CHAPTER IV

ELECTROMECHANICAL RESPONSE OF SILK FIBROIN HYDROGEL AND CONDUCTIVE POLYCARBAZOLE/SILK FIBROIN HYDROGEL COMPOSITES AS AN ARTIFICIAL MUSCLE

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Abstract

Pure silk fibroin (SF) hydrogel and composites of polycarbazole/silk fibroin (PCZ/SF) hydrogel were fabricated by solvent casting technique to investigate electromechanical properties, dielectric properties, and cantilever deflection properties as functions of electric field strength, SF concentration, glutaraldehyde concentration, and particle concentration in the blends. Electromechanical properties were characterized in oscillatory shear over a frequency range from 0.1 to 100 rad/s at electric field strengths ranging from 0 to 600 V/mm and at a temperature of 27 °C. For both pristine SF and the composite hydrogels, the storage modulus response ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G'_0$) increase dramatically with increasing electric field strength. The pristine hydrogel possesses the highest storage modulus sensitivity value of 5.87, a relatively high value when compared with other electroactive polymers. With the addition of conductive polycarbazole in SF hydrogel, the storage modulus sensitivity and the relative dielectric constant decrease; the conductive polymer thus provides the softening effect. In the deflection experiment with a cantilever fixture, the dielectrophoresis force and deflection distance increase monotonically with electric field strength, where the pure SF hydrogel shows the highest deflection distance and dielectrophoresis force.

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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 intended for animals and human-like robots. One type of electroactive materials is electroactive polymer [1]. Electroactive polymers offer promising and novel characteristics such as light weight, high energy density, and high flexibility. 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 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 silk fibroin 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, silk fibroin has been widely used in the pharmaceutical and medical fields [9]. The most popular morphology is to fabricate silk fibroin into a film type, because it is of a relatively easy preparation technique and the processing conditions can be controlled. Nevertheless, silk fibroin films have shown weak 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 variable conductivity, better thermal stability and mechanical properties [12]. Polycarbazole is one of the conductive polymers that has been interested in many applications, such as light-

emitting diodes, electrochromic displays, organic transistors, and rechargeable batteries [13].

In the present study, we are interested in fabricating an electroactive material from polycarbazole embedded in silk fibroin hydrogel. Also, it is of interest to study and test silk fibroin hydrogels and silk fibroin/polycarbazole composites for actuator applications. The mechanical properties, viscoelastic properties, electrical properties, and actuator performances were investigated and examined along with the effects of silk fibroin concentration, glutaraldehyde concentration, polycarbazole 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 used as received as dopant and solvent, respectively. Silk cocoons (Bombyx 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 to prepare silk fibroin solution. Sodium dodecyl sulfate (AR grade, Sigma-Aldrich) was used as surfactant. Glutaraldehyde solution 50 % in water (AR grade, Fluka) was used as the crosslinking agent. Deionized water was used in all the experiments.

2.2. Synthesis of polycarbazole

We followed the polycarbazole synthesis procedure of Gupta *et al.* [14] 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 silk fibroin (SF) solution

According to Kim *et al.* [15], 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 the room temperature, the extracted SF was dissolved in 9.3 M of lithium bromine solution at 60 °C for 4 h to yield a 20 %w/v solution. 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 silk fibroin (SF) and silk fibroin/polycarbazole (SF/PCZ) hydrogels

Pure SF hydrogels were prepared by diluting the SF solution to be 4 and 5 vol.%, then crosslinking concentrated SF solution with 0.01, 0.05, 0.1, 0.5, and 1 vol.% of glutaraldehyde solutions at room temperature. The crosslinked SF solutions were poured into plastic petri dishes (10 cm in diameter). The pure SF hydrogels were obtained after casting at a room temperature for a period of 2 days.

The composites of SF/PCZ hydrogels were prepared by mechanical blending of PCZ with SF solution. We dispersed PCZ powder into 10 ml of SF solution filled with 0.05 M of sodium dodecyl sulfate as the surfactant and further crosslinked with 0.01 vol.% of glutaraldehyde. The dispersion of particle was random. Concentrations of the highest electrical conductivity of PCZ in SF solution were 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 vol.%. The composite hydrogels were casted in a mold at a room temperature for 2 days before further characterizations.

2.5. Characterization and testing

The dedoped, doped polycarbazole (PCZ) and freeze-dried silk fibroin (SF) hydrogel were characterized by a FTIR spectrometer in order to identify their functional groups. The FTIR spectrometer (Thermo Nicolet, Nexus 670) was operated in the transmission mode with 64 scans and a resolution of ± 4 cm^{-1}, covering a wavenumber range between 400 and 4000 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. The thermal behavior of hydrogels was investigated by weighting a sample of 5-10 mg and loading into a platinum pan, and then heating under nitrogen flow with the heating rate of 10 °C/min from 30-900 °C.

Scanning electron micrographs were taken with a scanning electron microscope (Hitachi, S4800) to determine the morphology of PCZ in powder forms and SF/PCZ composites at various particle concentrations. The scanning electron micrographs of PCZ and SF/PCZ composites were obtained by using an acceleration voltage of 10 kV 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 in this experiment were 300 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution.

Electrical conductivity was measured by a meter which consists of two probes making contact on a surface of sample pellet. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage and the current change in the linear Ohmic regime were converted to the electrical conductivity of polymer using Eq. (1) as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s t} = \frac{I}{KVt} \qquad (1)$$

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

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known; we used silicon wafer chips (SiO_2). In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by Eq. (2) as follows:

$$K = \frac{\rho}{Rt} = \frac{I\rho}{Vt} \tag{2}$$

where K is the geometric correction factor, ρ the known resistivity of standard silicon wafer (Ωcm), t the film thickness (cm), R the film resistance (Ω), and I is the measured current (A).

A melt rheometer (Rheometric Scientific, ARES) was used to measure electromechanical properties. It was fixed with a custom-built copper parallel plate fixture diameter of 25 mm. DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver the electric field up to 4 kV. 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 polyimide (PI), [®]Kapton TH-012 (12 micron) was produced by and obtained from ©2006 Saint Gobain Performance plastic Corporation. The PI film is an excellent insulator up to 7 kV/mm for the breakdown voltage; a dielectric constant value of 3.3; volume resistivity $> 10^{16}$ S/cm. 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 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. The deformation frequency was carried out from 0.1 to 100 rad/s. 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 top and bottom sides of the specimen were coated with silver adhesive to improve the electrical contacts between the specimen and electrodes. The measurements were carried out at 300 K. The AC voltage applied was being varied between 1 and 10 V, depending on the materials. 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 pure SF hydrogel 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 (68 mm of length, 40 mm of width, and 2 mm of thickness). The gap between the pair of 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) which can deliver and electric field up to 25 kV. The output voltage from the high voltage power supply was calibrated using a Fluke 40 kV High Voltage Probe. A video camera was used to record the movement during experiment. Pictures were captured from the video and the deflection distances in x (d) and y axes (l) at the end of the specimen were determined by using the SemAfore software (version 5.21). The electric field strength was varied between 0 and 500 V/mm at the room temperature of 300 ± 1 K. Both the voltage and the current were monitored. The resisting elastic force of the specimens was calculated under electric field using the nonlinear deflection theory of a cantilever [16-20], which can be obtained from the standard curve between $(F_e l_0^2)/(EI)$ and d/l_0 ($l_0 =$ initial length of specimens) [19]; 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 the Young's modulus which is equal to $2G'(1 + v)$, where G' is the shear storage modulus taken to be G' (ω= 1 rad/s) at various electric field strengths, v is Poisson's ratio (0.5 for an incompressible), and I is the moment of inertia $1/12t^3w$, where t is the thickness of the sample and w is the width of the sample. The electrophoresis force can be calculated from the static horizontal force balance consisting of the elastic force, the corrective gravity force, and the buoyancy force, as in Eq. (3), according to Petcharoen and Sirivat [21]:

$$F_d = F_e + mg(sin\ \theta) - \rho Vg(sin\ \theta) \qquad (3)$$

where g is gravity constant (9.8 ms^{-2}), m the mass of the specimen, θ the deflection angle, ρ the density of the fluid , and V is the volume of displaced fluid.

3. Results and discussion

3.1. Characterization of polycarbazole (PCZ) and silk fibroin (SF) hydrogel

The FTIR spectra of the dedoped and doped polycarbazole were taken to identify the characteristic transmittance peaks. The characteristic peaks are at 3192, 1620, 1440, 1200, 825, and 700 cm^{-1}. These peaks can be assigned to the N-H stretching of the heteroaromatics; the C=C stretching of the aromatic compound; the C-N stretching of substitutions; the C-H in plane bending; the C-H deformation of trisubstituted benzene; , the C-H out-of-plane bending, respectively [14, 22].

The characteristic peaks in FTIR spectrum of freeze-dried SF hydrogels are at 3620, 2900, 1680, 1530, 1450, and 1250 cm^{-1}. These peaks can be assigned to the N-H stretching; the C-H stretching; the amide I (C=O stretching); the amide II (N-H bending and C-H stretching); the C-H bending; and the amide III (C-N stretching and C=O bending) due to the transformation from random coils to β-sheet structure, respectively [15, 23].

The TGA thermogram of dedoped PCZ shows a degradation peak at 700 °C corresponding to the backbone degradation. Whereas, doped PCZ thermogram shows

two degradation steps at 400 and 700 °C; they can be referred to the elimination of dopants and the decomposition of the polymeric chain [4].

The TGA thermogram of SF hydrogel shows two transitions temperature; the first transition at 60-100 °C refers to the loss of moisture and low temperature volatile species in the hydrogel; the second transition at 270-500 °C refers to the breakdown of the side chain group of amino acid residue and the silk fibroin degradation [25]. Percentage of weight loss of SF hydrogel slightly decreases with increasing amount of glutaraldehyde as the crosslinking agent.

The average particle diameters of dedoped and doped 100:1 PCZ are approximately 41.21 and 58.45 µm with the standard deviation of 1.15 and 1.16 µm, respectively. Fig. 1 shows the shapes of the dedoped and doped 100:1 PCZ particles; they are quite irregular in shape. Fig. 2 shows the dispersion of PCZ particles in silk fibroin hydrogels of 0, 0.01, and 0.1 vol.% of PCZ particles. The morphology of the dispersion is random.

The specific conductivity of dedoped and doped PCZ was measured by a custom-built two point probe (Keithley, Model 6517A). The specific conductivity of dedoped PCZ is 2.53×10^{-7} S/cm with a standard deviation of 9.24×10^{-9} S/cm. The specific conductivity of doped PCZ at $N_{HCl}:N_{CZ}$ equal to 1:1, 10:1, 100:1, 200:1, and 300:1 are 3.28×10^{-7}, 3.96×10^{-6}, 3.72×10^{-5}, 3.48×10^{-5}, and 4.28×10^{-6} S/cm with standard deviations of 1.02×10^{-7}, 1.26×10^{-6}, 3.26×10^{-7}, 8.50×10^{-7}, and 4.90×10^{-7} S/cm, respectively.

3.2. Electromechanical properties

3.2.1. Effects of silk fibroin (SF) concentration and glutaraldehyde (GTA) concentration

The effect of electric field strength on the rheological properties of the pristine silk fibroin (SF) hydrogels was investigated in a range of 0 to 1 kV/mm. Fig. 3. shows the storage modulus response sensitivity ($\Delta G'/G'_0$) of pure SF hydrogel prepared by 0.01, and 1.0 vol.% glutaraldehyde (GTA) crosslinked in 4 vol.% SF solutions and 0.01 vol.% GTA crosslinked in 5 vol.% SF solution vs. electric field

strength at a frequency of 100 rad/s, a strain of 0.1 % and a temperature of 300 K. The increases in the storage modulus response ($\Delta G'$) with electric field strength are nonlinear within the range of 0.25 to 1 kV/mm. The storage modulus response values of these samples at an electric field strength of 1 kV/mm are 3.08×10^5, 3.34×10^5, and 2.7×10^5 Pa, in which the initial storage modulus (G'_0) are 4.12×10^4, 9.93×10^4, and 1.10×10^5 Pa for the 0.01 vol.% GTA crosslinked in 4 vol.% SF solution, 1.0 vol.% GTA crosslinked in 4 vol.% SF solution, and 0.01 vol.% GTA crosslinked in 5 vol.% SF solution, respectively. Thus the storage modulus sensitivity ($\Delta G'/G'_0$) values are 7.48, 3.47, and 2.45 for the 0.01 vol.% GTA crosslinked in 4 vol.% SF solution, 1.0 vol.% GTA crosslinked in 4 vol.% SF solution, and 0.01 vol.% GTA crosslinked in 5 vol.% SF solution, respectively.

When an electric field is applied, induced dipole moments within the silk fibroin structure are generated, leading to intermolecular interactions. These intermolecular interactions induce the loss of free chain movements and thus chain rigidity, as indicated by the higher G' values [2, 26]. The electric field is clearly shown here to enhance the rigidity of the pure SF hydrogels. However, the storage modulus of SF hydrogel prepared by 0.01 vol.% GTA crosslinked in 5 vol.% SF solution improves slightly than those of SF hydrogels prepared by 0.01 and 1.0 vol.% GTA crosslinked in 4 vol.% SF solutions, due to its initially high rigidity in the absence of applied electric field. A higher electric field strength is expected to induce a higher dipole moment and to cause chain segment to pull themselves together in a tighter formation due to the greater electrostatic forces, as evidenced by dramatic increases in G' with electric field strength [27]. Increasing the amount of crosslinking agent reduces the reactive carbonyl and amine groups, which can generate dipole moments along SF chains. Therefore, the active sites which respond to the applied electric field is reduced which affects the storage modulus response and sensitivity.

In comparison with electroactive polymers and dielectric elastomers at an identical electric field strength 1 kV/mm, the styrene-isoprene-styrene triblock (D114P, D1164P, D1162P) exhibited the storage modulus sensitivity of 0.122, 0.102, and 0.050 [28], the uncrosslinked high-gel-strength gelatin exhibited the storage modulus sensitivity of 2.30 [29]. In our work, the pure SF hydrogels posse superior

responses and the sensitivity values which are an order of magnitude greater than those polymers, as shown in Table 1.

3.2.2. Effect of particle concentration

The electromechanical properties of the silk fibroin/polycarbazole (SF/PCZ) hydrogels were investigated in the range of 0-600 V/mm. Polycarbazole (PCZ) concentrations in silk fibroin (SF) hydrogel are 0, 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 vol.%. The storage modulus response ($\Delta G'$) values of the samples at an electric field strength of 600 V/mm are 2.42×10^5, 1.62×10^5, 9.36×10^4, 9.72×10^4, 1.02×10^5, 7.72×10^4, and 6.66×10^4 Pa with the initial storage modulus (G'_0) of 4.12×10^4, 5.88×10^4, 5.23×10^4, 6.09×10^4, 6.83×10^4, 6.81×10^4, and 6.87×10^4 Pa for the pure SF, the SF/PCZ (0.001 vol.% of PCZ), the SF/PCZ (0.005 vol.% of PCZ), the SF/PCZ (0.01 vol.% of PCZ), the SF/PCZ (0.05 vol.% of PCZ), the SF/PCZ (0.1 vol.% of PCZ), and the SF/PCZ (0.5 vol.% of PCZ) hydrogels, respectively. These results show the increase of the storage modulus response and storage modulus sensitivity ($\Delta G'/ G'_0$) with electric field strength for each sample. The mixing of PCZ into SF hydrogel shows the increase of G' with and without an electric field as a result of the effect of particles acting as fillers [30]. However, $\Delta G'$ and $\Delta G'/G'_0$ decrease with an increasing PCZ concentration, as shown in Fig. 4. This result here suggests that the decrease of the storage modulus sensitivity is due to the softening effect from water residues within the hydrogel specimen. The presence of water residues allow the PCZ induced dipole moments to move around as the electric field is applied and neutralize the significant polycarbazole particle interactions and SF induced dipole moments which would have been present as in previous work [31, 32].

Chotpattananont et al. [12] found that the storage and loss modulii of a polymer blend between polythiophene and polyisoprene increased with increasing polythiophene concentration. The electrically induced dipole moments created electrostatic forces between particles; the interaction can be physically thought of generating equivalent electric network stands which increase the storage modulus response and sensitivity. Kunanuruksapong and Sirivat [31] reported the storage

modulus sensitivity of poly(p-phenylene)/AR71 blends with increasing particle concentration increased linearly with the electric field strength.

3.2.3. Time dependence of the electromechanical response

We investigated the temporal characteristic of pure silk fibroin (SF) hydrogel and the silk fibroin/polycarbazole (SF/PCZ) hydrogel at PCZ concentration of 0.001 vol.% at electric field strength 600 V/mm in which the electric field was turn on and off alternately. The temporal characteristic of each sample was recorded in the linear viscoelastic regime at a strain of 0.1 %, and frequency of 100 rad/s.

Fig. 5 shows a comparison of the storage modulus (G') of the pure SF and of SF/PCZ (0.001 vol.% of PCZ) hydrogels during the time sweep test. For the pure SF hydrogel, G' increases rapidly when the electric field is on, and decreases instantaneously when the electric field is off. For the SF/PCZ (0.001 vol.% of PCZ) hydrogel, G' increases slightly when the electric field is on, but it does not recover to the original value. Our result here may suggest that there are some irreversible interactions of the dipole moments from PCZ particles and the carbonyl and amide groups along SF chains.

3.2.4. Relative dielectric permittivity of pure silk fibroin (SF) hydrogel and silk fibroin/polycarbazole (SF/PCZ) hydrogels

In general, the dielectric permittivity or dielectric constant of the materials arise due to the polarization of molecules and increases with the increase in its polarizability [32].The relative dielectric permittivities or the dielectric constants of pure silk fibroin (SF) hydrogel and silk fibroin/polycarbazole (SF/PCZ) hydrogels were measured at 300 K. Fig. 6 shows the relative dielectric permittivity versus frequency curves of the SF/PCZ hydrogels with various polycarbazole (PCZ) concentration to be 0, 0.001, 0.01, and 0.1 vol.%. The relative dielectric permittivities at the frequency of 20 Hz are 86.42, 77.95, 59.94, and 42.34 for the pure SF, the SF/PCZ (0.001 vol.% of PCZ), the SF/PCZ (0.01 vol.% of PCZ), and the SF/PCZ (0.1 vol.% of PCZ), respectively. The relative dielectric permittivities of

SF/PCZ hydrogels can be seen to increase with increasing frequency for all samples when the frequency is greater than 10^3 Hz. The increment of the relative dielectric permittivity with increasing frequency can be attributed to the ionic polarization that comes from the translation of polarization from water molecules inside the hydrogel. The plasticizing effect of increasing water content increase segmental mobility of polymeric chains, which reflected to the increase of dielectric permittivity due to the free charge motion and the shift of secondary α-relaxation to higher frequencies with stimultaneous increase of it relaxation strength. The effects of free charge motion are by far more striking. The α-relaxation in proteins is attributed to motion of alkyl sequences with participation of the polar amide and carbonyl groups and β-relaxation to associations of various dipolar groups and water [33]. In polar solvent, the polyions and counterions can easily dissociate from each other and associate with solvent molecule due to the relative large dielectric constant of the polar solvent, which can lead to the solubilization of polyelectrolytes as well as the very high degree of swelling of charge gels in polarsolvents [34]. Ntanrouli *et al.* [35] studied the dielectric permittivity of heteroarm star block terpolymer and reported that by increasing the dielectric permittivity of the medium, some ion dissociation and therefore repulsions along the protonated arm chains promote promote arm stretching, leads to overlap of the already compacted star. When an organic compound is mixed with water, the relaxation strength, relaxation time, and the distribution of the relaxation time are changed, because these relaxation parameters are related to the water structure of in the mixture. These factors may include the total the total size of solute particle, the overall shape of the solute molecule with respect to the water arrangement around it, the flexibility of the linear polymer chains, intra- and intermolecular hydrogen bonding, the formation of water bridges connecting two polar groups of solute via hydrogen bonds, and the enhancement of hydrogen bonds between those water molecules which are not connected to the polar groups of the solute and which may form small islands of isolated solvent [36].

3.4. Deflection responses

The deflection of the pure silk fibroin (SF) hydrogel and silk fibroin/polycarbazole (SF/PCZ) hydrogels was studied by vertically suspending the hydrogels in a silicone oil bath; a DC electric field was applied horizontally between two parallel flat copper electrodes. The electric deflection responses of pure SF, SF/PCZ (0.001 vol.% of PCZ), and SF/PCZ (0.5 vol.% of PCZ) hydrogels with an electric field strength of 500 V/mm were recorded by a video camera as shown in Fig. 7. Upon applying an electric field, the free lower end of the hydrogel deflects toward the anode side, depending on the electric field strength, that results from the effect of the non-symmetric charges. The pure SF hydrogel indicates an attractive interaction between the anode and the polarized carbonyl and amine groups, in which the SF structure possesses negative charge. The deflection distance and the dielectrophoretic forces of the pure SF hydrogel and the SF/PCZ hydrogels are shown in Fig. 8. The pure SF hydrogel shows greater deflection distance value than the SF/PCZ hydrogels. The hydrogels start to deflect at lower critical electric field strengths: 50, 75, and 125 V/mm for the pure SF, SF/PCZ (0.001 vol.% of PCZ), and SF/PCZ (0.01 vol.% of PCZ) hydrogels, respectively. Moreover, the SF/PCZ hydrogels shows a lesser deflection response under an applied electric field than the pure SF hydrogel because of its initial higher rigidity, or higher G'_0 value. Furthermore, the deflection distances and dielectrophoretic forces of the pure SF hydrogel and SF/PCZ hydrogels appear to increase stepwise with increasing electric field strength. The dielectrophoretic force of at electric field strength of 500 V/mm of the pure SF, SF/PCZ (0.001 vol.% of PCZ), and SF/PCZ (0.01 vol.% of PCZ) hydrogels is 9.19, 2.32, and 1.67 mN, respectively. The resultant dielectrophoretic forces of SF/PCZ hydrogels under the applied electric field are smaller than those of the pure SF hydrogel. Under the applied electric field, pure SF hydrogel can polarize and generate non-symmetric negative charges. Whereas, the polycarbazole has positive charges attached on the main chains, consequently the presence of positive charges diminishes the non-symmetric negative charges generated within the silk fibroin matrix. Therefore, the bendings and the dielectrophoretic forces of the SF/PCZ hydrogels under an electric field are less.

In our work, the maximum deflection distance and dielectrophoretic force are obtained with the pristine SF hydrogel at the electric field strength of 500 V/mm; they are 8.00 mm and 9.19 mN, respectively. In comparison with the previous works, the maximum deflection distance and dielectrophoretic force at 500 V/mm of styrene-isoprene-styrene triblock copolymer (D1114P) were 1.63 mm and 20.5 μN [28].The dielectrophoretic force of a gelatin hydrogel at 600 V/mm was 7.05 mN [30]. The dielectrophoretic force of a cellulosic gel at 500 V/mm was 4.63 mN at the deflection angle of 44 ° [37].

4. Conclusions

In this study, the electromechanical properties, dielectric properties, and the cantilever bending of pristine silk fibroin and silk fibroin/polycarbazole hydrogels were investigated at electric field strength varying from 0-600 V/mm. Polycarbazole was synthesized via the oxidative polymerization.

For the pure silk fibroin hydrogels, the storage modulus response ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G'_0$) increase dramatically with increasing electric field strength and show the highest storage modulus sensitivity value of 5.87. Increasing the amount of glutaraldehyde as the crosslinking agent causes the reduction of the storage modulus sensitivity value due to the decrease of reactive dipole moments from the crosslinking process.

For the silk fibroin/polycarbazole hydrogel system, particles of polycarbazole were embedded into silk fibroin hydrogels with the particle concentrations of 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 vol.%. The storage modulus response ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G'_0$) decrease with increasing particle concentration because water residues create the softening effect, neutralizing the electric-induced-dipole moments of the conductive polycarbazole particles, and generating movable induced dipole moments. The storage modulus sensitivity values of pure silk fibroin and silk fibroin/polycarbazole hydrogels are proportional to the relative dielectric permittivity values corresponding to the ionic polarization.

For the temporal response, there are some irreversible interactions from the remaining dipole interaction along silk fibroin and polycarbazole polymeric chains when the electric field is off.

For the deflection measurement, the deflection distances and the dielectrophoretic forces of the pure silk fibroin and silk fibroin/polycarbazole hydrogels increase with increasing electric field strength. The pure silk fibroin hydrogel shows greater deflection distance and the dielectrophoretic force, 8.00 mm and 9.19 mN, than those of fibroin/polycarbazole hydrogels.

Acknowledgements

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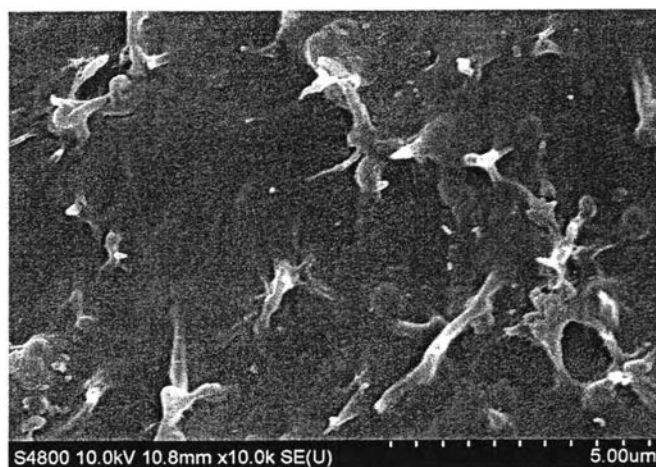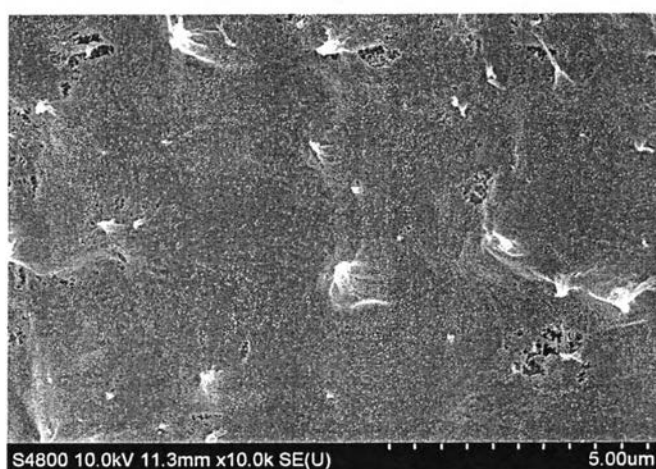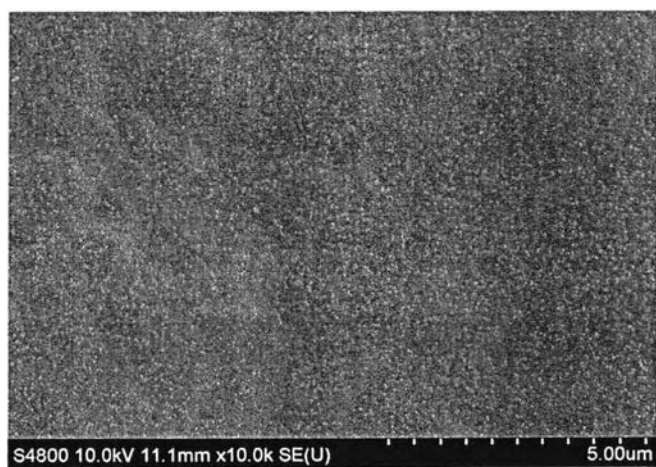[37] W. Kunchornsup, A. Sirivat, Sensor. Actuator. A 175 (2012) 155-164.
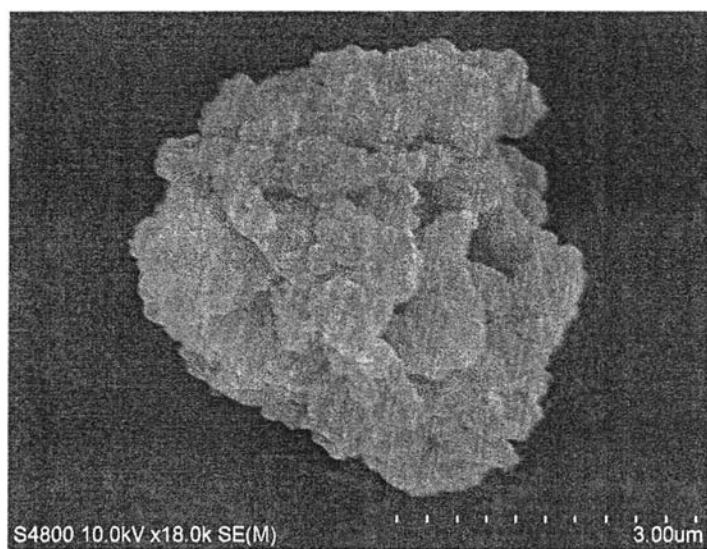
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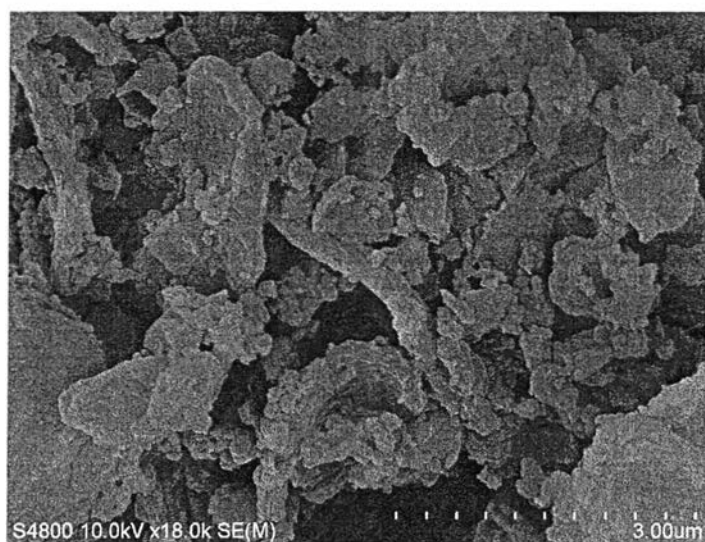
(b)

Fig. 1. SEM photographs of: (a) dedoped polycarbazole; (b) doped 100 :1 polycarbazole at magnification of 18000.

(a)

(b)

(c)

Fig. 2. SEM photographs of dispersion of polycarbazole (PCZ) particle in silk fibroin hygrogel: (a) 0 vol.%; (b) 0.01 vol.%; and (c) 0.1 vol.% of PCZ particle.
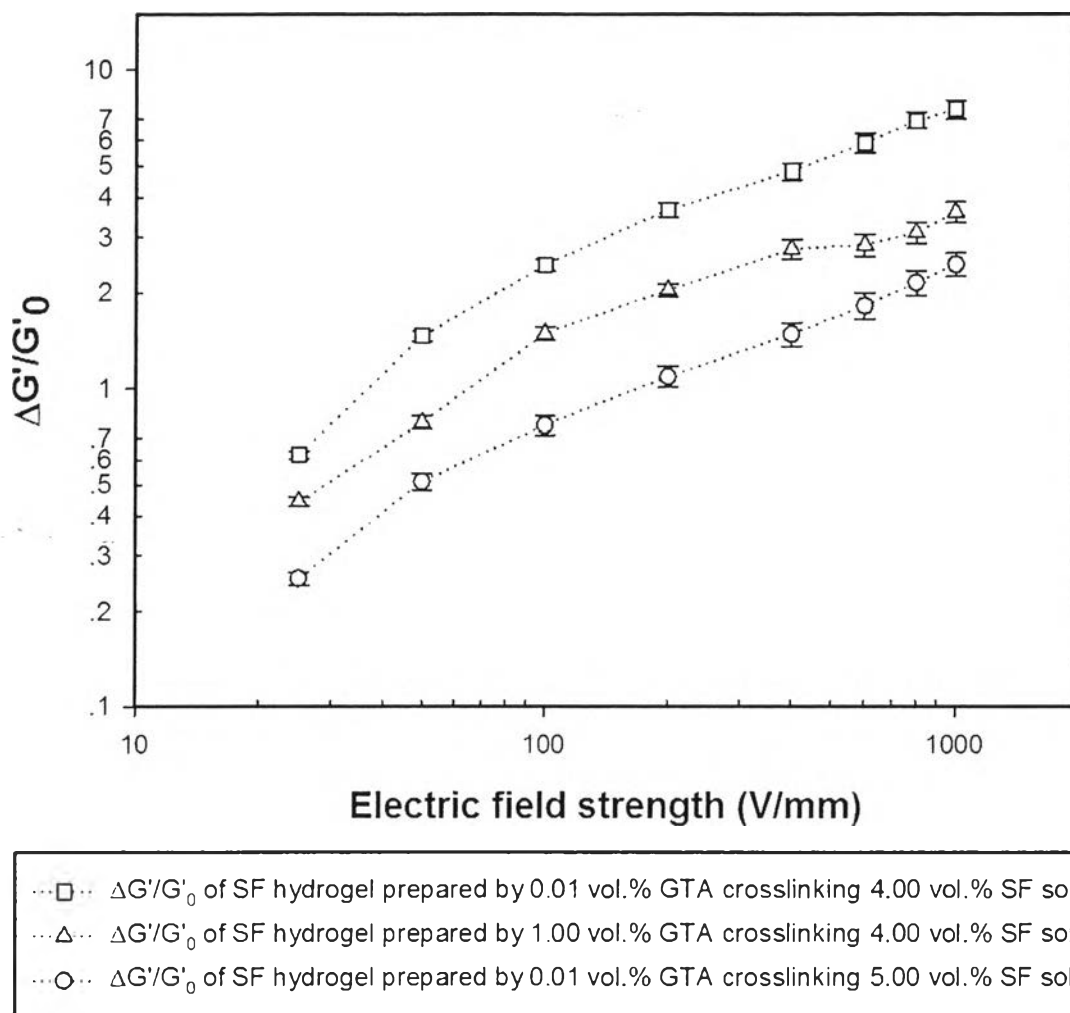
Fig. 3 The storage modulus sensitivity ($\Delta G'/G'_0$) vesus electric field strength of silk fibroin (SF) hydrogels prepared by various glutaradehyde (GTA) concentrations in 4 and 5 vol.% SF solutions, at strain 0.1 %, frequency 100 rad/s, temperature 300 K.
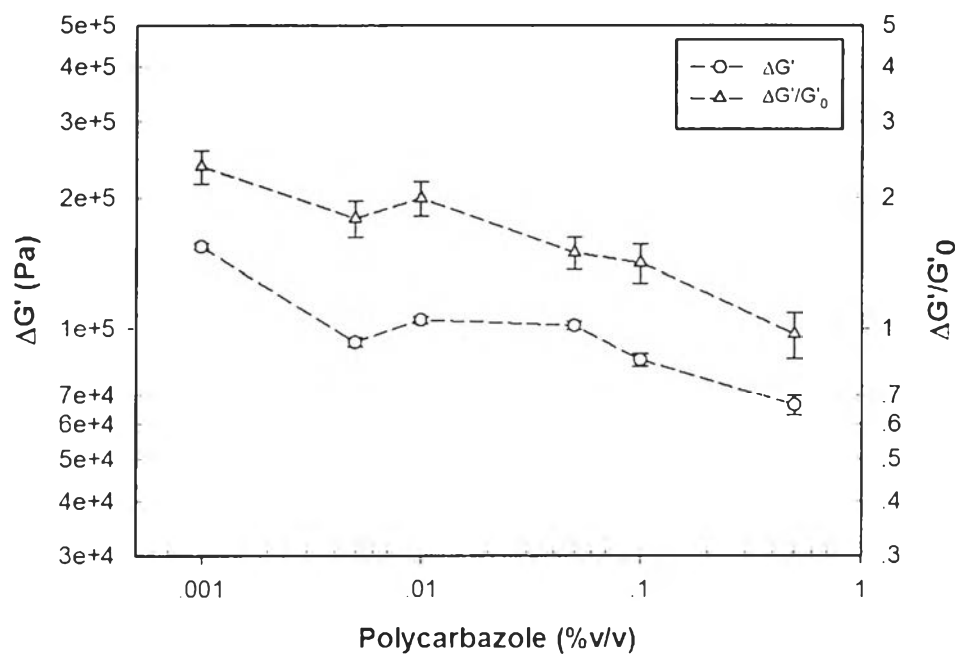
Fig. 4. Effect of polycarbazole concentration on the storage modulus response and the storage modulus sensitivity at strain 0.1 %, frequency 100 rad/s, electric field strength 600 V/mm, temperature 300 K.
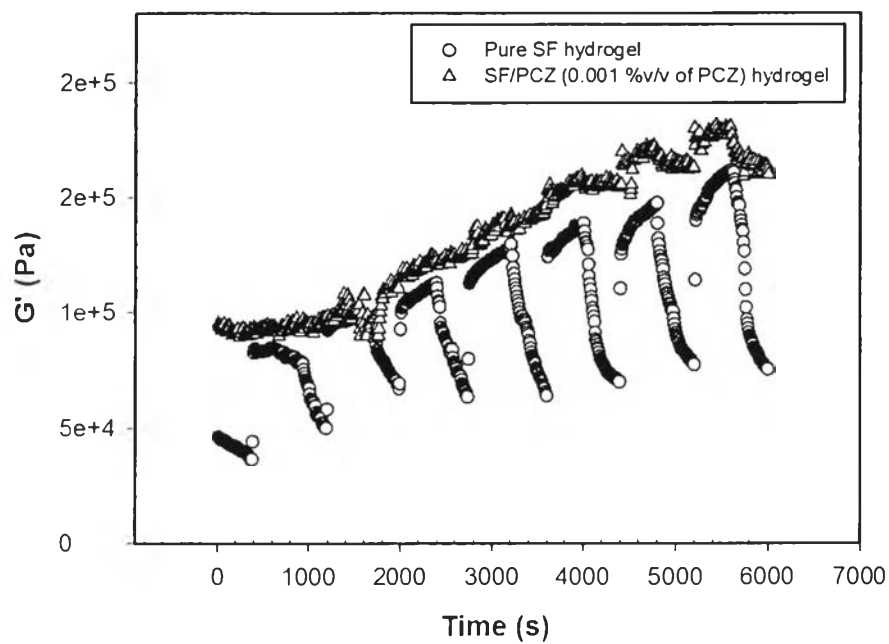
Fig. 5. Temporal responses of the storage modulus (G') of the pure silk fibroin (SF) hydrogel and the silk fibroin/polycarbazole (SF/PCZ) (0.001 %v/v of PCZ) hydrogel at strain of 0.15 %, frequency of 100 rad/s, electric field strength of 600 V/mm, temperature of 300 K.
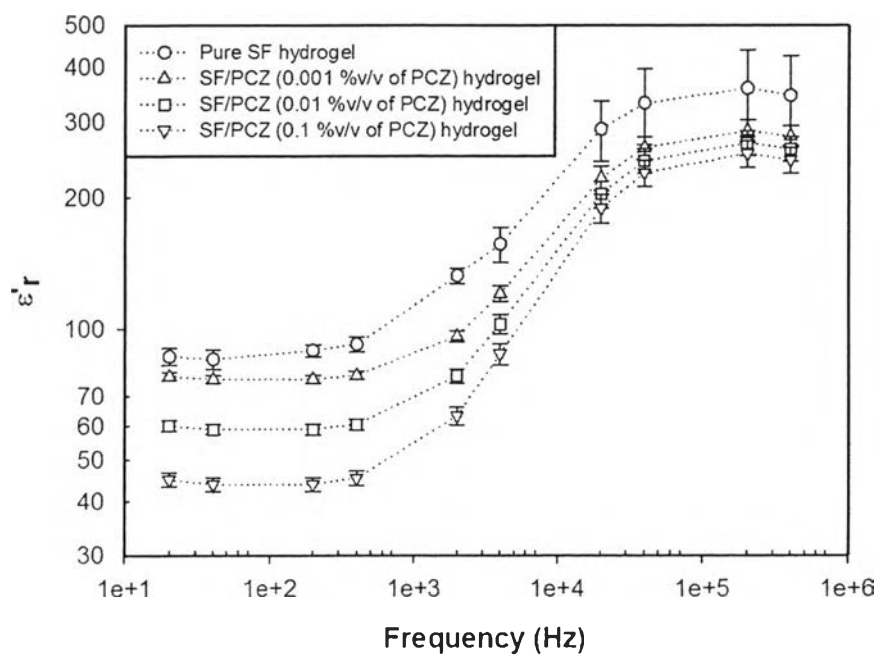
Fig. 6. Relative dielectric constant (ε_r') versus frequency of pure silk fibroin (SF) hydrogel, silk fibroin/polycarbazole (SF/PCZ) hydrogels with various polycarbazole (PCZ) concentration at temperature of 300 K.
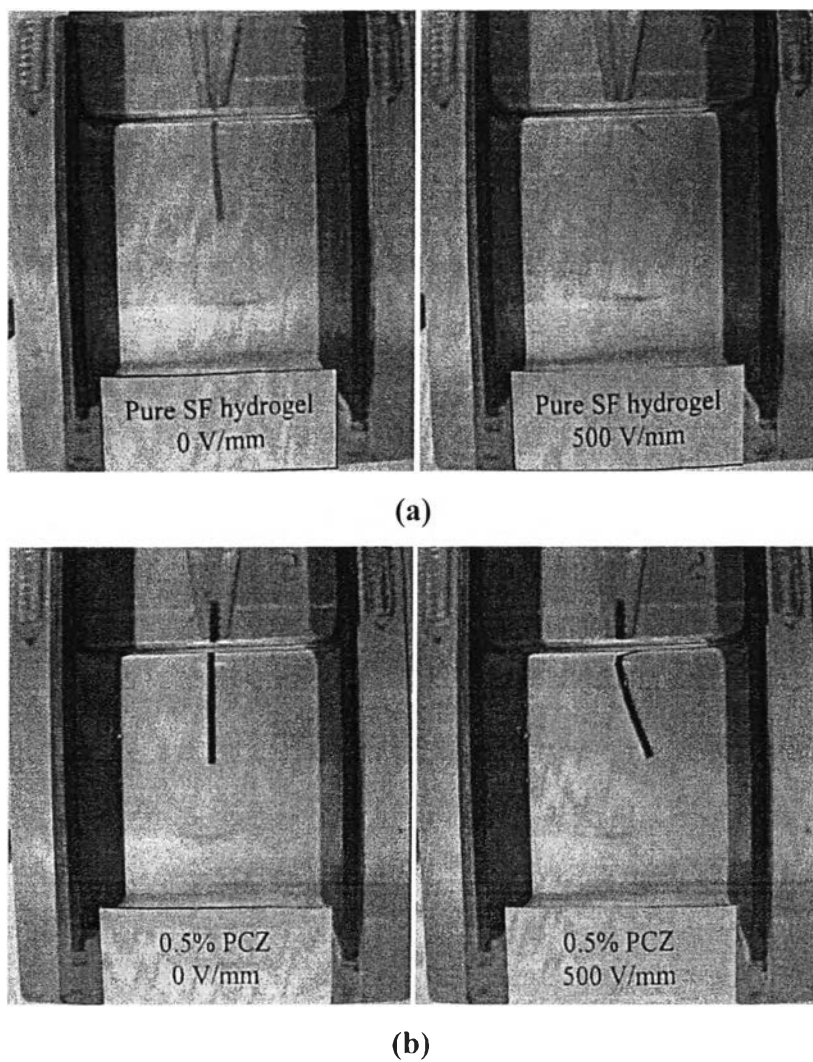
Fig. 7. Deflection of pure silk fibroin/polycarbazole (SF/PCZ) hydrogels at E = 0 and 500 V/mm: (a) pure SF hydrogel and (b) SF/PCZ (0.5 %v/v of PCZ) hydrogel.
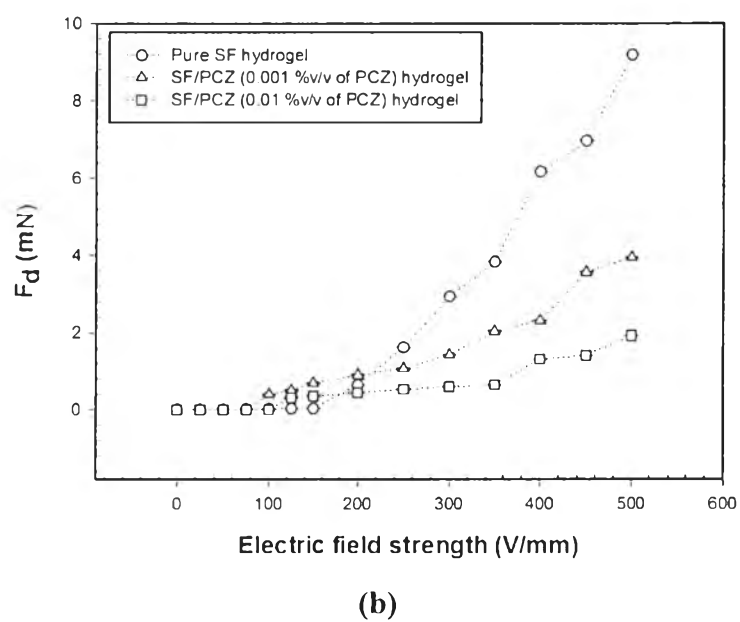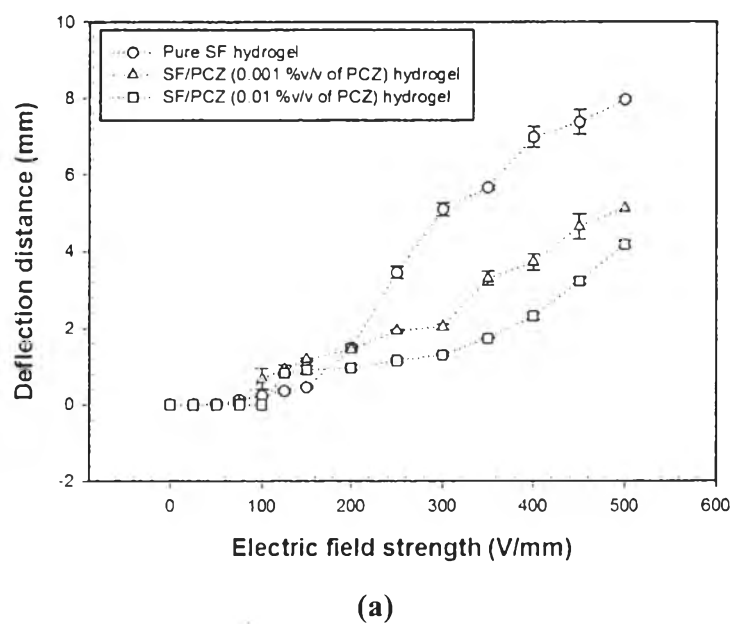
(a)

(b)

Fig.8. (a) Deflection distances of silk fibroin (SF) hydrogel, silk fibroin/polycarbazole (SF/PCZ) (0.001 vol.% of PCZ), and SF/PCZ (0.01 vol.% of PCZ) hydrogels at various electric field strengths. (b) Dielectricphoretic forces calculated through nonlinear deflection theory.

Table 1 Comparison of storage modulus sensitivities of pure silk fibroin (SF) hydrogel and electroactive materials

Material	Electric field strength (kV/mm)	Frequency (rad/s)	Storage modulus sensitivity ($\Delta G'/G'_0$)	Reference
SF hydrogel (0.01 vol.% GTA crosslinked 4 vol.% SF solution)	1	100	7.48	-
SF hydrogel (1.0 vol.% GTA crosslinked 4 vol.% SF solution)			3..47	-
SF hydrogel (0.01 vol.% GTA crosslinked 5 vol.% SF solution)			2.45	-
SF/PCZ (0.001 vol.% PCZ) hydrogel	0.6	100	2.75	-
SF/PCZ (0.005 vol.% PCZ) hydrogel			1.79	-
SF/PCZ (0.01 vol.% PCZ) hydrogel			1.60	-
SF/PCZ (0.05 vol.% PCZ) hydrogel			1.50	-
SF/PCZ (0.1 vol.% PCZ) hydrogel			1.33	-
SF/PCZ (0.5 vol.% PCZ) hydrogel			0.97	-
Styrene-isoprene-styrene triblock (D1114P)	1	1	0.122	[28]
Styrene-isoprene-styrene triblock (D1164P)			0.102	
Styrene-isoprene-styrene triblock (D1162P)			0.050	

Uncrosslinked high-gel-strength gelatin	1	100	2.30	[29]
3% crosslinked high-gel-strength gelatin			0.49	
AR71/Poly(p-phenylene) (10 vol.%)	1	1	0.306	[31]
AR71/ Poly(p-phenylene) (30 vol.%)			0.971	
Polyisoprene/Polythiophene (5 vol.%)	2	1	0.5	[32]
Polyisoprene/Polythiophene (20 vol.%)	2	1	1.10	