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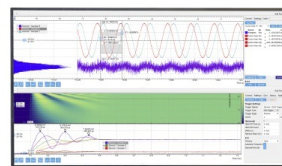
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# Characterization of Polyethylene Glycol Plasticized Carboxymethyl Cellulose-Ammonium Fluoride Solid Biopolymer Electrolytes

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**Abstract.** An attempt to increase the ionic conductivity of solid biopolymer electrolyte (SBE) from carboxyl methylcellulose (CMC) doped with 9 wt. % of ammonium fluoride (AF) has been made by the plasticizing with polyethylene glycol (PEG). Electrochemical Impedance Spectroscopy (EIS) was used to investigate the ionic conductivity of the CMC-AF-PEG SBEs. The study shows that the highest conductivity achieved is  $6.62 \times 10^{-7} \text{ S cm}^{-1}$  at room temperature for SBE with 25 % wt. PEG. X-Ray Diffraction (XRD) study proved that the highest conductive SBE has the highest amorphous nature which contributes to the high conductivity of the SBE. The interaction of CMC and AF was enhanced by the addition of PEG at C-O band in the CMC.

## INTRODUCTION

Since the earliest breakthrough of polymer-salt complexes by Wright in 1975 [1], there was a plethora of research focusing on the study and development of solvent free polymer electrolytes (SPEs). Extensive research on SPEs were driven by their advantages such as ease of preparation, light weight, leakage free, mechanically stable and flexibility for packaging design over gel/liquid counterparts [2]. SPEs have become promising materials for electrochemical device applications, namely, high energy density rechargeable batteries, fuel cells, supercapacitors, sensors and electrochromic displays [3]. Currently there are two types of polymers; natural polymers and synthetic polymers (petroleum based). Although synthetic polymers such as polyvinyl alcohols (PVA), polyethylene oxide (PEO) and polyacrylic acid (PAA) based electrolyte attracts more interest than natural based solid biopolymer electrolytes (SBEs) due to their high conductivity, the price of these materials is higher [3]. This turns the attention towards natural based SBEs which are much cheaper, easier to find and have eco-friendly properties. Natural based polymer electrolytes are usually made of starch, chitosan, cellulose, soy-based and sago [4-7]

Cellulose is one of the most abundance materials on earth which made it easy to get them at much cheaper price. One type of cellulose that are notably been used in many industries such as in foods, cosmetics, and pharmaceutical and recently popular in electronic devices are Carboxymethyl Cellulose or CMC. It is easily dissolved in water and have good characteristics as solid polymer electrolyte [8-10]. Introduction of plasticizer is one of popular methods to further increase the ionic conductivity of SBEs in addition to polymerization, ceramic fillers, and blending [11,12]. Some of most used plasticizing agent are ethylene carbonate (EC), propylene carbonate (PC), polyethylene glycol (PEG), dimethyl carbonate (DMC), glycerol and diethyl carbonate (DEC) [13].

The present work is aimed to synthesize the polyethylene glycol (PEG) plasticized carboxymethyl cellulose doped ammonium fluoride (NH<sub>4</sub>F) and to investigate the effect of plasticizer composition on the ionic conductivity, complexation and structural properties of the SBEs.

## MATERIALS AND METHODS

### Sample Preparation

Carboxymethyl cellulose (CMC) and ammonium fluoride (NH<sub>4</sub>F) were stirred in distilled water until homogenous. Different weight percentage (5-30 wt. %) of polyethylene glycol (PEG) is added into the CMC-NH<sub>4</sub>F solution and magnetically stirred until homogenous. The CMC-AF-PEG solution then casted into several petri dishes and dry in oven at 60°C. The calculation for weight percentage is calculated as follows:

$$\frac{x}{x+y} \times 100\% = wt\% \quad (1)$$

Here  $x$  is the weight of PEG and  $y$  is total weight of CMC + NH<sub>4</sub>F.

### Characterization

The samples will be characterized via Electrical Impedance Spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer in a frequency range between 50 Hz and 1 MHz. The SBE samples were cut into appropriate size and sandwiched between two stainless steel electrodes under spring pressure. The measurements were carried out at room temperature. The ionic conductivity of the SBEs can be calculated from the Equation 2.

$$\sigma = t/AR_b \quad (2)$$

Here  $A$  (cm<sup>2</sup>) is the electrode-electrolyte contact area of the film and  $t$  is its thickness.  $R_b$  is bulk resistance obtained from the complex impedance plot (Cole-Cole plot). X-Ray Diffraction (XRD) measurement was performed using Rigaku Mini Flex 2 XRD Diffractometer. Prior, samples were cut into a suitable size (2 cm × 2 cm) and then adhered onto a glass slide. The glass slide was placed in the sample holder and scanned at  $2\theta$  angles between 5° and 80° with X-rays of 1.5406 Å wavelength generated by a Cu K $\alpha$  source. Fourier Transform Infrared (FT-IR) study was done by using Shimadzu IRTracer-100 FTIR spectrometer. The SBEs were clamped in between germanium crystal and sample holder and scanned at frequency range from 700 to 4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolutions.

## RESULTS AND DISCUSSION

### Electrochemical Impedance Spectroscopy study

The ionic conductivity ( $\sigma$ ) of the SBEs were calculated using Equation 2 and were plotted in a graph on ionic conductivity against PEG content as shown in Figure 1. The highest ionic conductivity achieved is  $6.62 \times 10^{-7}$  S cm<sup>-1</sup> for sample PEG25. From the figure, the ionic conductivity of CMC-AF-PEG can be qualitatively explained by dividing the graph into several sections.

In the 1<sup>st</sup> section (0%-5%), the increase in  $\sigma$  at this region can be due to the increasing number of free mobile ions donated by AF with the addition of PEG. This made the number of conduction occurred increased in the polymer matrix hence increased the  $\sigma$ . The decreased  $\sigma$  at 5-10 can be referred to ion association in the polymer where, as the number of free mobile ions increased, the distance between the ions decreased hence they tend to form ion pairs due to the attractive interaction between ions.

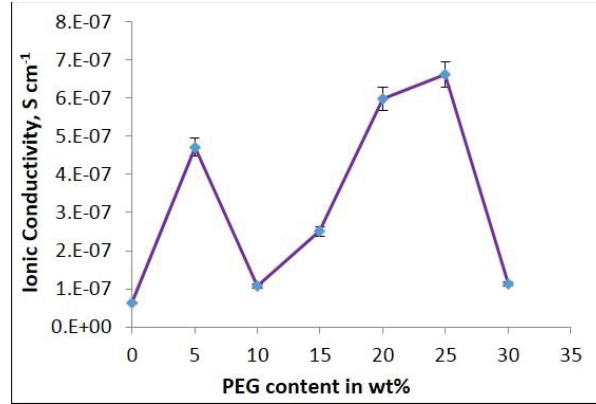


FIGURE 1. Ionic conductivity relative to PEG content

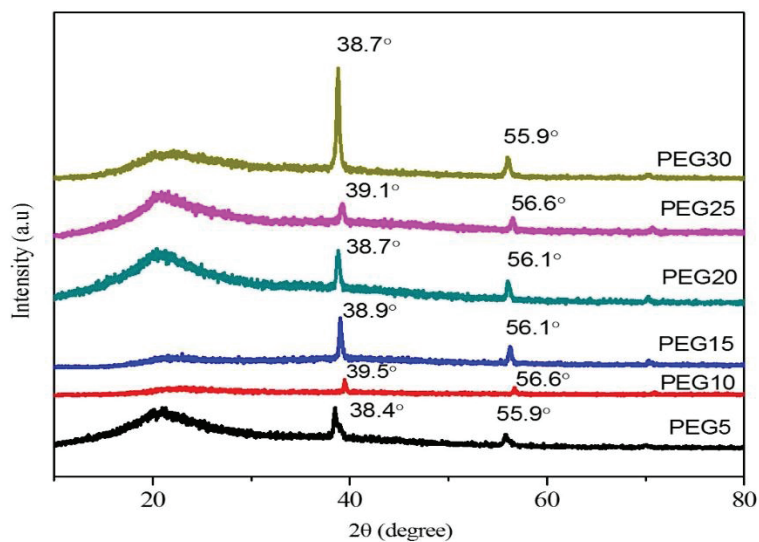
In 2<sup>nd</sup> section, (10%-30%), the increased conductivity from 10% to 25% and the decreased conductivity 25% to 30% can be noted as a common feature in solid polymer electrolytes. There are two explanations available for describing what happened in the polymer system. Firstly, according to Fuoss theory of triplet ion [14], the conductivity increased were contributed to the triplets because they are the dominating charge carriers at high concentration. Whereas in second theory (redissociation theory) the dominating charge is single ions which generated from the dissociation of ion pairs. The long-range electrostatic forces applied by the nearby dissociated ions which reduced the pair potential [15].

### X-Ray Diffraction study

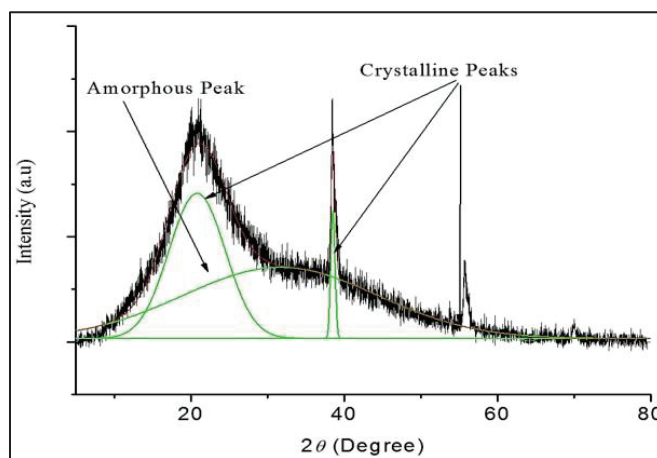
XRD study was done to determine the complexation between CMC-AF and PEG. Figure 2 shows the XRD diffraction of CMC-AF-PEG SBES. From Figure 3, it can be seen that there are two poly-crystalline peaks appeared which originated from the AF. The slightly shift of the peaks indicates the creation of salt-polymer complexes [24]. The mixture of amorphous and crystalline peaks reveals that the CMC-AF-PEG SBE has semi-crystalline structure. To further investigate the percentage of amorphous/crystalline in the SBE, the degree of crystallinity ( $X_c$ ) were determined.  $X_c$  were determine by deconvoluting the XRD diffraction of each SBE and then calculated using equation 3 [4]

$$X_c = \frac{T_c}{T_c + T_a} \times 100\% \quad (3)$$

Here  $T_c$  is total area under the graph of the crystalline peak and  $T_a$  is total area under the graph of the amorphous peak. Figure 4 shows the deconvolution of CMCAF-PEG5 SBE diffraction. Table 2 list the SBES with their respective degree of crystallinity,  $X_c$ . From the table, it is observed that sample CMC-AF-PEG-25 has the lowest value of  $X_c$ . According to Rahaman *et al.*, 2014 [17], the low value of  $X_c$  indicates high value of amorphous nature. This concludes that sample CMC-AF-PEG-25 has the highest amorphous nature hence explain the high ionic conductivity of the SBE. Sohaimy and Isa, 2015 [18] stated that the movement of free ions is restricted in amorphous region only and no movement occurred in crystalline region thus support the high ionic conductivity of the most amorphous SBE in this work.



**FIGURE 2.** XRD diffraction of selected SBE samples



**FIGURE 3.** XRD deconvolution of PEG5 SBE.

**TABLE 1.** Degree of crystallinity for all SBEs

Sample	$T_a$	$T_c$	$X_c$ (%)
CMC-AF-PEG-5	4322.22	2723.24	38.65
CMC-AF-PEG-10	1530.68	412.33	21.22
CMC-AF-PEG-15	2207.62	717.44	24.53
CMC-AF-PEG-20	7337.33	3870.32	34.53
CMC-AF-PEG-25	7650.31	1553.26	16.87
CMC-AF-PEG-30	2970.14	2483	45.53

### Fourier Transform Infrared Study

Through the Fourier Transform Infrared (FT-IR) study, the functional group and the structure of a molecule can be determined. In this work, FT-IR study were used to recognize the complexation occurred in the SBEs. From previous report by [19] has discussed the functional group in CMC, AF and CMC-AF respectively.

In CMC spectra, the stretching of O-H can be found at broad peak which centered at  $\sim 3363\text{ cm}^{-1}$  and the small peak at  $\sim 2893\text{ cm}^{-1}$  is the stretching of C-H which associated with the ring methane hydrogen [20]. Peak at about  $\sim 1591\text{ cm}^{-1}$  is the stretching mode of C=O in the backbone of CMC carbonyl group [21]. The peak at  $\sim 1415\text{ cm}^{-1}$  and  $\sim 1323\text{ cm}^{-1}$  can be attributed to O-H stretching and C-H bending respectively which denotes to the polysaccharide skeleton of CMC. The peak at  $\sim 1024\text{ cm}^{-1}$  is the C-O stretching. In  $\text{NH}_4\text{F}$ , stretching of N-H was found at  $\sim 3176\text{ cm}^{-1}$  and the bending of N-H was found at  $\sim 3028\text{ cm}^{-1}$ ,  $2823\text{ cm}^{-1}$  and  $\sim 1448\text{ cm}^{-1}$  [20]. In PEG spectra, the O-H stretching vibration was observed at  $\sim 3331\text{ cm}^{-1}$ . The peak at  $\sim 2870$  can be attributed to the stretching of C-H. The peak at  $\sim 1469\text{ cm}^{-1}$  and  $\sim 1390\text{ cm}^{-1}$  can be assign to the bending of C-H respectively. The stretching of C-O of first and secondary alcohol can be found at  $\sim 1062\text{ cm}^{-1}$  and  $\sim 1092\text{ cm}^{-1}$  respectively [22].

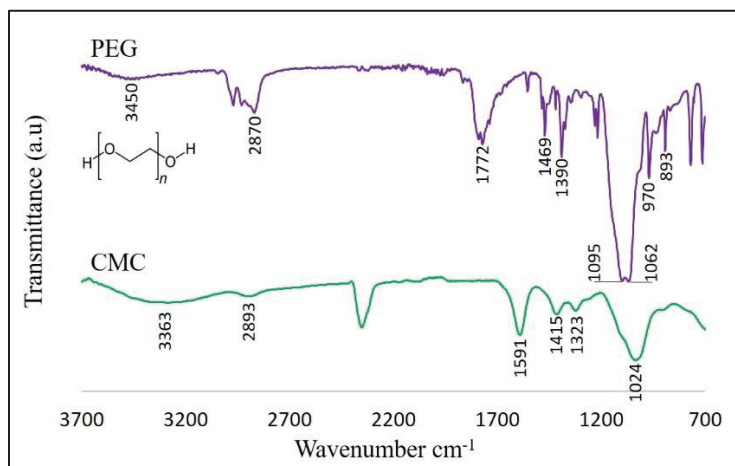


FIGURE 4. FT-IR spectra of CMC and PEG at ambient temperature.

Figure 5 depicts the FT-IR spectra of all SBEs at ambient temperature in range between  $800\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$ . From the figure, it can be seen that the C-O band at  $\sim 1043\text{ cm}^{-1}$  has slightly shifted to higher wavenumber to  $\sim 1049\text{ cm}^{-1}$  and the peak broaden respectively as the concentration of PEG increased. It is observed also that there is no additional peak appeared. Interestingly, from previous report by [20] the interactions between CMC and AF occurred at the C=O of CMC, but there are no interactions occurred in the present work as there are no peak shift or changes in intensity of the peak. With the introduction of PEG, it seems to promote the  $\text{H}^+$  ions from AF to interact more with O atom at C-O band.

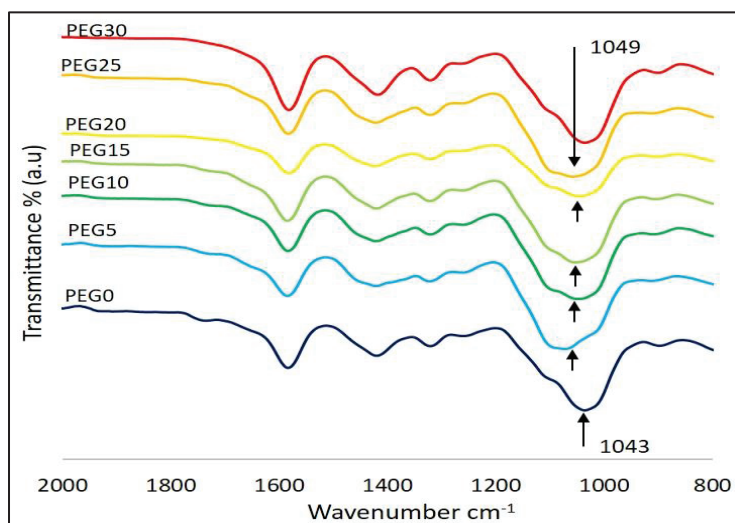


FIGURE 5. FT-IR spectra of all SBEs



## CONCLUSIONS

The CMCAF-PEG SBEs were successfully fabricated using solution casting technique. The highest ionic conductivity achieved is  $6.62 \times 10^{-7} \text{ S cm}^{-1}$  at room temperature for sample CMC-AF-PEG-25. The amorphousness of the SBE has significant contribution in increasing the ionic conductivity as seen in the XRD study where the most conductive SBE has the most amorphous nature. From FT-IR study, the addition of PEG promotes more interactions at C-O band of CMC and there are no new peaks emerged. All study shows that PEG is a good plasticizing agent as it increased the ionic conductivity and amorphousness of the SBE.

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