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Electrochemistry of interlayer supported polypyrrole tri-layer linear actuators

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ABSTRACT

Electro–chemo–mechanical deformation of polypyrrole doped with dodecylbenzenesulfonate (PPy/DBS), deposited electrochemically on chitosan and polyvinylidene fluoride (PVdF) substrates made conductive by chemically deposited poly(3,4-ethylenedioxythiophene) (PEDOT) are examined. The electronic conductivity and structural properties (by Raman and FTIR spectroscopy) of the chemically deposited PEDOT on chitosan film and PVdF membrane are characterized. The linear actuation response of PPy/DBS films on the two substrates in tetrabutylammonium trifluoromethanesulfonate in propylene carbonate electrolyte is investigated under isotonic (constant force) conditions. The goal of this study was to obtain novel linear actuators with mechanically stable tri-layer design and controllable strain, and to compare the effect of two completely different substrate materials on the properties of the conducting polymer coatings.

1. Introduction

Conducting polymer (CP) actuators are becoming of great interest for many applications including robotics [1,2], micro pumps, and valves [3,4] due to their low driving voltages [5], biocompatible characteristics [6,7] and micro fabrication potential [8,9]. Extensive research has been dedicated to the bending form of CP actuators in tri-layer or bi-layer design [10,11]. Nevertheless, for obtaining muscle-like behavior or for easier controllability, linear length change would be much more desirable than bending for robotic devices. Linear actuators can be fabricated from free-standing conducting polymer films with high actuation strains [12]. The obtainable strain depends upon the polymerization conditions [13] and choice of the electrolyte [14]. Unfortunately, the removed-from-electrode free-standing actuators are inherently asymmetric, as the outer and inner layers have different structure and electroactivity, leading to creep. Thin films have been typically used to ensure fast response, unfortunately such films are difficult to handle and fragile. Linear CP films are difficult to arrange in lamellar designs, therefore, several attempts have been made in recent years to obtain fiber actuators [15] or chemically oxidized CP in flexible interpenetrated network (IPN) matrix of polyethylene oxide and polybutadiene to obtain linear actuation properties [16]. An obvious drawback of this approach is the decreased strain caused by inclusion of the more restrained passive material; however, the passive layers also provide support and rigidity.

The goal of this work is to try the opposite approach—to obtain linear actuation starting from a tri-layer actuator design with a stretchable yet supporting middle layer. To allow evaluation of the proposed design, a commercially available polyvinylidene fluoride (PVdF) membrane and a custom made chitosan film were chosen as model materials due to their remarkable differences in structural, chemical, and physical properties. Several reports of using chitosan in combination with carbon nanotubes and conducting polymers have been published [17–19]; however, the focus has been on bending actuators. On these two substrates, a thin layer of poly(3,4-ethylenedioxythiophene) (PEDOT) was deposited by oxidative chemical polymerization to provide sufficient conductivity for the following electrochemical deposition of working material—polypyrrole (PPy). The approach of combined chemical–electrochemical synthesis has been recently developed utilizing oxidants such as ammonium persulfate (APS) or iron trichloride ($FeCl_3$) to allow the deposition of the main electrochemical CP on non-conductive materials [20,21]. To obtain conductive coating on the non-porous chitosan film, a new method has been developed in this work. The resulting electrodes were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and cyclic voltammetry. On top of the chemically coated substrate, PPy doped with dodecylbenzenesulfonate (PPy/DBS) was then electrodeposited. For bending tri-layer functionality,

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electronic separation of both electrode layers is essential, but in order to obtain linear actuation, the CP layers on either side are connected to form a single working electrode. The electro–chemo–mechanical deformation (ECMD) response of the tri-layer linear actuators based on PVdF (PPy-PEDOT-PVdF-PEDOT-PPy) and chitosan (PPy-PEDOT-chitosan-PEDOT-PPy) was investigated by electrochemical methods (cyclic voltammetry, square wave potentials) in 4-methyl-1,3-dioxolan-2-one (propylene carbonate, PC) solution of tetrabutylammonium trifluoromethanesulfonate ($TBACF_3SO_3$).

2. Experimental

2.1. Materials

Sodium dodecylbenzenesulfonate (NaDBS, 99%), chitosan (medium molecular weight, 75–85% deacetylated), 3,4-ethylenedioxythiophene (EDOT, 97%), PC (99%), acetic acid (97%), $TBACF_3SO_3$ (99%), $FeCl_3$ (97%), sodium hydroxide (NaOH, 99%), and ethan-1,2-diol (monoethylene glycol, MEG, 97%) were obtained from Sigma–Aldrich and used as supplied. MilliQ + water was used. Pyrrole (Py, 99%, Sigma–Aldrich) was distilled and stored under nitrogen at −20 °C prior to use. Commercial Durapore (Millipore) PVdF membranes (thickness 110 μm, hydrophilic, porosity 70%, pore size 0.1 μm) were used for PVdF-based samples.

2.2. Chemical synthesis

Chitosan polymer powder (2 wt.%) was dissolved in 2% acetic acid aqueous solution, poured into mold, dried in air followed by soaking in 0.2 M NaOH and drying in the oven at 60 °C overnight to obtain a film with thickness of approximately 110 μm. The oxidant solution (0.2 M $FeCl_3$ in PC) was heated to 60 °C. PVdF and chitosan were soaked in EDOT monomer solution in PC (with 4 vol.% water) and then dipped in the oxidant solution for 1 min. The resulting PEDOT-coated PVdF and chitosan were washed in methanol to remove excess monomer, oxidant, and loosely bound remains of PEDOT. The coated membranes were finally dried in a vacuum oven (2 mbar, 60 °C) for 4 h.

2.3. PPy/DBS electropolymerization

PPy/DBS was deposited galvanostatically ($0.1\,mA\,cm^{-2}$) on the above-described PEDOT-PVdF-PEDOT (Sample A) and PEDOT-chitosan-PEDOT (Sample B) working electrodes (surface area $2\,cm^2$) in a three electrode cell (with stainless steel sheet counter electrode and Ag/AgCl wire as the reference electrode), controlled by CH Instruments Inc. electrochemical workstation (model CHI440) from 0.2 M Py and 0.2 M NaDBS solution in mix of water and MEG (50:50 vol.%). The polymerization temperature was held constant at −18 °C. The electropolymerization was stopped after 40,000 s (11.1 h).

2.4. Electrochemical and ECMD measurements

Samples A and B were cut into 3 mm × 10 mm strips. 611A Dynamic Muscle Analysis Aurora Scientific Inc. was used for linear actuation measurements. The samples were immersed in an electrolyte solution and fixed to a polyvinyl chloride holder with a stainless steel sheet as the contact at the bottom end. The length of the films for actuation testing between the clamps was 1 mm. Each sample was preloaded for 2 h before the ECMD measurements with a constant force of 20.3 mN. The samples formed the working electrodes in a three-electrode setup (using Pt sheet counter electrode and Ag/AgCl (3 M KCl) reference electrode). The actuation measurements and the electrochemical characterization of the chemically coated substrates were performed in 0.1 M $TBACF_3SO_3$ in PC electrolyte during cyclic voltammetry (±1.0 V, scan rates 5, 10 and $50\,mV\,s^{-1}$) and square wave potentials (±1.0 V, frequency 0.1 Hz) using a CH Instruments electrochemical workstation (model CHI650C).

2.5. Scanning electron microscopy, Raman spectroscopy, FTIR, and sheet resistance

Scanning electron microscopy (SEM) micrographs of the chemically and electrochemically deposited CP layers were obtained using a CM-Instrument JCM-6000. The quality of the chemically synthesized PEDOT coatings on PVdF and chitosan was examined by Raman spectroscopy (Renishaw System 1000 microprobe, 785 nm excitation line obtained by Renishaw solid state diode red laser) and FTIR spectroscopy ($4000–600\,cm^{-1}$, Bruker Alpha with Platinum ATR). The sheet resistances of the dry Sample A and B as well as the chemically synthesized conductive PEDOT coatings on chitosan and PVdF were measured with a conductivity meter (LT Lutron, DM-9020) at several different locations of each film surface and the mean values with standard deviation were obtained.

3. Results and discussion

3.1. Conductive PEDOT coatings on PVdF and chitosan substrates

A metal-free approach was chosen for creating conductive coatings on the non-conductive PVdF and chitosan substrates. Due to the lower viscosity and higher aqueous solubility of Py monomer, it proved difficult to coat chitosan with Py in necessary amounts for successful polymerization in aqueous oxidant solution. At the same time, longer swelling in pyrrole causes decomposition of chitosan. To assure similar chemical synthesis conditions for both substrates and because of the higher conductivity of PEDOT as compared to PPy [21], EDOT was chosen for the chemical synthesis step. Chitosan depolymerizes in weakly acidic solutions in the presence of oxidants such as $NaNO_2$, APS or $FeCl_3$ [22,23], forming composites with CPs [24], the effect was observed in present chitosan films due to some residue of acetic acid left in the film after drying. To avoid the depolymerization reaction in aqueous solution, PC solution of $FeCl_3$ was used. In case of PEDOT on PVdF, it has been found that the formation of PEDOT partially inside of the pores of the substrate is necessary for obtaining sufficient adhesion [21]. Sheet resistances of the chemical coatings on PVdF and chitosan surfaces were found to be $4.0 \pm 0.6\,k\Omega/sq$ and $165 \pm 15\,k\Omega/sq$, respectively. As the adhesion of PEDOT on the non-porous and flat chitosan surface was as strong as that on PVdF, it is obvious that the adhesion mechanism must be different for the two. FTIR was used to try to understand the phenomena, the spectra of PEDOT coatings on PVdF and chitosan substrates are presented in Fig. 1.

Some characteristic FTIR spectrum peaks of PVdF (Fig. 1) are found at $1409\,cm^{-1}$ (β-phase CH_2 wagging deformation [25]), $1070\,cm^{-1}$ (α-phase CH_2 wagging deformation [25]), $877\,cm^{-1}$ (γ-phase CF_2 symmetric stretching [25]), 765 and $613\,cm^{-1}$ (α-phase CF_2 bending and skeletal bending [26]). Chemically polymerized PEDOT shows vibrations at $1507\,cm^{-1}$ (C=C stretching in doped polymer backbone [27]), $1084\,cm^{-1}$ (stretching modes of the ethylenedioxy group, 960, 835, and $691\,cm^{-1}$ of PEDOT are attributed to the C—S vibration modes in the thiophene ring [28]. The PEDOT and PVdF signals can be found (with minor shifts) in the PVdF-PEDOT spectrum, confirming deposition of a thin (transparent) PEDOT layer on PVdF membranes. In case of chitosan (Fig. 1), one could observe the N—H stretching at $3301\,cm^{-1}$; a characteristic double peak referring to chitosan-NHAc (acetyl) units consists of C=O stretching at $1651\,cm^{-1}$ and N—H bending at $1559\,cm^{-1}$;