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Potential of blend of kappa-carrageenan and cellulose derivatives for green polymer electrolyte application

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ABSTRACT

In this study, new biopolymer blend based on kappa-carrageenan and cellulose derivatives were prepared using solution casting technique. The cellulose derivative, carboxymethyl cellulose was produced from cellulose extracted from kenaf fibres. The cellulose derivative was blended with different wt% of kappa-carrageenan derivative to obtain free standing films. The properties of the prepared blend films were subjected to fourier transform infrared characterization, tensile test, scanning electron microscopy, dynamic mechanical analysis, electrochemical impedance spectroscopy and linear sweep voltammetry to investigate their structural, mechanical, viscoelastic and electrical behaviour. The FTIR result demonstrated that both polymers are compatible with each other. The mechanical properties of carboxymethyl kappa-carrageenan were enhanced with the addition of carboxymethyl cellulose. The polymer blend with wt% ratio of 60:40 yielded the most conductive film with conductivity of 3.25×10^{-4} S cm^{-1} and is expected to be the most suitable blend to be explored for polymer electrolytes application.

1. Introduction

With increasing trend to reduce environment impact caused by human activities, special interest is being paid to explore renewable biopolymer-based materials to replace conventional petroleum-based materials (Siracusa et al., 2008). Biopolymers have widely investigated due to being environmental friendly, nontoxic, and abundant in nature. Furthermore, it could overcome the main shortcoming of synthetic polymer, which is mostly insoluble in the solvents (Ma et al., 2007). Biopolymer materials show good potential to act as polymer hosts in polymer electrolytes due to their good biodegradability and compatibility with salts. Biodegradable biopolymer are attracted more attention as representative water-soluble polysaccharide in many research fields (Samsudin et al., 2012; Barbucci et al., 2000). There are several renewable resource-based biopolymers that are suitable to be used as host polymers in the polymer electrolytes. These include starch, cellulose, carrageenan, chitosan, etc. (Shukur et al., 2013; Samsudin and Isa, 2012; Samsudin et al., 2012; Kumar et al., 2012; Ramesh et al., 2011; Lu et al., 2009).

Kappa-carrageenan (κ-carrageenan) is one of the classes of carrageenan which extracted from certain species marine red algae (Tranquilan-Aranilla et al., 2012; Fan et al., 2011) while cellulose is the most abundant biopolymer which can be extracted inexpensively from plants (Klemm, 2006). κ-Carrageenan and cellulose can form cross-linking networks with other components in polymer electrolytes because of their rich hydroxyl group in their molecule structure (Yang et al., 2011). Moreover, hydroxyl group of the sugar rings allows substitution with other functional group. Polymers that show extensive hydrogen bonding appear to be more conductive than those that have few hydrogen bonds (Finkenstadt, 2005). To extent the use of κ-carrageenan and cellulose, chemical modification on κ-carrageenan and cellulose has been done in order to produce carboxymethyl κ-carrageenan (CMKC) and carboxymethyl cellulose (CMCE). The new derivatives of κ-carrageenan and cellulose are expected to have more number of oxygen atoms compared to the pristine κ-carrageenan and cellulose-fibre. These oxygen atoms may provide vacancies for cations and protons to coordinate. These will lead to high ionic conductivity and excellent

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thermal and chemical stability. Mobarak et al. (2012) reported that the ionic conductivity of modified κ-carrageenan increased by three orders magnitude as compared to the pristine κ-carrageenan. The conductivity achieved was 2.0×10^{-4} S cm^{-1} for CMKC (conductivity of κ-carrageenan was 5.3×10^{-7} S cm^{-1}). To the best of the author's knowledge, studies on CMKC/CMCE blend for use as host in polymer electrolytes have never been reported in the literature. In this study, CMKC and CMCE were synthesized from κ-carrageenan and cellulose-kenaf fibre. The synthesized CMKC and CMCE were then blended in different compositions. The aim of this study is to identify the best blend ratio for potential use as host in polymer electrolytes. The investigation was done using fourier transform infrared (FTIR), tensile measurement, scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) to obtain information of their structural, mechanical, viscoelastic and electrical behaviour.

2. Materials and method

2.1. Materials

Kenaf fiber was obtained from KFI Sdn. Bhd. Malaysia. κ-Carrageenan was supplied by Takarra Sdn. Bhd. Malaysia. Meanwhile, sulfuric acid (98%), sodium hydroxide (99%), sodium chlorite (80%), and glacial acetic acid (99.5%), isopropanol and monochloroacetic acid were purchased from Systerm-chemAR and Sigma–Aldrich. All materials were used without further purification.

2.2. Extraction of cellulose from kenaf fibre

In this work, cellulose was extracted from kenaf fibre by the following steps. The kenaf fibre was cut into small pieces, and then treated by an alkali treatment and bleaching process. For an alkali treatment, the small pieces of kenaf fibre was first treated with 4 wt% NaOH solution in a round bottom flask under mechanical stirring at 80 °C for 3 h. The process was repeated three times and refluxing was conducted throughout the process. The solution was then filtered several times using distilled water to remove alkali component. Following alkali treatment, the bleaching process was performed by adding aqueous chlorite (1.7 w/v%), acetic buffer solution and distilled water at reflux for 4 h. The mixture was allowed to cool and filtered using distilled water. The process was repeated thrice.

2.3. Preparation kappa-carrageenan and cellulose derivatives

CMKC and CMCE were synthesized according to the method proposed by Sun et al. (2008). κ-Carrageenan (or cellulose from kenaf fibres), sodium hydroxide, isopropanol and water were mixed together and alkalized at 50 °C for 1 h. Monochloroacetic acid dissolved in isopropanol was later added to the mixture. This solution mixture was then stirred for 4 h at 50 °C and then terminated by adding ethanol. The solid was filtered and rinsed with 70%, 80% and 90% ethanol solution and then vacuum dried at room temperature to form powder. The degree of substitution (DS) of the carboxymethyl for each sample was estimated using potentiometric titration (Fan et al., 2011).

2.4. CMKC/CMCE blend film preparation

Polymer blend films in this study were prepared by solution casting method. For the preparation of CMKC/CMCE blend with wt% ratio of 50:50, 0.5 g of CMKC powder was dissolved in acetic acid (1% v/v) at 40 °C. After 2 h, 0.5 g of CMCE was added and stirred for a few hours to form homogenous solution. The solution was then poured into Petri dishes and allowed to dry at room temperature for 2 weeks to obtain free standing films. The free standing films obtained were kept in a desiccator for further drying. The procedure was repeated to obtain other blends with CMKC:CMCE ratios of 60:40, 70:30, 80:20 and 90:10. The weight percentage of CMCE added to CMKC was calculated using the following equation;

$$\mathrm{wt_{CMCE}}\% = \frac{\mathrm{wt_{CMCE}}}{\mathrm{wt_{CMKC}} + \mathrm{wt_{CMCE}}} \times 100\% \quad (1)$$

where $\mathrm{wt_{CMKC}}$ and $\mathrm{wt_{CMCE}}$ are the weights of CMKC and CMCE respectively. The compositions of the samples and their designations are listed in Table 1.

Table 1
The compositions and designations of the CMKC/CMCE (wt%) blendfilms.

CMKC/CMCE blend	Samples designations
100/0	B0
90/10	B1
80/20	B2
70/30	B3
60/40	B4
50/50	B5

3. Characterization

3.1. Fourier transform infrared spectroscopy

FTIR spectroscopy was performed using PerkinElmer Frontier spectrophotometer. The spectrophotometer was equipped with an attenuated total reflection accessory with a germanium crystal. The studied sample was put on the germanium crystal and infrared light was passed through the sample in the frequency range from 4000 to 550 cm^{-1} with spectra resolution of 1 cm^{-1}. The FTIR data were recorded in the transmittance mode.

3.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy

The cross sectional morphology of the CMKC:CMCE films were studied using ZEISS EVO MA10 scanning electron microscope with an accelerating voltage of 10 kV. The blend films were sputter-coated with a thin gold layer before measurement. Elemental analysis of κ-carrageenan, cellulose and derivatives were examined with the energy dispersive X-ray (EDX) using Oxford Aztec X-Act EDX spectrometer.

3.3. X-ray diffraction

X-ray diffraction was performed to study the crystalline nature of κ-carrageenan, cellulose and its derivatives. The XRD spectra of the polymer electrolyte films studied in this work were recorded using a PANalytical in the 2θ range from 3° to 80°. The films were scanned with a beam of monochromatic Cu-Kα-X radiation of wavelength 1.5406 Å.

3.4. Dynamic mechanical analysis

The dynamic mechanical properties of CMKC/CMCE blend films were determined using PerkinElmer DMA 8000 in tension mode. Rectangular strip specimens (width 10 mm, length 20 mm) were used. The dual cantilever mode of deformation was used at the test temperatures ranging from −40 to 100 °C with a heating rate of 2 °C min^{-1}. The glass transition temperatures of samples were determined from the peak of the tan δ–T curves.