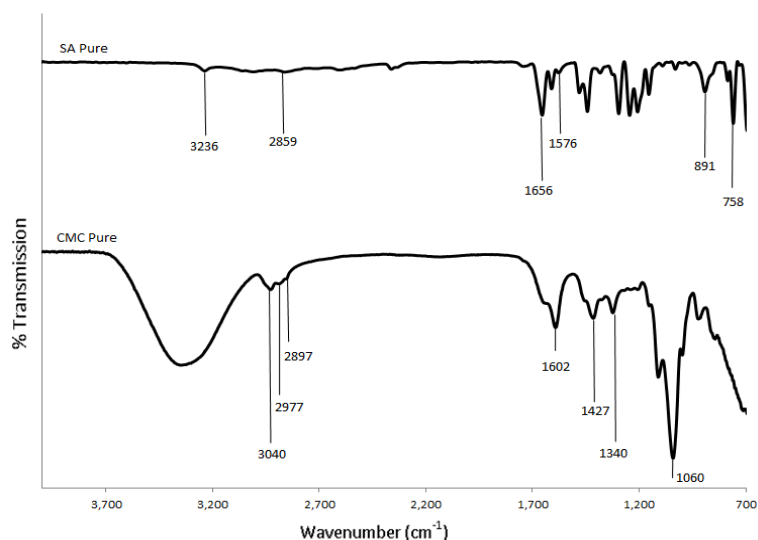


Figure 1: FTIR spectra of pure CMC and pure SA

SA was monohydroxybenzoic acid, a type of phenolic acid and a beta hydroxy acid. Salicylic acid formula is $C_6H_4(OH)COOH$. FTIR spectra of SA were shown in Figure 1. The FTIR study SA has been carried out in the 4000 to 700 cm^{-1} region. From the FTIR spectrum it stretching absorption of COOH group in primary two characteristic bands were observed at 758 , 891 , 1656 and 1576 cm^{-1} . The peak that appears at 3236 cm^{-1} was belong to vibrations of OH bonds. The peak at 2859 cm^{-1} was attributed to the C-O bands.

FTIR of CMC-SA biopolymer electrolytes

Figure 2, depicts the infrared spectrum of CMC-SA biopolymer electrolytes film. The spectrum shows the CMC doped with different wt. % of SA.

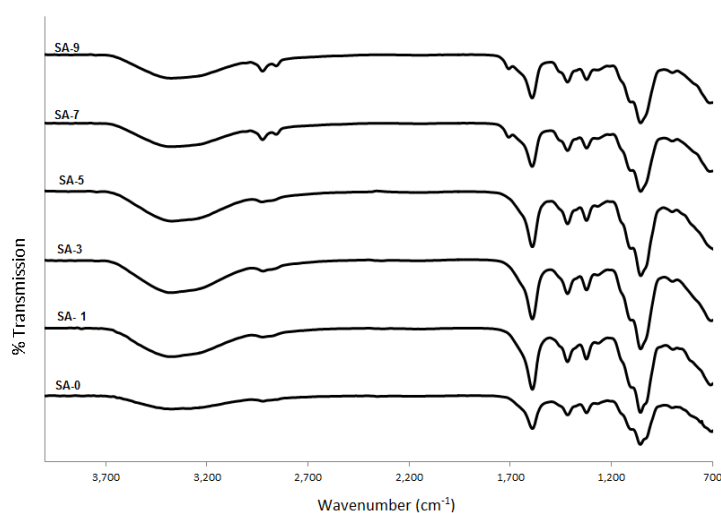


Figure 2: FTIR spectra of sample SA-0 to sample SA-9

From the Figure 2, it represents the interaction of CMC with the variation of SA concentration. This FTIR spectrum was taken in the range 700 cm^{-1} to 4000 cm^{-1} .

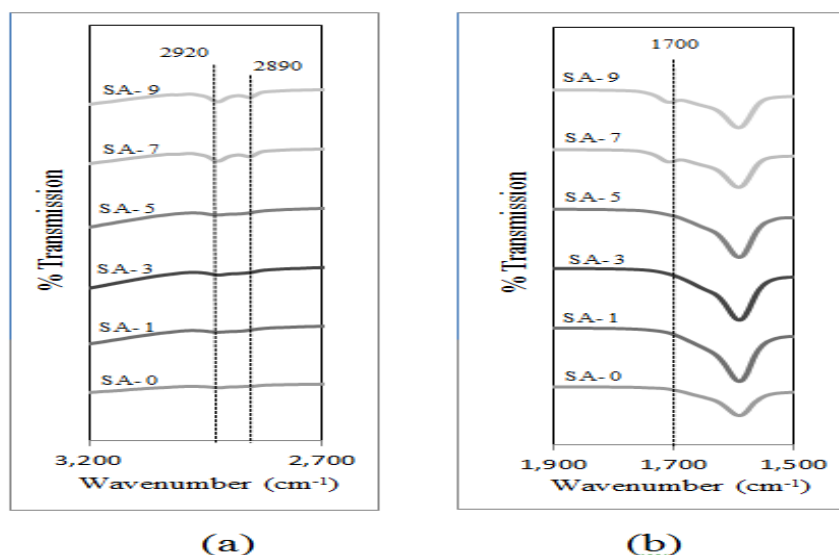


Figure 3: (a) CMC-SA IR spectrum in the region between 3200 cm^{-1} to 2700 cm^{-1} . (b) CMC-SA IR spectrum in the region between 1900 cm^{-1} to 1500 cm^{-1} .

From Figure 3, it can be observed that with increasing concentration of SA in the solid biopolymer system, a new peak emerged at 1700 cm^{-1} for the sample SA-7 and then increase until sample SA-9. The of COOH group from was 1656 and 1576 cm^{-1} shifted to the new peak at 1700 cm^{-1} . the peak was shifted to the higher wave number. Besides that, the two new peak was emerged from increasing the concentration of SA in the solid biopolymer system. The new peak was 2890 cm^{-1} and 2920 cm^{-1} . The peak that appears at 3236 cm^{-1} was belong to vibrations of OH bonds was shifted to the new peak at 2890 cm^{-1} and also was shifted to the peak at 2920 cm^{-1} .

Conductivity study of CMC-SA biopolymer electrolytes

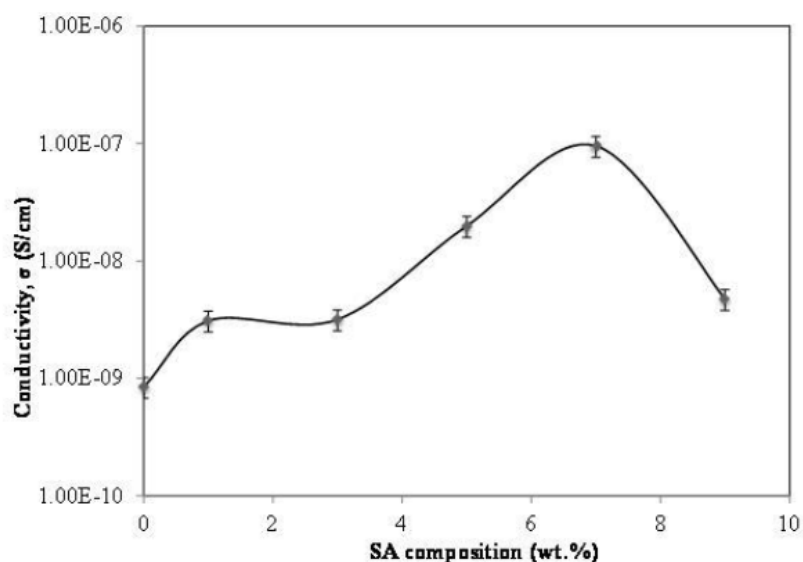


Figure 4: Conductivity versus SA composition at ambient temperature

Ionic conducting species concentration, cationic or anionic types charge carriers, the charge carrier's mobility and the temperature are several factors that influence the ionic conductivity [6, 7]. From Figure 4, it can be observed that the ionic, by addition of SA conductivity increases; this can be attributed to the increase in the number of mobile charge carriers. The highest conductivity at the

room temperature is $9.5 \times 10^{-8} \text{ Scm}^{-1}$ for sample SA-7 containing 7 wt. % of SA. With the addition of the more 7 wt. %, the conductivity starts to decrease. According to [8], the dependence of ionic conductivity on the salt concentration provides information on the specific interaction among the salt and the polymer matrix.

The temperature-dependent of ionic conductivity analysis was used to analyze the mechanism of ionic conduction of polymer electrolytes. Figure 5 shown the plot of log conductivity, σ versus $1000/T$ for the sample containing 0 wt.% to 9 wt.% of SA in temperature range 303 K to 393K..

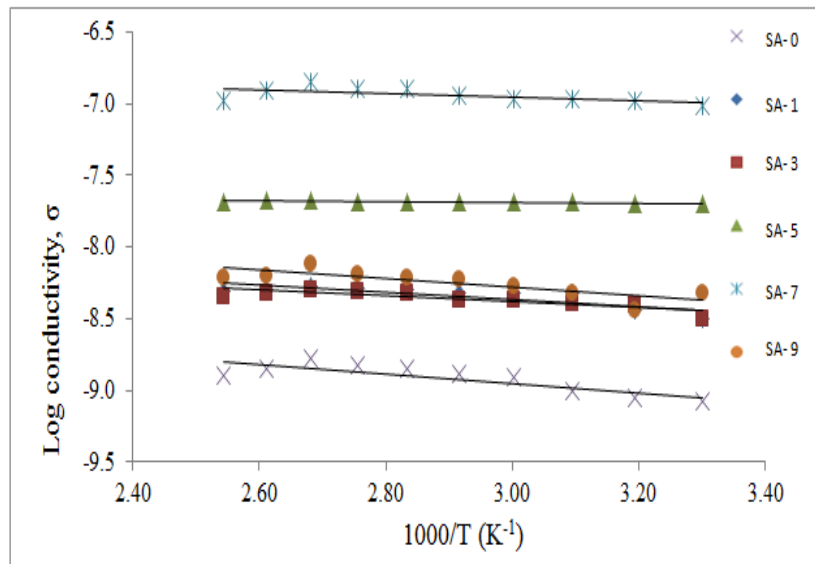


Figure 5: Plot of log σ vs. $1000/T$ for the CMC-SA system

From Figure 5, the linear relationship observed confirms that the variation in ionic conductivity with temperature obey the Arrhenius-type where the SPE system thermally activated process. It can be observed found that the proton conductivity of the SPE increases with increasing for all composition given by the relation:

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

where σ_0 is the pre-exponential factor, E_a the activation energy and k is the Boltzmann constant.

Designation	Activation Energy, E_a (eV)
SA-0	0.59
SA-1	0.54
SA-3	0.53
SA-5	0.47
SA-7	0.40
SA-9	0.50

The activation energy, E_a which is combination of the energy of defect formation and the energy for migration of ion was calculated from the slope of the log conductivity, σ versus $1000/T$ plot for all the samples. In the context of polymer electrolytes, the ion is usually “loosely bound” to site with donor electrons [9]. The movement from one site to another result in the conduction of

charge and the energy for this conduction is the E_a . When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site [6]. The E_a value for all samples is listed in Table 2. It was noticed from Table 2 that E_a for the conduction decreased gradually with increment an ionic conductivity of CMC-SA SBE system. Decreasing the value of E_a implies that the ions highly conducting samples require lower energy for migration. Since the ion transfer is greatly affected by the polymer segmental motion: an electrolyte with lower value of E_a implies rapid ionic conduction and then increase conductivity to the higher value. This is in agreement with the fact that the amount of ions in the biopolymer electrolyte increases with increasing in salt content, the energy barrier for the proton transport decreases and leading to a decrease in the activation energy. The low activation energy for CMC-SPE system is also due to the completely amorphous nature of polymer electrolyte that facilitates the fast H^+ ion motions in the polymer network [10].

Conclusion

Carboxy methylcellulose (CMC) based solid biopolymer electrolyte (SBE) was prepared by solution casting technique, with doping of different composition of salicylic acid (SA). XRD measurements confirmed that the SPE system predominantly amorphous in nature. The amount of SA has been found to influence the proton conduction and the high ambient temperature ionic conduction value of $9.50 \times 10^{-8} \text{ S cm}^{-1}$ has been obtained for CMC with 7 wt. % SA composition. The temperature dependence of ionic conductivity of these electrolytes exhibited Arrhenius behavior. FTIR studies was carried out to determine the dissociation of free protons (H^+) from the carboxyl group ($-COOH$) of SA.

Acknowledgments

The authors would like to thank all the members of Advanced Material Team and Ministry of Education Malaysia for financial support via FRGS and ERGS grant.

References

- [1] Nigmatullin, R., Lovitt, R., Wright, C., Linder, M., setälä, T.N. & Gama, M. (2004) Atomic force microscopy study of cellulose surface interaction controlled by cellulose binding domains. *Colloids and Surfaces B: Biointerfaces* 35 125-135.
- [2] Miller, K.S. and Krochta J.M . 1997. Oxygen and aroma barrier properties of edible films: A review. *Trends in Food Science & Technology*, Volume 8, Issue 7, July 1997, Pages 228-237.
- [3] Osman, Z., Ibrahim, Z. A., & Arof, A. K. (2001). Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes. *Carbohydrate Polymers*, 44, 167–173.
- [4] Su, J.F., Huang, Z., Yuan, X.Y., Wang, X.Y., Li, M. (2010) Structure and properties of carboxymethyl cellulose/soy protein isolate blend edible films crosslinked by Maillard reactions. *Carbohydrate Polymers*. 79, pp. 145–153.
- [5] AbouTaleb MF, Abd El-Mohdy HL, Abd El-Rehim HA (2009) Radiation preparation of PVA/ CMC copolymers and their application in removal of dyes. *Journal of hazardous materials*. 168, pp. 68-75.

-
- [6] Samsudin, A.S. & Isa, M.I.N. (2012). Structural and electrical properties of carboxy methylcellulose- dodecyltrimethyl ammonium bromide-based biopolymer electrolytes system. *International Journal of Polymeric Materials*, 61, 30-40.
- [7] Ellen Raphael, César O. Avellaneda, Bruno Manzolli & Agnieszka Pawlicka. (2010). Agar-based films for application as polymer electrolytes. *Electrochimica Acta*, 55, 1455-1459.
- [8] Yahya, M.Z.A. & Arof, A.K. (2003). Effect of oleic acid plasticizer on chitosan- lithium acetate solid polymer electrolytes. *European Polymer Journal*, 30, 897-902.
- [9] Buraidah, M.H., Teo, L.P., Majid, S.R. & Arof, A.K. (2009). Ionic conductivity by correlated barrier hopping in NH₄I doped chitosan solid electrolyte. *Physica B*, 404, 1373-1379.
- [10] Rozali, M.L.H., Samsudin, A. S., Isa, M.I.N. (2012). Ion Conducting Mechanism of Carboxy Methylcellulose Doped With Ionic Dopant Salicylic Acid Based Solid Polymer Electrolytes *International Journal of Applied Science and Technology* Vol. 2 No. 4.