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Biopolymer electrolytes based on blend of kappa-carrageenan and cellulose derivatives for potential application in dye sensitized solar cell

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In this work, carboxymethyl kappa-carrageenan was used as the principle host for developing new biopolymer electrolytes based on the blend of carboxymethyl kappa-carrageenan/carboxymethyl cellulose. The blending of carboxymethyl cellulose into carboxymethyl kappa-carragenan was found to be a promising strategy to improve the material properties such as conductive properties. The electrolyte samples were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, dynamic mechanical analysis, electrochemical impedance spectroscopy, ionic transference number measurement and linear sweep voltammetry in order to investigate their structural, thermal and electrochemical properties. Impedance study showed that the ionic conductivity increased with the increment of ammonium iodide concentration. The highest room temperature ionic conductivity achieved was $2.41 \times 10^{-3}\ S\ cm^{-1}$ at 30 wt% of the salt. The increment of conductivity was due to the increase of formation of transient cross-linking between the carboxymethyl kappa-carrageenan/carboxymethyl cellulose chains and the doping salt as indicated the T_g trend. The conductivity was also attributed by the increase in the number of charge carriers in the biopolymer electrolytes system. The interactions between polymers and salt were confirmed by FTIR study. The transference number measurements showed that the conductivity was predominantly ionic. Temperature dependent conductivity study showed that conductivity increased with the reciprocal of temperature. The conductivity-temperature plots suggested that the conductivity obeyed the Vogel–Tammann–Fulcher relation and the activation energy for the best conducting sample was 0.010 eV. This system was used for the fabrication of dye sensitized solar cells, FTO/TiO_2-dye/CMKC/CMCE-$NH_4I + I_2$/Pt. The fabricated cell showed response under light intensity of $100\ mW\ cm^{-2}$ with efficiency of 0.13% indicating that the blend biopolymer system has potential to be applied in dye sensitized solar cell.

1. Introduction

Polymer based electrolyte materials are of great interest due to their many interesting properties such as flexibility and ease of preparation into films of large surface area. Even though many studies on polymer electrolytes have been done, most of the studies reported in the literature used petrochemical based polymers, which are associated to the environmental issues and high cost. In order to reduce the dependence of petrochemical based polymer for electrolytes, bio based polymers may be applied as hosts [1–3]. The bio based polymers are also promising candidates that meet different requirements. However, single biopolymers may not offer good mechanical and physical or chemical properties to meet wide range of device applications. Incorporation with other natural bio based polymer has shown favourable result such as good conductive properties. Buraidah and Arof reported that the conductivity of $3.73 \times 10^{-7}\ S\ cm^{-1}$ for the system containing 55 wt% chitosan-45 wt% NH_4I increased to $1.77 \times 10^{-6}\ S\ cm^{-1}$ upon blending with 27.5 wt% of PVA. This result was attributed to the additional complexation sites and amorphous nature of PVA [4].

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Among the biopolymers, kappa-carrageenan (*k*-carrageenan) and cellulose are of interest since they are abundant in nature, renewable, biocompatible and cost effective. *k*-carrageenan is a family of linear sulphated polysaccharides that are extracted from red edible seaweeds [5] while cellulose is the most abundant biopolymer which can be extracted inexpensively from plants, some animals, fungi, algae and bacteria [6]. *k*-carrageenan and cellulose can form cross-linking networks with other components in polymer electrolytes ascribed to their hydroxyl group rich molecular structure [7]. Polymers that show extensive hydrogen bonding appear to be more conductive than those that have few hydrogen bonds [8].

Recent trend and strategies in research are geared towards functionalization of known materials. Carboxymethylation of polysaccharides is one of the widely studied conversions that leads to development of new biopolymers with very promising properties [5]. Chemical modification of *k*-carrageenan and cellulose are carried out via the substitution of carboxymethyl group in the polymer molecules. The derivatives obtained differ significantly from the parent *k*-carrageenan and cellulose but the biodegradability are still maintained. The *k*-carrageenan and cellulose derivatives have more number of oxygen, compared to the parent polymers, and thus can provide more vacancies for cations or proton to coordinate [9]. The application of CMCE are mainly found as host in electrolyte systems [3,10–12]. In an earlier article, we have reported the use of kenaf based CMCE for polymer electrolytes application. The CMCE/(20 wt%) CH_3COONH_4 exhibited the highest conductivity of $5.77 \times 10^{-4}\,S\,cm^{-1}$ at room temperature [12]. Other researchers also investigated cellulosic electrolytes for dye sensitized solar cell (DSSC) application [13,14]. Paolo et al. [13] characterized the photovoltaic performance of cellulose-based gel electrolytes in DSSCs. A maximum photoconversion efficiency of 3.33% was obtained for the DSSC employing a gel prepared with 2 wt% of LiI, iodine (10 wt% of the whole weight of iodide), 5 wt% of micro-cellulose, 10 wt% of TBP and a MPII/EMISCN (volume percentage ratio of 50/50). Meanwhile, Bella et al. [14] used CMCE and microfibrillated cellulose (MFC) as bio-sourced fillers in quasi-solid electrolytes for polymeric DSSC. They obtained efficiency of 5.18% for their DSSC fabricated using CMCE-based gel-polymer electrolyte. Meanwhile their DSSC employing MFC-based polymer electrolyte membrane exhibited efficiency of 7.03%.

The aim of this study was to develop electrolytes based on the blend of derivatives of *k*-carrageenan and cellulose for potential use as electrolytes in solid-state DSSC. To the best of the author's knowledge, study on biopolymer electrolytes based on carboxymethyl kappa-carrageenan (CMKC)/carboxymethyl cellulose (CMCE) blend for use as electrolytes in solid-state DSSC application has never been reported in the literature. In this work, CMKC and CMCE were synthesized from *k*-carrageenan and kenaf fibre. The synthesized CMKC and CMCE were then blended and doped with ammonium iodide (NH_4I). NH_4I was chosen as a doping salt because it has potential to be used as salt in polymer electrolyte together with iodine (I_2), especially for the DSSC electrolytes. It also has low lattice energy and larger anionic size which are favorable for giving high ionic conductivity [15].

The investigation of the electrolytes were done using Fourier transform infrared (FTIR), dynamic mechanical analysis (DMA), electrochemical impedance spectroscopy (EIS), ionic transference number measurement (TNM) and linear sweep voltammetry (LSV) in order to study the interaction between polymer and salt, thermal, electrical and electrochemical characteristics of CMKC/CMCE blend electrolyte films. The best conductive CMKC/CMCE blend based electrolyte was used to fabricate DSSC.

2. Experimental

2.1. Materials

k-carrageenan was supplied by Takarra Sdn. Bhd., Malaysia. Meanwhile, kenaf fibers were obtained from KFI Sdn. Bhd., Malaysia. Sulfuric acid (98%), sodium hydroxide (99%), sodium chlorite (80%), and glacial acetid acid (99.5%), isopropanol, monochloroacetic acid, NH_4I, iodine (I_2), di-tetrabutylammonium cis-bis(isothiocynato) bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) (N719) and platinum (Pt) were purchased from SYSTERM-chemAR and Sigma–Aldrich. The TiO_2 paste DSL 18 NR-AO was supplied from Dyesol.

2.2. Synthesis of carboxymethyl kappa-carrageenan and carboxymethyl cellulose

In this work, cellulose was extracted from kenaf fibres by the following steps. The 50 g of kenaf fibres were cut into small pieces, and then treated by an alkali treatment and bleaching process. CMKC and CMCE were synthesized according to the method proposed by Sun et al. [16]. 10 g of *k*-carrageenan/5 g of cellulose-kenaf fibres, sodium hydroxide, isopropanol and water were mixed together and alkalized at 50 °C for 1 hour. Monochloroacetic acid dissolved in 20 ml of isopropanol was later added to the mixture. This solution mixture was then stirred for 4 hours at 50 °C and then terminated by adding 70% ethanol. The solid was filtered and rinsed with 70%, 80% and 90% ethanol solution and then vacuum dried at room temperature to form powder.

2.3. Preparation of biopolymer blend salt film

The biopolymer blend based on CMKC/CMCE electrolyte films were prepared by adding different weight percentages of NH_4I (10 - 50 wt%) to solutions containing 1 g of CMKC/CMCE of mass ratio 60: 40%. Based on our preliminary study, it was found that this ratio produced CMKC/CMCE film with the lowest glass transition, T_g and highest room temperature conductivity. 50 ml of 1% of acetic acid was used as the solvent. The weight percentage of salt was calculated using the equation:

$$wt_{NH_4I}\% = \frac{wt_{NH_4I}}{wt_{CMKC} + wt_{CMCE}} \times 100\% \tag{1}$$

where wt_{NH4I}, wt_{CMKC}, and wt_{CMCE} are the weights of salt, CMKC and CMCE respectively. The solutions were stirred at room temperature for a few hours and poured into Petri dishes and left to evaporate slowly to form films. The prepared films with thickness between 0.20 mm to 0.30 mm were then kept in a vacuum desiccator to ensure that the films were completely dried before measurement.

2.4. Characterization of materials

2.4.1. Fourier transforms infrared spectroscopy

FTIR spectroscopy was performed using Perkin Elmer Frontier spectrophotometer in order to study the interactions of the biopolymer host and the doping salt. The spectrophotometer was equipped with an Attenuated Total Reflection accessory with a germanium crystal. The sample was put on the germanium crystal and infrared light was passed through the sample in the wavenumber range from 4000 to 550 cm^{-1} at a resolution of 1 cm^{-1}. The FTIR data were recorded in the transmittance mode.

2.4.2. Dynamic mechanical analysis

The dynamic mechanical properties of CMKC/CMCE-NH_4I films were determined using Perkin Elmer DMA 8000 in tension mode.