Artificial Muscle Material with Fast Electroactuation under Neutral pH Conditions

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A novel artificial muscle material based on an acrylic acid/acrylamide hydrogel blended with a conductive polypyrrole/carbon black composite was prepared. The material was optimized in terms of its electroactuation response by varying the acrylic acid content, the blending concentration of the conductive composite, and the intensity of the electric field. The artificial muscle material showed a fast and reversible electroactuation when a low potential was applied. Further, the artificial muscle was incorporated into a microfabricated pumping device that exhibited reproducible flow rates, thus demonstrating its potential usefulness in bio-micro-electro−mechanical systems (BioMEMS) applications.

Introduction

Electroactuated polymeric hydrogels are attractive materials that may find a broad range of applications such as for microactuators in bio-micro-electro-mechanical systems (BioMEMS). To date, however, the practical applications of these hydrogels in vivo remain very limited. The requirements of such an application dictate biocompatibility, fast and reversible actuation at physiological pH, low power consumption, high mechanical integrity, and extended lifetime.[1] A variety of polymeric hydrogels,[2,3] including poly(vinyl alcohol),[4] acrylic acid,[5−7] polyacrylamide,[8] and combinations of the above[9] have been developed that are capable of electroactuation. Although there are a number of polymeric materials with excellent actuating characteristics, they have a number of drawbacks which limit their usefulness in in vivo applications. For example, the materials reported thus far work in nonphysiological pH media (i.e, in acidic[10] or basic[4] solutions), need application of high voltages,[5,7,11,12] or have slow response times.[6,13,14] To that end, we report the development of a novel polymeric hydrogel-based artificial muscle composite that can be electroactuated in a fast (5 s or faster) and reversible manner under neutral pH conditions by application of a low voltage (1 V or less). The new material shows superior performance characteristics and is suitable for a variety of BioMEMS applications, such as electrosensitive soft microvalves, microactuation systems, and micropumps.

Experimental Section

Materials. Acrylic acid, acrylamide, polypyrrole composite with 20% w/w carbon black *N,N′*-methylenebisacrylamide, potassium persulfate, and *N,N,N′,N′*-tetramethylethylenediamine were purchased from Aldrich (Milwaukee, WI) and used as received.

Preparation of Artificial Muscle Composite. The artificial muscle material was prepared by mixing 5 mL of deionized water, the desired weight ratio of acrylic acid and acrylamide based on a total monomer content of 2 g, either 0.02 or 0.04 g of polypyrrole composite with carbon black, 0.15 g of *N,N′*-methylenebisacrylamide, 0.05 g of potassium persulfate, and 0.05 g of *N,N,N′,N′*-tetramethylethylenediamine. After curing at 80 °C, the hydrogels were preconditioned in the 0.15 M NaCl test solution for at least 24 h.

Electroactuation Measurement. Cylindrical samples of the artificial muscle with dimensions of 4 mm diameter and 10 mm long were tested in an electrochemical cell. The hydrogel samples were placed between two platinum electrodes of 12 × 25 mm at a 1-cm distance from each electrode. The Pt electrodes were covered with dialysis membrane, which redirected the flow of any O_2 and H_2 gases generated from water electrolysis away from the material. A BAS 100B/W electrochemical station (Bioanalytical Systems) and a Ag/AgCl reference microelectrode (BAS) were used for the application of the potential. The electroactuation measurements of the artificial muscles were performed in triplicate, $n = 3$. Rectangular micromuscle structures with dimensions of 400 μm wide, 400

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μm thick, and 2500 μm long were also tested in a miniaturized cell, using 3 × 6 mm gold foil electrodes kept at a distance of 5 mm. One end of the micromuscle was immobilized on a glass support using silicone grease as the fixing agent, while the other end was free to move under electroactuation. An inverted microscope and a CCD camera interfaced to a computer were employed to record the electroactuation experiments.

Fluid Release Experiment. A rectangular hydrogel sample of dimensions 2 × 4 mm and 12 mm long was used for the fluid release experiment. One end of the hydrogel was immobilized on a poly(methyl methacrylate) (PMMA) support between two platinum electrodes of 12 × 25 mm at a 2 cm distance. The free end of the muscle was positioned on the surface of a circular PMMA microreservoir of 8.13 mm diameter and 635 μm depth. The reservoir, filled with a colored aqueous solution using red food coloring for ease of visualization and covered with a flexible poly(dimethyl siloxane) membrane, was connected to an empty calibrated microchannel with a cross section of 254 × 254 μm (0.01 × 0.01 in). The whole setup was immersed in a 0.15 M NaCl solution in a transparent glass cell. When electroactuated, the hydrogel bent downward, thus pushing the membrane covering the reservoir, pumping the fluid from the reservoir into the calibrated microchannel. The pressure applied by the artificial muscle on the membrane of the reservoir to observe the minimal fluid release was determined by measuring the force applied by the muscle, as derived from the measurement of the mass change, while performing the experiment on an analytical balance.

Results and Discussion

Effect of Chemical Composition on the Electroactuation Response of the Material. The artificial muscle hydrogel precursor consisted of acrylic acid, acrylamide, and a polypyrrole/carbon black composite (PPy/CB). The cylindrical hydrogel sample was placed perpendicular to the electric field and showed parabolic-shape bending toward the cathode when a 3 V potential was applied for 2 min (Figure 1). Once the applied potential was interrupted, the bent muscle relaxed to the initial state. When the polarity of the electrodes was reversed, the muscle bent in the opposite direction, demonstrating reversible electroactuation. The bending angle of the artificial muscle was dependent on the chemical composition of the material. It was observed that the higher the acrylic acid content, the higher the bending angle of the hydrogel (Figure 2A). The artificial muscle based on the 65% (w/w) acrylic acid composition presented a bending angle of 15.0 ± 0.2° (n = 3) when 3 V were applied for 2 min. It was observed that further increase in the acrylic acid content results in an increase of the hydrogel response (i.e., larger bending angles) at the expense of the mechanical stability of the muscle (data not shown). Therefore, the composition that contained 65% (w/w) acrylic acid was selected for further studies. An additional parameter that was investigated when optimizing the artificial muscle composition was the incorporation of a conductive polymer such as polypyrrole on carbon black. It was postulated that this additive should increase the ionic conductivity of the hydrogel composite, thus enhancing its electroactuation capabilities. Indeed, Figure 2B shows that the bending angle of the hydrogel containing a 4% (w/w) PPy/CB was higher (23.5 ± 0.6°) than that corresponding to the 1% (w/w) PPy/CB-based material used in Figure 2A (15.0° bending angle). In addition, the hydrogel composed of 4% (w/w) carbon black alone presents a significantly lower response (15.8 ± 0.9° bending angle) than its PPy/CB counterpart. As expected, the response of a control

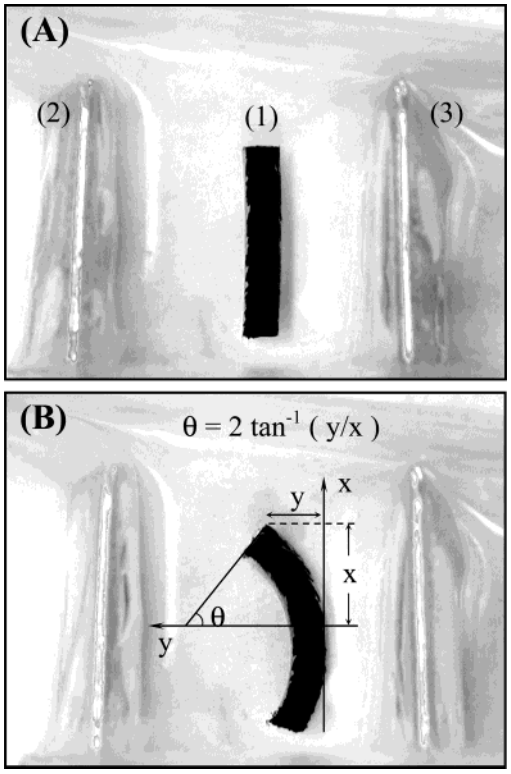

Figure 1. Hydrogel in a 0.15 M NaCl solution under (A) no applied potential and (B) electroactuation by application of 3 V during a time period of 2 min [(1) cylindrical hydrogel sample; (2) Pt counter electrode; and (3) Pt working electrode]. A Ag/AgCl electrode was used as a reference (not shown). The bending angle (θ) of the hydrogel was calculated by determining the position of the end of the hydrogel on the x−y coordinate.

artificial muscle with no PPy/CB or carbon black was smaller (bending angle of 10.3 ± 0.9°), which demonstrates that PPy/CB increased the response of the hydrogel under electroactuation.

Effect of the Electric Field on Electroactuation Response. The effect of the electric field on the electroactuation of the artificial muscle was also examined. The observed bending angle of the optimized muscle placed at a 1 cm from each electrode was 23.5° after 2 min of application of a 3 V potential. Decreasing the distance of the material from each electrode to 0.5 cm resulted in a decrease of the response time of the hydrogel to 30 s and an increase of the bending angle to 28°. In contrast, an increase in the distance of the hydrogel muscle from each electrode to 2 cm worsened significantly the hydrogel response; the bending angle observed was only 2° after 3 V was applied for 2 min. The effect of the electrolyte concentration on the artificial muscle response was also investigated. The hydrogel did not respond when the electrolyte concentration was decreased by 4 orders of magnitude from 0.15 M to 1.5 × 10^{-5} M NaCl. Finally, lowering the voltage from 3 to 1 V resulted in an increase of the response time of the muscle from 2 to 15 min.

Artificial Muscle Electroactuation Induced by Changes in Osmotic Pressure. It is generally thought that the deformation of a hydrogel under the application of a potential is due to the electrophoretic movement of ions, developing a concentration gradient, and inducing

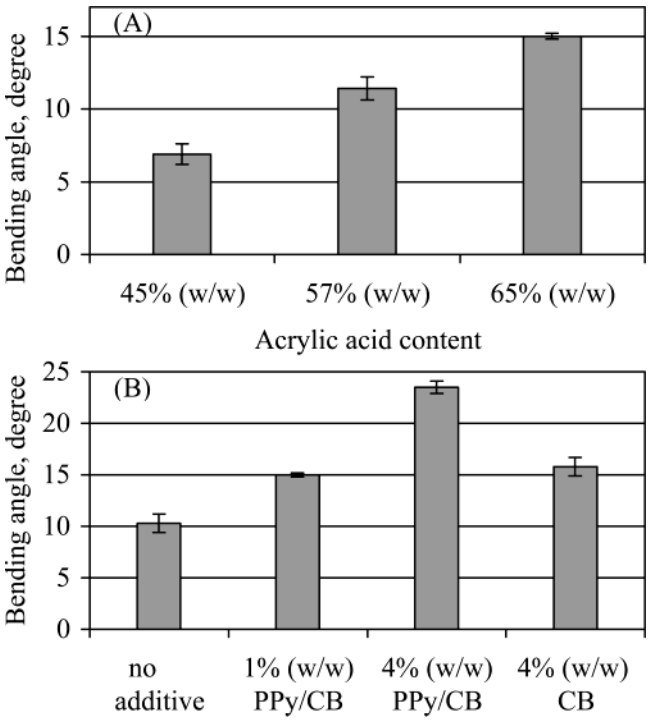

Figure 2. Effect of the content of the chemical constituents (A) acrylic acid and (B) additive [carbon black (CB), polypyrrole/carbon black additive (PPy/CB), or no additive] on the bending angle of the artificial muscle. The muscle was electroactuated by the application of 3 V for 2 min in a 0.15 M NaCl solution. [The hydrogels in part A are based on a 1% (w/w) PPy/CB, the designated amount of acrylic acid, and the corresponding amount of acrylamide up to a total of 90% (w/w) monomer content. The hydrogels in part B are based on a 3:1 acrylic acid to acrylamide weight ratio, and the designated amount of additive. All results represent averages and standard deviations from three measurements.]

changes in osmotic pressure.[15,16] Further, we demonstrate the effect of important parameters, such as that of the intensity of the applied electric field and the chemical composition of the material, on the electroactuation response of the hydrogel. Our experiments were performed in part to evaluate the validity of this mechanism. Indeed, consistent with the proposed mechanism we show for the first time that the addition of the conductive additive polypyrrole/carbon black composite improves the electroactuation response of the material.

Fast Electroactuation of Artificial Micromuscle. To determine whether the artificial muscle material developed here could be employed in a BioMEMS type actuator configuration, the mechanical dynamic characteristics of a miniaturized rectangular micromuscle with dimensions of 400 × 400 × 2500 μm were examined. In one experimental configuration, one end of the micromuscle was fixed on a glass support while the other end was free to move under electroactuation. The applied voltage was cycled between +1 and −1 V (scan rate 200 mV/s) for 12 continuous cycles. Figure 3 shows that the micromuscle bends "in tune" with the applied voltage. The response time, defined as the time to reach

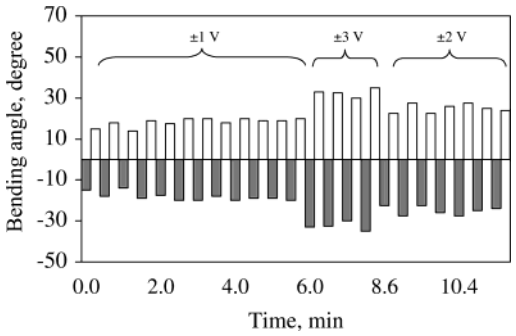

Figure 3. Bending of a micromuscle with a 400 μm × 400 μm cross section as a function of the applied voltage (either ±1, ±3, or ±2 V). The application of negative potentials (darker bars) results in bending of the hydrogel toward the opposite direction (denoted by the negative bending angles) than that when positive potentials (white bars) are applied (denoted by the positive bending angles).

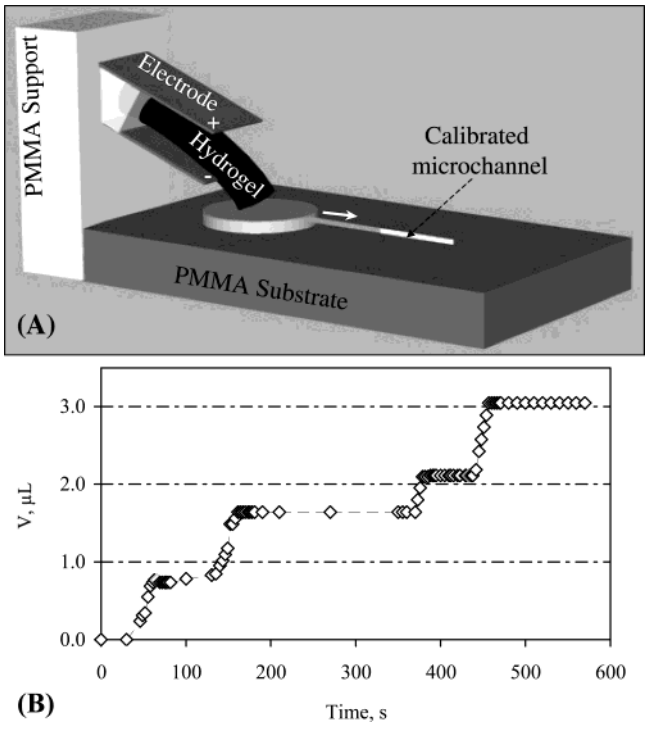

Figure 4. Microfluidic release in a rectangular calibrated microchannel (254 μm × 254 μm cross section) by the electroactuated artificial muscle. (A) Experimental setup showing the hydrogel, the Pt electrodes, and the PMMA support and substrate; the arrow indicates the direction of the flow of fluid in the microchannel when force is applied); the whole setup is immersed in the testing medium of 0.15 M NaCl; (B) Volume of fluid released under electroactuation of the artificial muscle by the application of four discrete pulses of 4 V.

maximum bending upon application of a voltage step, was in all cases less than 5 s. The application of 1 V results in the bending of the hydrogel toward the counter electrode (serving as the cathode) with a bending angle of 18°. The cycling of the potential by the application of −1 V results in the return of the muscle to the initial aligned position and further bending in the opposite direction (toward the working electrode now serving as the cathode), which is denoted by the negative bending angle of −18°. It should be noted that the application of such a low voltage prevents any O_2 or H_2 gas evolution from water electrolysis, ameliorating the suitability of this material for use in BioMEMS applica-

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tions. The application of higher potentials (2 and 3 V) showed an expected improvement in the response of the material, with bending angles of 25° and 32°, respectively. In addition, it was observed that the characteristics (bending angle and response time) of the micromuscle were enhanced when compared to the muscle of the same composition with larger dimensions of 4 × 10 mm (discussed in Figure 2B). Therefore, the characteristics of the composite can be further improved by scaling down the dimensions of the artificial muscle. It should be noted also that the examined micromuscle behaved in a similar manner even after 5 months of storage in the test medium, which demonstrates the high stability of this material.

Application of Artificial Muscle Material for Fluid Pumping. The utilization of the new artificial muscle material in BioMEMS systems was further demonstrated by employing the artificial muscle in the μL-range release of fluid in a calibrated microchannel. The experimental setup used is shown in Figure 4A. The artificial muscle was immersed in the 0.15 M NaCl solution and placed on the surface of a microreservoir covered with a flexible poly(dimethyl siloxane) membrane. Under electroactuation, the bent hydrogel pushes the surface of the membrane covering the reservoir, pumping fluid from the reservoir into the calibrated microchannel. To observe minimal fluid release, the artificial muscle needed to exert a 1.95 Pa pressure on the membrane of the reservoir. Figure 4B demonstrates the volume of the fluid released by the application of four discrete pulses of 4 V. The surface tension of the liquid within the microchannel was such that no fluid leakage was observed when the voltage between pulses was set to zero. Flow rates were calculated from the slopes of the corresponding four segments of the volume vs time plot. The flow rate was reproducible, 2.85 ± 0.23 μL/min with 8% RSD ($n = 4$), and shows the potential applicability of this system as a μL pumping actuator with low power requirements.

Conclusions

A novel artificial muscle material with superior characteristics composed of acrylic acid, acrylamide, and polypyrrole/carbon black composite was prepared. This composite shows fast (response times of 5 s or less) and reversible bending under electroactuation with a low applied voltage (1 V or less) in neutral pH conditions. The artificial muscle presented is a versatile material that can find many applications in the field of BioMEMS.

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