ELECTRICALLY RESPONSIVE MATERIAL BASED ON CARRAGEENAN HYDROGEL AS AN ACTUATOR

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ABSTRACT

Actuator is a mechanical device that can change electrical energy into mechanical energy. It produces a large deformation under activated energy. Generally, electric field is often used to induce material deformation and certain electroactive polymers can offer large mechanical responses under electric field. The electromechanical properties of the carrageenan hydrogels were studied under the effects of electric field strength, carrageenan types namely κ, ι, and λ, and operating temperature. The numbers of charged sulfated groups per carrageenan repeating unit of the κ-carrageenan, ι-carrageenan, and λ-carrageenan are one, two, and three, respectively. The electromechanical response of the carrageenan increased with increasing sulfated groups; the λ-carrageenan hydrogel provided the highest storage modulus sensitivity of 4.0 under applied electric field strength of 800 V/mm. The pristine ι-carrageenan hydrogel composites also showed higher dielectrophoretic forces and higher deflections relative to those of the pristine κ-carrageenan hydrogel.

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INTRODUCTION

Hydrogels are three dimensional networks that can absorb a lot of water. Hydrogel features include a high degree of hydration, swelling ability, biocompatibility, and a high internal diffusivity of small molecules. The EAPs components allow a fine control of the electrical stimulus. The EAPs distinct properties are the electrical and optical properties, especially the high electrical conductivity. These properties can be altered and controlled through stimulations such as electricity, light, and pH (Huang et al., 2008). Carrageenans are well known for their gel-forming and thickening properties. Carrageenan comprises a family of linear water-soluble sulfated polysaccharides extracted from red seaweeds. Carrageenans have the ability to form thermoreversible hydrogels and are extensively used as a gelling agent in food and pharmaceutical industries (Piculell, 1995). These biopolymers are an anionic polysaccharide, their structure contains galactose, 3,6-anhydrogalactose units, carboxy and hydroxy groups and ester sulfates. Carrageenans are very sensitive to the acid and oxidative breakdowns, and the cleavage of the glycosidic linkages increases with temperature and time. Carrageenan hydrogels are investigated for their electrical properties,
mechanical properties, and actuator performances under the effects of carrageenan types and electric field strengths.

EXPERIMENTAL

A. Materials
Kappa carrageenan (κ-carrageenan: Thai Food and Chemical Co., LTD, Food grade), Iota carrageenan (ι-carrageenan: Sigma-Aldrich, AR grade), and Lambda carrageenan (λ-carrageenan: Sigma-Aldrich, AR grade) were used to fabricate hydrogels. Deionized water was used in all experiments.

B. Preparation of Carrageenan Hydrogels
A carrageenan was dissolved in distilled water (0.97 %v/v) at 60 ºC under continuous stirring for 3 h. The solution was kept under vigorous stirring at room temperature. Then, the solution was transferred to a plastic petri dish (10 cm in diameter). The carrageenan hydrogel was obtained after allowing water evaporation at room temperature for 48 h and was kept at 4 ºC in a plastic bag for retaining water.

C. Characterization
Transmission Electron Microscope
TEM (LEO, 906 E) was used to examine the morphological structure and the dispersion of the P3HT in the κ-carrageenan hydrogels. Small pieces of gels were chemically fixed in 2 %w/w glutaraldehyde and 0.1 %w/w ruthenium (ammoniated ruthenium oxychloride) salt solutions, and post fixed with 1%w/w OsO₄ in the same salt solutions. Samples were dehydrated in acetone series, followed by an infiltration in resin, LR White, and polymerized. Thin sections of 70 nm were cut with a diamond knife and stained with uranyl acetate and lead citrate. The samples was attached onto brass-stubs and an accelerating voltage of 80 kV was used. Images were taken at the magnifications of 10000-80000 times.

Thermal Gravimetric Analyzer (TGA)
A Thermal Gravimetric Analyzer (DuPont, TGA 2950) was used to determine the amount of moisture content and the decomposition temperatures of the carrageenan hydrogels. The thermal behaviour was investigated by weighting a sample of 4-10 mg, placed it in a platinum pan, and then heated under nitrogen flow with the heating rate 10 ºC/min from 30-900 ºC.

D. Electromechanical Properties
The electromechanical properties of the carrageenan hydrogels was measured by a rheometer as functions of electric field strength. The melt rheometer (Rheometric Scientific, ARES) was fitted with a custom-built copper parallel plate fixture (sample
A DC voltage was applied with a DC power supply (Instek, GFG8216A), which could deliver electric field strength to 800 V/mm. A digital multimeter was used to monitor the voltage input. In these experiments, the oscillatory shear mode was applied and the dynamic moduli (G' and G") were measured as functions of frequency and electric field strength. The polyimide (PI), ®Kapton TH-012 (12 micron) was obtained from ©2006 Saint Gobain Performance Plastic Corporation. PI sheets were placed on both sides of a sample before testing to prevent the current leakage. Strain sweep tests were first carried out to determine the suitable strains to measure G' and G" in the linear viscoelastic regime. The appropriate strain was determined to be 0.03% for all samples. The temporal response experiments were also carried out at 800 V/mm to evaluate the equilibrium time and recoverability of the hydrogels. The frequency sweep tests were next carried out to measure G' and G" of each sample as functions of frequency. The frequency was varied from 0.1 to 100 rad/s. Prior to each measurement, the carrageenan hydrogel samples were pre-sheared at a low frequency under an electric field for 20 min to ensure the formation of equilibrium polarization before the G' and G" measurements.

RESULTS AND DISCUSSION

A. Characterization

Figure 1 shows TEM micrographs of the carrageenan hydrogels. In Figure 1, it can be seen that the κ-carrageenan and τ-carrageenan hydrogels show three dimensional networks of double helical structures, while the λ-carrageenan shows a random coil structure. The three dimensional network of the κ-carrageenan is the most dense, followed by the τ-carrageenan and the λ-carrageenan; the latter shows a random coil (the least aggregation). The double helical formation is generated through a physical interaction (H-bonding) in crosslinking chains into a three dimensional network, where the double helical junction zones connect stretches of disordered carrageenan chains (Anderson et al., 1969 and Rees et al., 1969). The higher amount of sulfate ions along the carrageenan structure tends to induce the higher electrostatic repulsion between the polymer chains resulting in a less dense double-helix chain formation (Tako et al., 2015). The λ-carrageenan has the highest amount of sulfate ions (three -SO₃⁻ per repeating unit) followed by the τ-carrageenan (two -SO₃⁻ per repeating unit) and the κ-carrageenan (one -SO₃⁻ per repeating unit), thus resulting in different double helical formations.
Figure 1 TEM images at magnification of 80000x of 0.97 %V/V carrageenan: (a) κ-carrageenan; (b) ι-carrageenan; and (c) λ-carrageenan.

B. Electromechanical Properties

Figure 2(a) shows a comparison of storage moduli ($G'$) during the time sweep tests. For all samples, $G'$ increases rapidly when the electric field is on. Then, $G'$ decreases instantaneously when electric field is off. The induction times of the κ, ι, and λ-carrageenans are about 8000, 8000, and 5000 seconds, respectively and the recovery times are 2000, 2000, and 1500, respectively. Under applied electric field, the ionic polarization occurs from the water ions, the orientation polarization occurs from the sulfate and hydroxyl groups, and possibly shear induced carrageenan-chain alignments are generated. These induced dipole moments interact to produce the ‘electrostrictive effect’ (Kunchornsup et al., 2012; and Petcharoen et al., 2013, incresing material rigidity and $G'$). The different induction times can be related to the state of carrageenans. The shortest induction time of the λ-carrageenan to reach the polarization equilibrium is obtained from the vis cose liquid state when compared with the crosslinked κ and ι-carrageenans (Piculell et al., 2006). Figure 2(b) shows the storage modulus ($G'$) and the storage modulus sensitivity ($ΔG'/G'_0$) versus electric field of the κ-carrageenan, ι-carrageenan and λ-carrageenan hydrogels at frequency 100 rad/s and at 300 K. Both $G'$ and $ΔG'/G'_0$ of each carrageenan hydrogel increase monotonically with applied electric field between 0 and 400 V/mm. Beyond the electric field of 400 V/mm, $G'$ and $ΔG'/G'_0$ of the κ-carrageenan slightly decrease, but for the ι and λ-carrageenan hydrogels they continue increase. It can be noted that the λ-carrageenan provides the highest $ΔG'/G'_0$ of 4.01. The increase of the storage modulus ($G'$) and the storage modulus sensitivity ($ΔG'/G'_0$) of the carrageenan hydrogels below 400 V/mm are directly related the the electrostrictive effect (Thongsak et al. 2011; Hiamtup et al., 2008; Niamlang et al., 2008; Tungkavet et al., 2012; and Kunchornsup et al., 2014). Above the electric field strength of 400 V/mm, $G'$ and $ΔG'/G'_0$ of the κ-carrageenan slightly decrease because of the denaturation of the double helix coil to a random coil (Xianwei et al., 2014). The high
electric field disrupts the intra-helical interaction of H-bonding (three H-bonding per pitch) leading to the change of the double helical coil to a random coil. The \( G' \) and \( \Delta G'/G_0' \) of the \( \iota \)-carrageenan increases to be higher than the \( \kappa \)-carrageenan because of the higher sulfate groups per repeating unit leading to an enhanced polarization. In addition, the intra-helical interaction of the \( \iota \)-carrageenan is stronger than the \( \kappa \)-carrageenan. The \( G' \) and \( \Delta G'/G_0' \) of the \( \lambda \)-carrageenan increase monotonically with electric field strength because of its random coil conformation which can be easily polarized relative to others leading to more dipole moments generated at a low electric field. Moreover, the \( \lambda \)-carrageenan provides the highest \( \Delta G'/G_0' \) at a high electric field because it has the highest sulphate groups and a lower rigidity without electric field.

![Image](image.png)

**Figure 2** Temporal response tests and the storage modulus \( G' \) (a) and the storage modulus sensitivity \( \Delta G'/G_0' \) of carrageenan hydrogels; \( \kappa \)-carrageenan; \( \iota \)-carrageenan; and \( \lambda \)-carrageenan hydrogel.

**CONCLUSIONS**

The electromechanical properties and the deflection responses of the carrageenan hydrogels and P3HT-\( \kappa \)-Carrageenan hydrogel blends were investigated as functions of electric field strength varying from 0-800 V/mm. For the carrageenan hydrogels, the \( G' \) and the \( \Delta G'/G_0' \) generally increased with increasing electric field strength. The \( \Delta G'/G_0' \) of \( \lambda \)-carrageenan hydrogel was higher than the \( \iota \) and \( \kappa \)-carrageenans.

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REFERENCES


