Structural Properties of Cellulose Acetate From Oil Palm Empty Fruit Bunch Doped With LiClO$_4$ As Biopolymer Electrolyte

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Abstract. Cellulose acetate biopolymer electrolyte from oil palm empty fruit bunch doped with LiClO$_4$ was synthesized by solution casting method. Structural properties of this biopolymer electrolyte were characterized by Fourier Transform Infra Red (FTIR) and X Ray Diffraction (XRD). Result of FTIR analysis, the addition of LiClO$_4$ caused shifted in wavenumber to the lower wavenumber in C=O functional group and shifted in wavenumber to the higher wavenumber in C-O functional group. Based on the results of XRD analysis, the presence of LiClO$_4$ caused the crystalline phase of cellulose acetate to be a more amorphous phase. These indicated an intermolecular interaction between cellulose acetate and LiClO$_4$ and LiClO$_4$ dissociate in polymer matrix of cellulose acetate.

1. Introduction
The usage of lithium-ion batteries increased in daily life, especially in electronic equipment. This lifestyle caused an enhancement amount of battery waste that it was dumped into the environment. Battery waste leads to contamination of hazardous heavy metals and liquid. Environmental-friendly and recycling of battery materials become more concern for further research [1-2].

Solid polymer electrolytes are being part of the battery that it is found in the lithium-ion battery. Polymer electrolyte from easily degraded materials (biopolymers) is more considered to develop in research for supporting waste reduction and green environment. Biopolymer electrolytes are generally from derivatives of polysaccharides such as cellulose, alginate, and carrageenan [3-6]. Cellulose sources can be obtained from plants and plantation waste, for example, oil palm empty fruit bunch. The processing of oil palm produces solid waste of oil palm empty fruit bunches around 22-24% of the total waste [7]. Extracted cellulose from oil palm empty bunches was then modified to cellulose acetate by acetylation reaction [8-9].

Various modifications were made to improve the characteristics of cellulose acetate as a biopolymer electrolyte in lithium-ion batteries. These were begun with varying the type of lithium salts, adding plasticizers and mixing with other polymers [10-12], [3]. These characteristics include conductivity, mechanics, and thermal resistance. These characteristics are influenced by the interaction of the
constituent components in the polymer electrolyte, especially the host polymer with lithium salts. The interaction is also useful to determine compatibility or miscibility between components in biopolymer electrolyte [13-14].

The presence of interaction can be revealed through analysis of the structural properties of biopolymer electrolyte. The structural properties were characterized by FTIR analysis by confirming changes in its functional groups and XRD analysis by its crystallinity. Therefore in this paper is aim to know the effect of LiClO₄ on cellulose acetate synthesized from oil palm empty fruit bunches cellulose extract on its structural properties characterized by FTIR and XRD.

2. Materials And Methods

2.1 Materials

Oil palm empty fruit bunch were obtained from Pontianak, West Kalimantan. All chemicals were from analytical standard and purchased from Material Physical Chemistry Laboratory. All chemicals were used without further purification.

2.2 Methods

Preparation of Cellulose Acetate/LiClO₄

Biopolymer electrolytes were prepared by mixing cellulose acetate solution in chloroform and LiClO₄ in methanol and stirred for 4 hours until homogenous with composition 85% cellulose acetate and 15% LiClO₄ (%w/w). Cellulose acetate was synthesis from acetylate cellulose extract and cellulose was extracted from oil palm empty fruit bunch. Synthesis of cellulose acetate and extracting cellulose based on Nurhadini and Arcana [9]. Biopolymer electrolyte solution was casted in glass plate and evaporated the solvent until dried. Thin biopolymer electrolyte was characterized by FT-Infra Red (FTIR) analysis and X-Ray Diffraction (XRD) analysis.

3. Result And Discussion

3.1 FTIR Analysis

FTIR analysis was used to identify the interaction of LiClO₄ with cellulose acetate by observing peak functional group absorption. The existence of this interaction can be characterized by changes in absorption peak, namely shifting wave numbers, the emergence of new peaks or changes in absorption intensity. Figure 1 is an FTIR spectrum of cellulose acetate and cellulose acetate which is added 15% LiClO₄ shown in the spectrum with wave numbers 1850-1300 cm⁻¹ and 1300-600 cm⁻¹.

Based on Figure 1, it showed that the absorption pattern of pure cellulose acetate and cellulose acetate with LiClO₄ had different vibration absorption in their functional group. The spectrum of cellulose acetate has peak absorption of carbonyl group (C=O) symmetric stretching at 1738 cm⁻¹, which is shifted to 1734 cm⁻¹ when it was added 15% LiClO₄. The peak shifted also occurred from 1371 cm⁻¹ to 1374 cm⁻¹ was assigned to vibration stretching of C-CH₃. These peaks shifted indicated the presence of interaction between Li⁺ with polymer backbone. Another evidence interaction Li⁺ with cellulose acetate were peak shifted at 1221 cm⁻¹ and 1036 cm⁻¹. The peaks of pure cellulose acetate at 1221 cm⁻¹ and 1036 cm⁻¹ was due to stretching vibration of C–O from primer alcohol and stretching vibration of C-O from acetyl group, respectively. These peaks have been shifted to 1229 cm⁻¹ and 1048 cm⁻¹ when cellulose acetate with addition LiClO₄. The interaction of Li⁺ and cellulose acetate indicated that the presence intermolecular interaction between cellulose acetate and LiClO₄ by complexation interaction [9], [15]. The list of assignment of cellulose acetate and cellulose acetate with LiClO₄ was presented in Table 1.
Figure 1. FTIR spectrum of (a) cellulose acetate and (b) cellulose acetate with 15% LiClO$_4$; (I) The peaks at 1850 cm$^{-1}$ – 1300 cm$^{-1}$ and (II) the peaks at 1300 cm$^{-1}$ - 600 cm$^{-1}$

Table 1. The assignment of cellulose acetate and cellulose acetate with 15% LiClO$_4$

| Assignment    | Cellulose Acetate Wavenumber (cm$^{-1}$) | Cellulose Acetate with 15% LiClO$_4$ Wavenumber (cm$^{-1}$) |
|---------------|------------------------------------------|----------------------------------------------------------|
| C=O           | 1738                                     | 1734                                                     |
| C –CH$_3$     | 1371                                     | 1374                                                     |
| C – O         | 1221                                     | 1229                                                     |
| C – O         | 1036                                     | 1048                                                     |
| CH$_2$ rocking | 901                                      | 901                                                      |
| ClO$_4^-$      | -                                        | 623                                                      |

The existence of ClO$_4^-$ ions in the polymer matrix was observed with a peak at 623 cm$^{-1}$. According to Sim et al (2010) vibrational frequencies of LiClO$_4$ at 616 cm$^{-1}$ and 633 cm$^{-1}$ (doublet) in signature area. A peak 616 cm$^{-1}$ was attributed to free ClO4 ions and the tiny shoulder at 633cm$^{-1}$ [16]. In this study, it indicated LiClO$_4$ dissociation and form complex with the polymer matrix in cellulose acetate [15].
3.2 X-Ray Diffraction Analysis

XRD analysis was characterization to study crystallinity in structural properties of biopolymer electrolyte. The XRD diffractogram of cellulose acetate and cellulose acetate with 15% LiClO₄ was shown in Figure 2.

![Figure 2. XRD Diffractogram of CA and CA with 15% LiClO₄](image)

Crystalline peaks of cellulose acetate were observed range at 2θ = 9° – 27°. In this study crystalline peaks of cellulose acetate was shown at 2θ = 18° and 22° in Figure 2. These peaks intensity was decreased when cellulose acetate was added with 15% LiClO₄. These reducing peaks intensity lead to a broad peak due to LiClO₄ soluble in cellulose acetate. It was suggested that interaction cellulose acetate with LiClO₄ lead to enhance amorphous phase in cellulose acetate. Amorphous phase in cellulose made ion moving more freely in polymer matrix and increased polymer electrolyte conductivity [9]

Conclusion

The presence of LiClO₄ in cellulose acetate from acetylating cellulose extract in oil palm empty fruit bunch affect structural properties of cellulose acetate that it is analyzed by FTIR and XRD. Presence of LiClO₄ in cellulose acetate effect shifted wavenumber of C=O and C – O stretching vibration. Also it cause increase amorphous phase in cellulose acetate. It indicated that presence interaction between LiClO₄ and cellulose acetate and LiClO₄ dissociate in polymer matrix of cellulose acetate.

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