Materials Science and Engineering C 56 (2015) 1–8

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Electromechanical response of silk fibroin hydrogel and conductive polycarbazole/silk fibroin hydrogel composites as actuator material

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ARTICLE INFO

Article history:
Received 19 February 2015
Received in revised form 22 April 2015
Accepted 9 June 2015
Available online 12 June 2015

Keywords:
Silk fibroin
Hydrogels
Polycarbazole
Actuator
Biopolymer

ABSTRACT

Pure silk fibroin (SF) hydrogel and polycarbazole/silk fibroin (SF/PCZ) hydrogels were fabricated by solvent casting technique to evaluate electromechanical responses, dielectric properties, and cantilever deflection properties as functions of electric field strength, SF concentration, glutaraldehyde concentration, and PCZ concentration in the blends. Electromechanical properties were characterized in oscillatory shear mode at electric field strengths ranging from 0 to 600 V/mm and at a temperature of 27 °C. For both the pristine SF and SF/PCZ hydrogels, the storage modulus response ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G'_0$) increased dramatically with increasing electric field strength. The pristine hydrogel possessed the highest storage modulus sensitivity value of 5.87, a relatively high value when compared with other previously studied electroactive polymers. With the addition of conductive PCZ in SF hydrogel, the storage modulus sensitivity and the relative dielectric constant decreased; the conductive polymer thus provided the softening effect under electric field. In the deflection response, the dielectrophoresis force and deflection distance increased monotonically with electric field strength, where the pure SF hydrogel showed the highest deflection distance and dielectrophoresis force.

1. Introduction

Development of artificial muscle has received interests based on biologically inspired actuators or devices which possess electromechanical responses. The applications of artificial muscles are presently intended for animals and human-like robots. Electroactive polymer is one type of electroactive material [1]. Electroactive polymers offer novel and promising characteristics such as light weight, high flexibility, and high energy density. The examples of electroactive materials are dielectric elastomers [2], electrostrictive papers [3], conductive polymers [4], electrorheological fluids [5], ionic polymer gels [6], and ionic polymer metal composites [7].

Silk fibroin (SF) is a protein biopolymer derived from silkworm (*Bombyx mori*), consisting of light (~25 kDa) and heavy (~350 kDa) chains of polypeptides and linked by disulfide bond. The amino acid composition of SF primarily consists of glycine (43%), alanine (30%), and serine (12%) [8,9]. Due to a wealth of merits, such as biocompatibility, biodegradability, mechanically superior, amenable to aqueous or organic solvent processing, SF has been widely used in the medical and pharmaceutical fields [9]. The most popular morphology is to fabricate SF into a film type, because it is of a relatively easy preparation technique and the processing conditions can be controlled. However, SF films have shown low mechanical properties because of the brittleness in the dry state, which limits the actuator applications [10,11]. Recently, composites of conductive polymers and biopolymers have been of keen interest due to better thermal stability and mechanical properties, variable conductivity [12]. Polycarbazole (PCZ) is one of the conductive polymers that has been interested in many applications, such as electrochromic displays, rechargeable batteries, light-emitting diodes, and organic transistors [13]. However, toxicity of polycarbazole has not been fully investigated. It has been reported that polycarbazole was a stable substance, but it was incompatible with the strong oxidizing agent such as hydrogen peroxide, sulfuric acid, and silver oxide [14].

In the present study, the objective was in fabricating an electroactive material from conductive PCZ embedded in SF hydrogel. Also, it is of interest to study and test SF hydrogels and SF/PCZ hydrogel under electric field for actuator applications. The electromechanical properties, electrical properties, and actuator performances were investigated and examined along with the effects of SF concentration, glutaraldehyde concentration, PCZ concentration, and electric field strength.

2. Experimental

2.1. Materials

Carbazole (AR grade, Merck) was used as the monomer. Ammonium persulfate (AR grade, Sigma-Aldrich) was used as the oxidant. Hydrochloric acid 37% and dichloromethane (AR grade, RCI Labscan) were

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http://dx.doi.org/10.1016/j.msec.2015.06.005
0928-4931/

used as received as the dopant and solvent, respectively. Silk cocoons (*B. mori*) were obtained from Chul Thai silk Co., Ltd. Sodium carbonate (AR grade, Riedel-de Haën) was used to extract sericin and wax. Lithium bromide anhydrous (AR grade, Sigma-Aldrich) was used for preparing silk fibroin solution. Sodium dodecyl sulfate (AR grade, Sigma-Aldrich) was used as the surfactant. Glutaraldehyde solution 50% in water (AR grade, Fluka) was used as the crosslinking agent. Deionized water was used in all experiments.

2.2. Synthesis of PCZ

We followed the polycarbazole synthesis procedure of Gupta et al. [15] using carbazole, ammonium persulfate, hydrochloric acid, and dichloromethane. The reaction was carried out at room temperature. 1.2 M of ammonium persulfate was dissolved in 50 ml of 0.5 M hydrochloric acid solution and 60 mM of carbazole monomer was dissolved in 50 ml of dichloromethane. The aqueous and non-aqueous solution were mixed and stirred for 6 h to get a green slurry solution. After filtering, the green precipitate was collected and dried in a vacuum oven. Dedoping polycarbazole was performed by stirring the obtained polycarbazole in 0.1 M of ammonium hydroxide solution and doped again with concentrated hydrochloric acid. The mole ratio of hydrochloric acid to carbazole (N_{HCl}:N_{CZ}) was adjusted to be 1:1, 10:1, 100:1, 200:1, and 300:1.

2.3. Preparation of SF solution

According to Kim et al. [16], a SF aqueous solution was prepared by boiling silk cocoons for 30 min in 0.02 M of sodium carbonate and then rinsed thoroughly with water to extract sericin and wax. After drying at room temperature, the extracted SF was dissolved in 9.3 M of lithium bromine solution at 60 °C for 4 h. This solution was dialyzed in water using a cellulose acetate membrane (Pierce, MWCO 3500) for 2 days. The final concentration of the SF solution was about 7% w/v, which was determined by weighing the remaining solid after drying.

2.4. Fabrication of pure SF and SF/PCZ hydrogels

Pure SF hydrogels were prepared from the SF solutions of 4 and 5 vol.%. The crosslinked SF solutions were prepared by adding 0.01, 0.05, 0.1, 0.5, and 1 vol. of glutaraldehyde at room temperature (27 °C). The crosslinked SF solutions were poured into petri dishes. The pure SF hydrogels were obtained after casting at room temperature for 2 days. The pure SF hydrogels can be referred to as 01SF, 05SF, 10SF, 50SF, and 1SF hydrogels, respectively from the 4 vol.% SF solution.

The SF/PCZ hydrogels were prepared by mixing PCZ with a SF solution. PCZ powder was dispersed into 10 ml of the SF solution (01SF) filled with 0.05 M of sodium dodecyl sulfate as the surfactant and with 0.01 vol.% glutaraldehyde. Concentrations of the highest conductivity PCZ in the SF solution were 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 vol.%. The SF/PCZ hydrogels were casted in a mold at room temperature for 2 days before further characterizations. The SF/PCZ hydrogels can be referred to as 01SF/001PCZ, 01SF/005PCZ, 01SF/01PCZ, 01SF/05PCZ, 01SF/1PCZ, and 01SF/5PCZ, respectively.

2.5. Characterization and testing

The dedoped PCZ and freeze-dried SF hydrogel were characterized by a FTIR spectrometer to identify the functional groups. The FTIR spectrometer (Thermo Nicolet, Nexus 670) was operated in the transmission mode with 64 scans and a resolution of $\pm 4\ cm^{-1}$ using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material.

A thermal gravimetric analyzer (Thermo, TGA Q50) was used to determine the amount of moisture content and decomposition temperatures of PCZ and SF hydrogel. PCZ powder and hydrogel samples with a typical weight of 5–10 mg were loaded and then heated under nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 900 °C.

Scanning electron micrographs were captured with a scanning electron microscope (Hitachi, S4800) using an acceleration voltage of 10 kV to investigate the morphology of PCZ in powder form and SF/PCZ hydrogels with magnifications of 10,000 and 18,000, respectively.

Particle sizes of PCZ were determined by using a particle size analyzer (Malvern, Mastersizer). The lenses used was 300 mm. Electrical conductivity was measured by a meter which consisted of two probes making contact on a surface of sample pellet. The probes were connected to a source meter (Keithley, Model 6517A) supplying a constant voltage and for reading current. The applied voltage and the resultant current in the linear Ohmic regime were converted to the electrical conductivity using Eq. (1) as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s t} = \frac{I}{KVt} \tag{1}$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity (Ω cm), R_s is the sheet resistivity (Ω), I is the measured current (A), K is the geometric correction factor, V is the applied voltage (V), and t is the pellet thickness (cm).

A melt rheometer (Rheometric Scientific, ARES) was used to evaluate electromechanical properties. It was fixed with a copper parallel plate fixture diameter of 25 mm. DC voltage was applied with a DC power supply (Instek, GFG 8216A). A digital multimeter (Tektronix, CDM 250) was used to monitor the voltage input. The samples were prepared in the configuration of polyimide–hydrogel–polyimide sandwich to prevent the shortening of the circuit. The insulating polyimide (PI), ®Kapton TH-012 (12 μm) was obtained from ©2006 Saint Gobain Performance Plastic Corporation. In these experiments, an oscillatory shear strain was applied and the dynamic modulus (G′) was measured as a function of the frequency and electric field strength. Strain sweep test was first carried out to determine the suitable strains to measure G′ in the linear viscoelastic regime. The appropriate strain was determined to be 0.1% for the pristine SF hydrogels and SF/PCZ hydrogels. The temporal response experiments were carried out at 300 K. Then, the frequency sweep tests were carried out to measure G′ of each sample as a function of frequency and electric field strength. In each measurement, each SF hydrogel was pre-sheared at a low frequency (0.038 rad/s) and then the electric field was applied for 15 min to ensure the steady state condition before the G′ measurement.

The relative dielectric permittivity was measured by an LCR meter (HP, model 4284A) connected to the melt rheometer with a 25 mm parallel plate fixture. The thickness of the sample was 1 mm with the diameter of 25 mm. The measurements were carried out at 300 K. The electric permittivity at a frequency of 20 Hz was divided by 8.85 pF/m of dielectric permittivity of free space to obtain the relative dielectric permittivity or the dielectric constant.

The dielectrophoresis forces were determined by measuring the deflection distances of the pristine SF hydrogels and SF/PCZ hydrogels in the vertical cantilever fixture under electric field. The specimens were vertically immersed in the silicone oil (viscosity = 100 cSt) between parallel copper electrode plates. The gap between the electrodes was 30 mm. A DC voltage was applied with a DC power supply (Goldsun, GPS 3003B) connected to a high voltage power supply (Gamma High Voltage, model UC5-30P and UC5-30N). A video camera was used to record the movement during experiment. The deflection distances in x (d) and y axes (l) at the end of the specimen were determined by using the SemAfore software. The electric field strength was varied between 0 and 500 V/mm at the room temperature of 300 ± 1 K. The resisting elastic force of the specimens was calculated under electric field using the nonlinear deflection theory of a cantilever [17–21], which can be obtained from the standard curve between $(F_e l_0^2)/(El)$ and d/l_0 (l_0 = initial length of specimens) [20]; F_e is the elastic force, d is the deflection distance in the horizontal axis, l is the deflection distance in the vertical axis, E is