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Influence of carrageenan molecular structures on electromechanical behaviours of poly(3-hexylthiophene)/carrageenan conductive hydrogels

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ABSTRACT

The κ , ι , and λ carrageenans were fabricated by solution casting as soft and electrically responsive actuators. The poly(3-hexylthiophene) (P3HT) was added as a dispersed phase to improve the electrical and electromechanical properties of the pristine carrageenan hydrogels. The electromechanical properties of the carrageenan hydrogels were investigated under the effects of electric field strength, carrageenan type namely κ , ι , and λ , operating temperature, and P3HT concentration. The electromechanical responses of the pristine carrageenans increased with increasing sulfated groups present; the λ -carrageenan hydrogel provided the highest storage modulus sensitivity of 4.0 under applied electric field strength of 800 V/mm. With increasing temperature, the double-helical structure of the κ -carrageenan hydrogel changed into a random coil leading to the increase in the storage modulus response. On the other hand, the P3HT/ κ -carrageenan hydrogel blend at 0.10%v/v P3HT provided the high storage modulus sensitivity of 2.20 at the electric field strength of 800 V/mm. The higher dielectrophoretic forces were due to the additional P3HT electronic polarization, but lower deflections relative to those of the pristine κ -carrageenan hydrogel. Both κ - and λ -carrageenans with the double helical structures are shown here as possible candidates to be fabricated as electroactive hydrogels for actuator or biomedical applications.

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1. Introduction

Electroconductive hydrogels (ECHs) belong to a class of multifunctional smart materials with potential applications such as tissue engineering [1], actuators [2], and bioactive electrode coating [3]. The ECHs consist of a conducting polymer embedded within a three-dimensional crosslinked polymer-based network. The combination of the properties of electroactive polymers (EAPs) and the swelling/deswelling capabilities of the hydrogels enables various biomedical applications [4]. As an example of the ECHs, Justin et al. (2010) [5] prepared ECHs by using poly(HEMA)-based hydrogels embedded with polypyrrole. The hydrogel matrix was expandable to allow the movement of the pyrrole monomers and other ions through the gel leading to the high electrical conductivity of the ECHs.

Hydrogels are generally three-dimensional networks that naturally absorb water. Hydrogel features include a high degree of hydration, swelling ability, biocompatibility, and high diffusivity for small

molecules. These properties can be altered and controlled through stimulations such as electricity, light, and pH [6].

The EAPs distinct properties are the electrical and optical properties especially the high electrical conductivity. The EAPs belong to the class of polymers possessing a π conjugation along the polymer backbone: polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTH) [4].

Carrageenans belong to a family of linear water-soluble sulfated polysaccharides extracted from red seaweeds. Carrageenans are known to possess the gel-forming and thickening properties; they have the ability to form thermo-reversible hydrogels which are extensively used as a gelling agent in food and pharmaceutical industries [7]. These biopolymers are anionic polysaccharides; their structures contain 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.

Poly(3-hexylthiophene) (P3HT) is one widely-studied EAPs because of its high charge carrier mobility (>0.1 cm²/Vs), chemical and thermal stability, ease of fabrication, and commercial availability. Furthermore, it can be synthesized from various methods that enable a production of highly regioregular P3HT with controlled molecular weight. In a

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previous work, the nanoparticle conductive polymer was shown to provide high electrical conductivity [8]. It may be noted that the electrical conductivity of a conductive polymer has been known to depend on many factors: the degree of doping, the oxidation state, the particle morphology and size, the crystallinity, the inter- and intra-chain interactions, the molecular weight and effective conjugation length, or the content of surfactants and other stabilizers [9].

Recently, there have been considerable attentions in the synthesis of nano-conducting/biopolymer composites with high electrical conductivity. Sasso et al. (2010) [10] prepared electroactive PPy/chitosan composite nanospheres and highly conducting PPy/cellulose nanocomposite films; they evaluated the mechanical strength, flexibility, durability, electrical conductivity, loading capacity, and ion exchange speed. In another previous work, it has been suggested that a potential application is as bioactuators consisting of nanoparticle conductive polymers and biohydrogels [11].

In the present work, 3-hexylthiophene was chosen to be synthesized to obtain an electroactive polymer nanoparticle by chemical oxidation via emulsion polymerization. One objective of the study was to utilize P3HT as a conductive filler to be embedded in carrageenan hydrogels as the matrix phase. A small amount of P3HT was added as a dispersed phase to improve the electrical and electromechanical properties of the carrageenan hydrogels. Carrageenan hydrogels and P3HT/ κ -carrageenan hydrogel blends were investigated for the electrical properties, mechanical properties, and actuator performances under the effects of carrageenan types, P3HT/carrageenan hydrogel ratios, and electric field strengths.

2. Experimental

2.1. Materials

3-hexathiophene monomer (Sigma-Aldrich, AR grade) was used as a monomer. Iron (III) chloride (FeCl_3 ; Sigma-Aldrich, AR grade) was used as an oxidizing agent. Chloroform (RCI Labscan, AR grade) was used as a solvent. Dodecylbenzene sulfonic acid (DBSA; Sigma-Aldrich, AR grade) was used as a surfactant. 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.

2.2. Polymerization of poly(3-hexylthiophene)

P3HT nanoparticles was synthesized in a 250 ml double-jacketed glass reactor with a mechanical stirrer. The reaction temperature was 40 °C as maintained by a thermostat, and the stirring rate was 300 rpm. The reaction procedure was as follows: DBSA (0.017 mol, 3.0 g) was dissolved in 50 mL of chloroform and added to the reactor. The 3-hexylthiophene monomer (0.143 mol, 2.0 g) was added into the DBSA solution. FeCl_3 (5.77 g) in 100 mL of chloroform was added to the reactant mixture solution, and then the mixture was stirred for 12 h at 40 °C. The obtained polymer was collected by filtration and then washed with methanol; then it was dried in a vacuum oven at 80 °C for 24 h. Under the procedure above, the obtained P3HT spherical particle size and conductivity were 554 ± 37.6 nm and 71.0 ± 2.07 S/cm, respectively.

2.3. Preparation of carrageenan hydrogels

The three carrageenans were dissolved in distilled water (0.97%v/v) at 60 °C under continuous stirring for 3 h. Then, the solutions were transferred to petri dishes (10 cm of diameter). The carrageenan hydrogels were obtained after allowing water evaporation at room temperature for 48 h and were kept in plastic bags at 4 °C to retain the water

content. The κ and ι -carrageenans formed hydrogels, whereas the λ -carrageenan remained in the viscous liquid state at room temperature.

2.4. Preparation of P3HT/ κ -carrageenan hydrogel blends

A κ -carrageenan solution in distilled water (0.97%v/v) was prepared at 80 °C under continuous stirring. The P3HT: κ -carrageenan ratios in the aqueous solutions were 0.1%v/v, and 1.0%v/v. The solutions were then transferred to petri dishes for casting at room temperature for 48 h to obtain the hydrogel blends.

2.5. Characterizations

2.5.1. Fourier transform infrared spectrometer

A Fourier transform infrared spectrometer, FT-IR (Nicolet, Nexus 670) was used to characterize the functional groups of the carrageenan hydrogels and P3HT/carrageenan hydrogels. This technique was used to identify the absorption modes with 32 scans with a resolution of ± 4 cm^{-1} , covering a wavelength range of 4000–400 cm^{-1} .

2.5.2. Scanning Electron microscope

SEM (Hitachi, S4800) was used to examine the morphological structures and the dispersion of the P3HT particles in the κ -carrageenan hydrogel. The samples were attached onto brass-stub and platinum plated, an accelerating voltage of 80 kV was used, and images were taken at the magnifications of 20,000–40,000.

2.5.3. Transmission electron microscope

TEM (LEO, 906 E) was used to examine the morphological structure and the dispersion of the P3HT particles in the κ -carrageenan hydrogel. Small pieces of gels were chemically fixated in the 2%w/w glutaraldehyde and 0.1%w/w ruthenium (ammoniated ruthenium oxychloride) salt solution, and post fixated with 1%w/w OsO_4 in the same salt solution. The gels were then dehydrated in acetone series, followed by the infiltration of a resin, the LR White. Thin sections of 70 nm thickness were cut with a diamond knife and stained with uranyl acetate and lead citrate. The samples were then attached onto brass-stubs. An accelerating voltage of 80 kV was used, and the images were taken at the magnifications of 10,000–80,000 times.

2.5.4. Thermal gravimetric analyzer (TGA)

A thermal gravimetric analyzer (DuPont, TGA 2950) was used to characterize thermal properties of the synthesized P3HT and to determine the amounts of moisture content and the decomposition temperatures of the carrageenan hydrogels. The thermal behaviour was investigated by weighting each sample of 4–10 mg, placed it in a platinum pan, and then heated under nitrogen flow with the heating rate 10 °C/min from 30 to 900 °C.

2.5.5. Electromechanical properties

A melt rheometer (Rheometric Scientific, ARES) was fitted with a custom-built copper parallel plate fixture (sample size: 25 mm in diameter, and ~1.5 mm in thickness). A DC voltage was applied from a DC power supply (Instek, GFG8216A), in which it could deliver the electric field strength up to 800 V/mm. 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) sheets, @Kapton TH-012 (12 micron) as obtained from ©2006 Saint Gobain Performance Plastic Corporation, were placed on both sides of each sample to prevent the electrical 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 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 then carried out to measure G' and G'' of each sample

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