Soft Linear Electroactive Polymer Actuators based on Polypyrrole

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ABSTRACT

There is a growing demand for human-friendly robots that can interact and work closely with humans. Such robots need to be compliant, lightweight and equipped with silent and soft actuators. Electroactive polymers such as conducting polymers (CPs) are “smart” materials that deform in response to electrical stimulation and are often addressed as artificial muscles due to their functional similarity with natural muscles. They offer unique possibilities and are perfect candidates for such actuators since they are lightweight, silent, and driven at low voltages. Most CP actuators are fabricated using electrochemical oxidative synthesis. We have developed new CP based fibres employing both vapour phase and liquid phase electrochemical synthesis. We will present the fabrication and characterisation of these fibres as well as their performance as linear actuators.

Keywords: Conducting polymers; Polypyrrole; Poly (3,4-ethylenedioxythiophene), Fibre-actuators; Chemical synthesis; Vapour phase polymerization, Electrochemical deposition.

1. INTRODUCTION

There is a growing demand for human-friendly robots that can interact and work closely with humans. Robots, and also exoskeletons and prosthetics, have come a long way during the last decades due to technological advances in material science, microelectronics, and systems control. Several semi-autonomous walking humanoid robots have been created, such as the famous Honda ASIMO and HRP-4[1, 2], that are envisioned as General Purpose Robotic Co-workers, for instance to play a major role in taking care of the aging population. Exoskeletons that either enhance human performance or aid (or even restore) disabled people to walk and carry out everyday tasks are becoming commercially available (Ekso Bionics' Suit)[3]. Additionally, prosthetics, such as artificial hands (iLimp from Touch Bionics Inc.)[4] or arms (DEKA Research)[5], have become more complex and mimic lost functions rather well. However, these devices are driven by electric motors or pneumatic actuators making them noisy, heavy, stiff and non-compliant. Conducting polymers (CPs) deliver high stresses, typically more than 5 MPa, exceeding that of mammalian skeletal muscles that deliver stresses of 0.35MPa[6, 7]. The delivered strains of CPs at a small load are moderate, typically 1-10% compared to ~20% strain of natural muscles, although strains up to 35% have been demonstrated for a few cycles[8]. CPs offer unique possibilities and are perfect candidates for soft actuators since they are lightweight, silent, and driven at low voltages. The actuating principle of CPs resembles that of natural muscles, being electrically controlled, wet, and soft. CPs undergo a volume change upon electrochemical oxidation or reduction by applying a low potential of 1-2 V. The volume change is predominantly caused by the insertion or ejection of ions and solvent into the polymer matrix[9] (Figure.1). Since the volume change is based on ion and solvent motion, the CP actuators need an ion source/sink to operate. This may be a salt solution or an ionic liquid embedded in a polymer matrix that allows operation in normal atmosphere and also results in a major increase in cycle life time [10, 11]. Moreover, CPs are known to be biocompatible, making these actuators well suited for applications within cell biology and medical devices, such as steerable catheters [12-14].

Figure 1. Scheme of electrochemical oxidation and reduction of polypyrrole

In most cases, an electrochemical synthesis route is the preferred method to synthesize CPs for actuator applications. It has the advantage of producing the material directly on an electrode facilitating further analysis, and hence eliminating processability problems. Moreover, the electrochemical route has the advantage to allow a good control of the polymer thickness, morphology and degree of the polymer doping by controlling the synthesis parameters such as the quantity of charge passed during the deposition process. However, therein also lies a problem: the substrate has to be electrically conductive. When the substrate is electrically non-conductive, the deposition of metallic electrode layers for electrochemical synthesis of CPs is required. In addition, metal electrodes are often troubled by the delamination phenomena at the metal/polymer interface[15, 16] and/or increase in stiffness[17]. Here, novel, linear CP fibre-actuators that are electrically conductive and electrochemomechanically switchable, based on soft fibres are presented. The methodology for the preparation of the metal-free fibre-actuators is based on a two-step chemical-electrochemical combined CPs synthesis[18]. First a chemically synthesized PEDOT “seed-layer” is deposited to form an electrically conductive electrode surface, allowing the following electrochemical deposition of the main, actuating polypyrrole (PPy) layer (Figure 2). To achieve a uniform coating of the PEDOT seed-layer, vapour phase polymerization (VPP) of poly (3,4-ethylenedioxythiophene) doped with tosylate (PEDOT: Tos) was employed. There is much interest in the VPP method because it provides high control over CP film thickness, uniformity and density. Moreover, it has been shown that VPP PEDOT, as a softer material with a higher conductivity, can reduce IR losses along the actuator ensuring a highly electroactive electrochemical CP layer with a homogeneous distribution throughout the actuator.

2. EXPERIMENTAL DETAILS

Materials

Pyrrole (Py, Sigma-Aldrich) and 3,4-ethylenedioxythiophene (EDOT, H C Starck) were freshly distilled at reduced pressure and stored in the dark under inert atmosphere at low temperature. Sodium dodecylbenzenesulfonate (NaDBS) was received from TCI Europe (Purity > 95%). Fe (III) tosylate was received from HC Stark as a 55 wt. % CB55 solution in n-butanol. A Lyocell™ cellulose based fibre was used for the fabrication of actuator.

Preparation of fibre-actuators

The methodology for the preparation of actuator is based on a two-step PEDOT-PPy chemical-electrochemical synthesis. The chemically synthesized first PEDOT seed-layer forms a conductive electrode surface, allowing the following controllable electrochemical deposition of the main thick PPy layer.

Oxidative vapour-phase polymerization of EDOT. VPP PEDOT was carried out in a vacuum single-chamber set-up as shown in Figure 2. The soft fibre was initially coated with the oxidant ferric tosylate in n-butanol. The coated fibre was then transferred to the polymerization chamber containing Petri dish with 100 μ l of freshly distilled EDOT and maintained at 40°C for 30 min. Thereafter the coated fibre was taken out, thoroughly washed with methanol and dried at room temperature/1 mm Hg for 2 h.

Electrochemical synthesis of PPy. Electrochemical synthesis of electroactive PPy on the chemically synthesized PEDOT was carried out in the three electrode configuration containing pyrrole (0.1 M) as a monomer and NaDBS (0.1 M) as a dopant dissolved in MilliQ filtered water (18.2 M Ω) (Figure 2). The chemically coated fibre was used as working electrode, gold coated polyethylene (PET) substrate was selected as counter electrode and a KCl saturated Ag/AgCl as reference electrode. Chronoamperometric synthesis route at constant potential (0,7 V) was employed to generate the PPy using an Ivium Compacte potentiostat.

Figure 2. Design and fabrication schematic of CP fibre. 1. EDOT vapour phase polymerization 2. Electrochemical deposition of PPy

Electromechanical characterisation

Electromechanical characterisations of the fibre-actuators were performed using a three-electrode system consisting of a KCl saturated Ag/AgCl reference electrode, a gold coated PET substrate counter electrode. A 0.1 M NaDBS aqueous solution was employed as electrolyte. Diametrical strain measurements of the fibre-actuators was recorded by Mitutoyo LSM-501H contactless Laser Scan Micrometer (LSM), controlled by a display unit (Mitutoyo LSM-6100) and the output signal was fed to the potentiostat, see Figure 3A. The diametrical strain set-up and measurement procedures are described in more detail in [19, 20]. The generated force of the CPs fibre-actuator sample was measured with a Dual Mode Lever System 300B (Aurora Scientific), see Figure 3B. Similar to diametrical strain measurements, the sample was activated using a three-electrode system. The potential was scanned between 0.3 V and -1 V to drive the sample between the oxidized and reduced states.

Figure 3: Illustration of experimental set-up for (A) diametrical strain measurement with a laser scanning micrometer (LSM) and (B) for electrochemical force output measurements of CPs fibre-actuators

3. RESULTS AND DISCUSSION

CP fibre-actuators

The CP fibre-actuator synthesis and their electromechanical actuation mode are respectively illustrated in Figure 2 and Figure 3. Actuators were prepared according to the new two-step chemical-electrochemical CP synthesis. Typically, the commercially available Baytron C solution of Fe (Tos)₃ (40 wt% in butanol) was applied to the 400µm thick Lyocell fibre. The coated fibre was then placed in a gas-phase polymerization chamber together with 100 µl of EDOT monomer liquid. The polymerization chamber was then sealed and evacuated to 1 mPa at 40°C in order to accelerate the VPP process. Next, in order to obtain good-quality actuating PPy layer, electropolymerization was carried out chronoamperometrically in a three-electrode electrochemical cell at a constant potential 0.7 V. Using the chemically synthesized PEDOT seed-layer as the anode, this synthetic pathway ensures metal-free CP fibres. On the basis of the Lyocell fibre geometry, the electrodeposited fibres demonstrate the ability to act as linear actuator during the electromechanical actuation. Figure 4.A shows an uncoated and Figure 4.B the coated Lyocell fibre, clearly demonstrating the regular and uniform deposited conducting polymer. Indeed, as can be seen even the small cellulose microfibrils that comprise the fibre are coated with a uniform black PPy film. The fibre surface morphology was found to be an important parameter as the coated fibre will be used in electromechanical applications. The average electronic resistivity of the conducting fibre is 126 Ω.cm which is relatively high and sufficient for an actuator implementation.

Figure 4. Optical microscope images of (A) uncoated and (B) the coated Lyocell fibre

Characterization

The diametrical response of these CP fibre-actuator was observed using the laser scanning micrometer. By measuring the charge induced swelling, we observed that the fibre-actuator radial expansion occurred during the cathodic wave indicating that the cation motion (including solvent) is the main driving mechanism in these actuators. The curves in Figure 5.A shows a typical time response under rectangular wave of applied voltage at 0.3 to -1 V versus Ag/AgCl for a period of 200 s. The actuators showed the large perpendicular diameter change of 23 µm. To allow the comparison with other CP actuator materials, diametrical strain was calculated according to equation 1.

$$\varepsilon = \frac{\Delta L}{L} \quad (1)$$

Where ε is the diametrical strain, L the diameter of the CP-fibre actuator, and ΔL the measured diameter change. The calculated diametrical strain is ~ 6 %. This value is slightly inferior to those described previously[20]. The lower strain can be explained that the core inactive Lyocell diameter has been included in the calculation. The

PPy growth progresses inside the fibre, making it difficult to accurately define the core diameter for the strain calculations as done previously [19]. The resulting CP fibre-actuators were also characterized in terms of linear force output using a Dual Mode Lever System 300B as shown schematically in Figure 3.B. The curve in Figure 5 B presents the resulted output force as a function of the time under square wave potential varying from 0.3 to -1V versus Ag/AgCl. As can be seen, the CP fibre-actuator shows output force in the range of hundreds of μN . The corresponding stress is $\sim 100 \text{ N/m}^2$ which is less than other values found in the literature[21]. Likewise, analysis of the stress generated by the CP fibre-actuator depends upon the fibre diameter chosen to calculate the cross-sectional area. Indeed, using the total thickness of the CP fibre-actuator instead of the thickness of the PPy, leads to a lower calculated stress value.

Figure 5. (A) Diametrical strain measurements and (B) Force output measurements during charging and discharging of CP fibre-actuators (thickness=430 μm) between 0.3 V and -1 V for 200s.

4. CONCLUSION

We have demonstrated a new method to obtain metal-free fibre-actuators comprising conducting polymers and soft Lyocell based fibres. The CP fibre-actuators were prepared using a two-step PEDOT-PPy chemical vapor phase-electrochemical polymerization. The chemically synthesized PEDOT seed-layer forms an electrically conductive electrode surface, allowing the following well-controllable electrochemical deposition of the main working layer of the conducting polymer material while also ensuring good adhesion between the fibre and the conducting polymers. The CP fibre-actuators have been characterized as linear actuators in terms of diametrical strain and linear force output and have demonstrated strain up to 6% and output forces in the range of hundreds

of μN . Characterisation of the linear electroactive elongation and strain is on-going. This two-step synthesis method result in the first demonstration of novel linear soft actuators employing electroactive polymer fibres. This experiments provides a novel, simple and efficient alternative for novel soft actuators not only for soft robotics but also for instance for exoskeletons and prosthetics.

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