Spectroscopic Study on the Film of Polyvinyl Alcohol and Carboxymethyl Cellulose as Polymer Electrolyte Materials

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Abstract. Polymer electrolytes have emerged as a powerful platform in the progress of more efficient energy storage devices. In this study, polymer electrolyte materials (PEM) was successfully prepared using drop casting method. A spectroscopic study of the film were prepared by varying the ratio of the volume (PVA/CMC) at 100/0, 75/25, 50/50, 25/75 %. The functional groups were investigated using fourier transform infrared (FTIR) spectroscopy. The crystallinity degree obtained by X-ray diffraction (XRD). Their transparency degree were observed by UV-Vis spectroscopy. The ionic conductivity studies obtained by electrochemical impedance spectroscopy (EIS).

1. Introduction

The advancement of more efficient energy storage devices using polymer electrolytes (PE) has emerged as a strong platform. PEM attracts the attention of many researchers because of its excellent nature for use in low electrical devices such as batteries [1]. Petroleum-based polymer applications that provide losses such as high costs, depletion of petroleum resources and trigger environmental problems [2]. Therefore, efforts are needed to develop biopolymer-based electrolyte polymers as an alternative use of petroleum.

Recently, carboxymethyl cellulose (CMC) has attracted attention as a promising substitute in electrolyte systems because it is a cost-effective and harmless material [3]. CMC is a cellulose derivative obtained by inserting a carboxymethyl group (CH2COOH) into the cellulose chain [4]. The polyvinyl alcohol (PVA) is one of the potential candidates in the application of composite films due to its hydrophilicity properties. Beside that, PVA has the structure where its carbon chain backbone has attached hydroxyl group (-OH) to methane carbon. These characteristics make it an important source of intermolecular attraction to form PEM. These characteristics make it an important source of intermolecular attraction to form PEM [5]. Therefore, CMC and PVA have potential towards the development of PEM [6]. In this study, we showed the effect of adding CMC content to PVA by adopting a mixing technique. Then, The PVA/CMC films are then characterized using FTIR, XRD, UV-Vis, and EIS to find out functional groups, crystallinity, transparency and ionic conductivity, respectively.
2. Method
2.1. Materials
The raw materials used in this study are poly(vinyl alcohol) (Mw = 146,000-186,000 g/mol) at 99+ % hydrolyzed purchased Sigma-Aldrich from USA. Sodium-Carboxymethyl cellulose (CMC) of chemical grade purchased Sigma-Aldrich from USA. The Aquadest as a solvent for polymer material.

2.2. Preparation of Films
The PVA/CMC films were prepared by drop casting in teflon stainless. It was prepared from different weight percentage ratios of both PVA and CMC. The 2 % PVA solution prepared by 2 gr of PVA dissolved in 100 ml of aquadest and stirred at 500 rpm for 2 h at 85 °C. The 1 % CMC solution prepared by 1 gr of CMC dissolved in 100 ml of aquadest and stirred at 500 rpm for 4 h at 80 °C. The PVA/CMC film prepared by varying the ratio of volume at 100/0, 75/25, 50/50, and 25/75 % and stirred at 500 rpm for 15 min to have good homogeneity for mixture with temperature at 80 °C. The PVA/CMC solution were casted into teflon stainless (diameter 6 cm) and oven-dried at 30 °C for 24 h. The dried films were peeled from teflon stainless and characterized.

2.3. Characterization
Ja The functional groups measurement using fourier transform infrared spectroscopy (FTIR). The crystallinity degree measurement using X-ray Diffraction in Shimazu XRD-7000, provide with a Cu Kα radiation (λ=0.154 nm) at 40 kv and 30 ma in the 2theta range of 5° until 60° at a speed of 2° min⁻¹. The transparence degree measurement by UV-Vis spectroscopy in the wavelength range 200-600 nm. The ionic conductivity measurement using electrochemical impedance spectroscopy in a HIOKI 3522-50 LCR HiTESTER under room temperature with a range frequency of 50 Hz to 1 MHz. The ionic conductivity was determined using equation (1), and while the resistance value was obtained using equation (2) [7].

\[
\sigma = \frac{t}{RA} \tag{1}
\]

\[
R = \frac{1}{G} \tag{2}
\]

Where \( t \) is a thickness of the sample, \( A \) (cm²) the cross-sectional area of the film, \( R \) is resistance, and \( G \) is conductance value was obtained from LCR meter. The thickness of the PEM was found of 0.0002 cm using a micrometerect.

3. Results and Discussion
A The physical appearance on the PVA/CMC film obtained from this study is illustrated in Figure 1. The sample prepared showed transparent, free standing and flexible behavior as a solid film.

![Figure 1](image-url)
3.1 Chemical and Structure Analysis

Complexation interactions that occur between PVA and CMC are observed through FTIR spectroscopy shown in Figure 2. Addition of CMC causes the disappearance and shifts of several peaks, which shows that the complexation of interactions between PVA and CMC is formed. This complexation can change the molecular chain that affects its physical properties, which are characterized by increasing or decreasing electrical properties [8].

![Figure 2. The FTIR spectra of the PVA/CMC films](image)

The absorption band at C-C, C-O-C, -OH, -CH2, -COO-, C=O, -CH, and -OH is very clearly observed the occurrence of complexation which causes the intensity and wave numbers to decrease or shift [2,9–11]. The complexity between PVA and CMC is shown in Table 1. PVA can interact with CMC through intermolecular H-bonds in the presence of active sites so as to reduce the intensity of the absorption peak [10]. The absorption band at the peak of 1097.24 1/cm shifts to 1086.43 1/cm because the ether (C-O-C) connection containing oxygen sites is able to form intermolecular H-bonds with other molecules such as PVA with CMC [2]. The absorption band at the peak of 1658 1/cm (C=O acetate) at 100/0 disappears when the addition of CMC, this confirms the CMC deformation into the PVA. This observation is similar to the research conducted by Ali et al., It was reported that changes in intensity and shifts in peak wave numbers occur when CMC composition increases [10]. It is clear that all changes shown confirm the interaction of complexity between PVA and CMC.

**Table 1.** List of vibrational Modes of PVA/CMC films

| 100/0 (1/cm) | 75/25 (1/cm) | 50/50 (1/cm) | 25/75 (1/cm) | Functional groups |
|--------------|--------------|--------------|--------------|------------------|
| 853          | 852          | 852          | 850          | Stretch C-C      |
| 1097         | 1098         | 1094         | 1086         | Bending C-O-C   |
| 1333         | 1330         | 1328         | 1327         | Bending –OH     |
| 1422         | 1420         | 1419         | 1418         | Scissoring -CH2 |
| 1566         | 1592         | 1595         | 1596         | Asymmetrical -COO- |
| 1658         |              |              |              | Stretching C=O  |
| 2943         | 2942         | 2942         | 2941         | Stretching –CH1 |
| 3307         | 3219         | 3216         | 3293         | Stretching –OH  |
3.1.1. Crystallinity Degree Analysis
The XRD patterns obtained for the PVA/CMC (100/0, 75/25, 50/50, and 25/75 %) is shown in Figure 3. The two maximum intensity diffraction peak exist around 2theta angles is \( \sim 19.6 \) and \( \sim 44.5 \). The main peak occured at \( \sim 19.6 \), corresponded to the typical reflection of the PVA. The Another weak peak was observed at \( \sim 44.5 \), confirmed the semi-crystalline structure. An increase in CMC volume causes the diffraction peak at \( \sim 19.6 \) to decrease so that the structure of the PVA/CMC film becomes more amorphous. However, diffraction peaks of PVA/CMC films are weakened and broadened with an increase in CMC content, which shows a decrease in crystallinity or dominance of the amorphous phase [11]. The two polymers applied in this study are generally semi-crystalline materials due to the occurrence of both crystalline and amorphous regions [2].

![Figure 3. X-ray diffraction pattern of the PVA/CMC films](image)

3.2 Transparance Degree Analysis
One of the indicators to determine the possibility of mixing two or more compositions in a mixture film can use a degree of transparency measurement. Light transmittance from PVA/CMC films at wavelengths of 200-600 nm is shown in Figure 4. The transmittance curve decreases clearly with each...
CMC composition increasing. This result means that the CMC composition is relatively increased in the film, which decreases the degree of transparency of the film.

Figure 4. Transmittance spectra of the PVA/CMC films

3.3 Ionic Conductivity Analysis

The ionic conductivity measurement is carried out to determine the effect of adding CMC into the PVA. Based on the results of the previous XRD analysis, it was proven that the PVA crystallinity was measured after the incorporation of CMC. The relationship between crystallinity and ionic conductivity is further investigated. The ionic conductivity is illustrated in Figure 5, which shows a decrease in ionic conductivity when CMC is mixed by PVA gradually. The value of ionic conductivity PVA/CMC % (100/0, 75/25, 50/50, 25/75 %) are $1.74 \times 10^{-4}$ S/cm, $1.31 \times 10^{-4}$ S/cm, $9.17 \times 10^{-5}$ S/cm, and $1.022 \times 10^{-7}$ S/cm, respectively. Perhaps this decrease is due to the higher amorphous phase which was confirmed from the XRD analysis. These results are dissimilar with those found by Saadiah et al., The higher amorphous phase confirmed from XRD causing an increase in the value of ionic conductivity [2]. Ramli and Isa., [12] and also Hafiza and Isa., [13] reported similarly, an increase in ionic conductivity can be caused by an increase in amorphous in the sample, which encourages ion transport.
4 Conclusion
The PVA/CMC based PEMs were successfully carried out by the mixing method. The highest and lowest ionic conductivity of PEM was achieved to the sample with the PVA/CMC ratio at 100/0 % and 25/75 %, namely $1.74 \times 10^{-4}$ S/cm and $1.022 \times 10^{-7}$ S/cm. The addition of CMC in PVA reduces the value of ionic conductivity in the sample, which is also represented by an increase in the amorphous degree of PVA.

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