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Enhanced actuation performance of silk-polypyrrole composites

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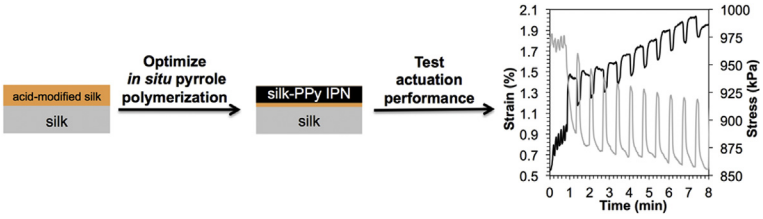
HIGHLIGHTS

- Improved synthesis procedures were identified to produce more conductive silk-polypyrrole biocomposite bilayer actuators.
- Optimized films exhibited a dramatic improvement in electrochemical stability under extended cycling.
- Devices generated twice as much stress and 6× the amount of strain during linear electrochemical actuation.

GRAPHICAL ABSTRACT



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ABSTRACT

Recently we have shown that a composite material of silk and the conducting polymer polypyrrole (PPy) has promising characteristics for use as a bending bilayer actuator. In this study, the reaction conditions were varied for the *in situ* incorporation of polypyrrole into silk films during pyrrole polymerization. While surface morphology and mechanical properties were minimally affected, polymerization conditions were identified where the resistivity, stability of the films during storage and stability during prolonged electrochemical cycling were dramatically improved. When fabricated into bilayer-type electromechanical actuation devices, stress and strain generation, as well as the stability during repeated actuation, was found to be superior for silk-polypyrrole composite films with improved electrical properties.

1. Introduction

Conductive polymers such as polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PAni) have drawn significant interest for use as soft actuator materials in biomedical devices such as micropumps [1–4], steerable catheters [5–7], microvalves and blood vessel connectors [5]. Electromechanical actuation of these materials is controlled electrochemically by applying a positive or negative bias to the polymer film in the presence of an electrolyte. The electrolyte ions provide a charge balance that allows for the oxidation or reduction of the polymer backbone. The flux of these ions (and accompanying solvent molecules) within the polymer matrix results in expansion or contraction. When adhered to an inactive support material in a bilayer-type structure, the expansion and contraction of the conducting polymer layer can result in a bending movement [5].

Extensive research, particularly with PPy, has shown that many conductive polymers are biocompatible [8–10], but actuators made solely of conductive polymers are typically too brittle to serve as electrode structures independent of support scaffolding

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[10–12]. Actuators fabricated from composites or blends of conducting polymers and a variety of synthetic support polymers have been reported in the literature [5,13,14]. However, there are still very few actuators that have been constructed using biocompatible or biodegradable materials [15–18], and performance of these devices has only been characterized in highly acidic conditions [15,17], organic solvents [14], or with synthetic electrolytes [16,18]. Therefore, further development of biocompatible devices that also function in biologically relevant environments (water with electrolytes such as Na^+, K^+, Cl^-, HPO_4^{2-}, etc.) is needed in order to fully realize the biomedical applications described above.

Our group recently reported that PPy can be incorporated into solid films made of silk fibroin [19,20], a biodegradable material with desirable mechanical properties for actuators. Silk fibroin provides high tensile strength and toughness to the composite material due to the highly crystalline anti-parallel β-sheets formed by the fibroin protein [21,22]. Silk is also elastic and lightweight, both necessary qualities of an effective soft-tissue actuator. Covalent incorporation of anionic sulfonic acid groups into the silk protein was found to encourage the formation of an interpenetrating network between the silk and cationic PPy, resulting in a robust composite structure that is incapable of delamination [19]. Bilayer devices were fabricated from these silk-PPy composite materials, and electromechanical actuation was demonstrated [20]. However, high potentials of ±3 V were required to effectively actuate these first-generation silk-PPy devices due to their relatively high sheet resistivities (~10^2–10^3 Ω/sq). The films also degraded significantly with successive electrochemical cycling, which resulted in limited actuator performance [20].

The performance of conducting polymer actuators can be dramatically influenced by the conductivity and electrochemical stability of the film. If the film has low conductivity, a large voltage drop occurs down the length of the film and only regions nearest the contact may be exposed to potentials high enough to result in electrochemical doping [23]. This reduces the ion exchange capacity and lowers the actuation efficiency of the films [24]. Minimizing degradation is also essential, as polymer actuators intended for biomedical applications will be repeatedly oxidized and reduced in aqueous environments during device operation.

Here, we achieve improved conductivity and stability of silk-PPy composite devices through optimization of the *in situ* deposition of PPy into silk films during oxidative pyrrole polymerization. Reaction conditions varied include oxidant type, oxidant loading and reaction time. The resulting film morphologies were evaluated using scanning electron microscopy (SEM) and the mechanical properties were compared. Conductivity measurements and cyclic voltammetry were used to evaluate stability of the films during storage and with prolonged electrochemical cycling. Finally, the stress and strain generated by the silk-PPy composite films during actuation were measured. Polymerization conditions were identified where conductivity and electrochemical stability of the resulting silk-PPy composite films were dramatically improved, which in turn led to enhanced stress and strain response and cycling lifetime of actuator devices fabricated from these materials.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Aldrich, Sigma or Fluka and used without further purification. Cocoons from the *Bombyx mori* silkworm were purchased from Mulberry Farms in Fallbrook, CA.

2.2. Preparation of silk-PPy bilayer devices

Silk-PPy bilayer devices were prepared as previously described [19,20] with slight modifications. Briefly, an aqueous silk solution (7–8% w/v) was drop cast on a silicone mat, air dried to form a film approximately 50 μm in thickness, and then soaked in 70% (v/v) ethanol overnight to produce a water-insoluble silk film. The surface of the film was chemically modified to covalently attach sulfonic acid groups as previously described [20], while the method for depositing PPy within the films during an *in situ* polymerization was modified. Films were submerged in an aqueous solution containing 52 mM pyrrole and 5.2 mM of *para*-toluenesulfonic acid. $FeCl_3$ or $Fe(OTs)_3$ (at either a 3:1, 1:1, 1:2 or 1:5 pyrrole:oxidant molar concentration) was added to initiate polymerization, and the solution was left to react for 1 or 2 h at rt. The films were then sonicated in nanopure water for 1 min to remove any excess PPy from the surface of the films. For imaging and initial electrochemical characterization, films were subjected to the chemical modification procedures described above while free-floating in solution, resulting in modification of both faces of the film. To create bilayer films for actuation experiments, PPy was selectively deposited only on one side of the silk films by adhering the films to the bottom of a Petri dish as previously described [20].

2.3. SEM imaging

Topography and cross-sections of silk films were visualized using a Vega TS 5136 MM. Films were fractured in liquid nitrogen to image cross sections, and all samples were mounted with carbon tape on aluminum stubs. Acid-modified films (no PPy) were sputter coated with 10 nm of a gold/palladium mixture prior to imaging with SEM. The composite films were not coated so that the depth of PPy penetration could be visualized. Without sputter coating, regions of the film that contain the conductive PPy appear darker, while the insulating silk in the center appears white due to charging in the electron beam. Bilayer films used for actuation that only have PPy deposited on the porous face were difficult to image due to extreme charging of the insulating silk layer. Therefore, films that were modified on both sides were used for cross-sectional imaging to minimize charging, so the dark interpenetrating network is evident on both sides of the film.

2.4. Electrical and electrochemical characterization

Sheet resistivity of the PPy-modified side of bilayer films was measured in ambient atmosphere with a Lucas Labs Pro-4 four-point resistivity probe (Signatone SP4-40045TBY tip) powered by a Keithley 2400 SourceMeter. Each film was measured four times and the average sheet resistivity of these measurements was calculated. Cyclic voltammetry (CV) was carried out as previously described [20] in an aqueous supporting electrolyte solution of phosphate buffered saline (PBS, 0.1 M phosphate, 0.15 M NaCl, pH 7.2). The area of film exposed to electrolyte was approximately 65 mm^2. Scans were initiated at 0 V and swept between ±1.0 V at a scan rate of 50 mV/s.

2.5. Stress and strain generated during actuation

To measure the stress and strain generated during actuation, an Aurora Scientific 300C-LR dual-mode muscle lever system equipped with a 600A Digital Controller was employed (see diagram in Supplementary Information). Potentials and currents were applied or recorded using a Keithley Sourcemeter 2400 controlled by LabView. Polyimide tape was used to affix a copper contact and fishing line to the top of the films (typical film dimensions: