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Poly(Vinyl Alcohol)/Poly(Acrylic Acid) Hydrogel in a dc Electric Field: Swelling, Shape Change, and Actuation Characteristics

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Abstract

Poly(vinyl alcohol) (PVA)/Poly(acrylic acid) (PAA) hydrogel can be utilized as a biomimetic actuator and coating material for tissue-implant interface, when employing an electrical stimulus. The swelling, shape change, and actuation characteristics of PVA/PAA hydrogel in a range of dc electrical fields were determined to find the optimal electric field for the hydrogel application as biomimetic actuator and coating materials. The hydrogel samples were prepared by dissolving PVA and PAA in deionized water at 4 wt% and mixed together at 1:1 ratio. Two custom made experimental setups were fabricated; one used for the measurement of swelling ratio of the hydrogels; and the other used for the shape changes or actuation characteristics of the hydrogels. Swelling experiments show increased swelling ratios of the hydrogel due to 10 V, 20 V, and 30 V electric fields. The rate of increment of the swelling ratio of hydrogel samples under 10V was higher compare to those samples under 20 V and 30 V. The width and height changes of rectangular shapes and maximum deflection along the length of hydrogel sample due to a range of electric fields (0-30V) were measured using an optical microscope. Incremental shape change up to a specific threshold value (around 10V) was observed due to electric stimulus. Electrostatic actuation pressure of hydrogel samples under 10V was higher compare to those samples under 20 V and 30 V. These results suggested that optimal performance of PVA/PAA hydrogel can be achieved around 10V.

Keywords

Poly Vinyl Alcohol; Poly Acrylic Acid; Ionic Hydrogel; Swelling Effect; Shape Effect; Actuation

Introduction

Ionic hydrogel is a copolymer of an N-substituted methacrylamide or acrylamide, a cross-linking heterogeneous agent [Luo *et. al.*, 2007]. This polymer can deform elastically and can have equilibrium water content approximately 80%. Ionic hydrogels demonstrates a discontinuous volumetric change above a specific threshold of an external stimulus such as pH, temperature, ionic strength or concentration of organic solvent. Structural support and controlled shape for the swelling hydrogel can be achieved by such ionic hydrogel. The

volume, shape and deflection changes of the ionic hydrogel can be utilized for the fabrication of micro or nano scale actuation devices, which mimics the conversion of chemical or electrical energy into mechanical energy. Researchers have developed such actuator based on rapid electric field-associated bending deformation of a cross-linked hydrogel of poly(vinyl alcohol) chains entangled with poly(acrylic acid) [Dumitriu, 2001]. PVA/PAA hydrogel is an ionic hydrogel that changes shape when placed under an electrical stimulation [Jabbari *et al.*, 2007].

The tissue-biomaterial interface is the weakest place in the grafted hard-soft tissues interfaces such as bone-cement [Khandaker *et al.*, 2011]. Little research has been conducted on enhancing the integration of hard-soft engineered tissue scaffolds. A strong interface between a biomaterial and the surrounding tissue is integral to an artificial graft's functionality and long-term performance. Presuming this interface can be strengthened, it would have great medical applications. Tissue-biomaterial interfaces made with nano surface roughness and physically stimulated biomaterials may enhance the cell dependent mechanical integration of the interfaces more than those interfaces made with nano smooth and physically non-stimulated biomaterials. It has been found that hydrogels that undergo mechanical deformation enhances osteoblast cellular attachment and proliferation [Toworfe *et al.*, 2010]. Small physical forces can enhance the tissue-biomaterial interface by increasing the chondrocyte densities at the interface of tissue-biomaterial constructs. Lu *et al.* [Lu *et al.*, 2009] investigated a new approach for improving the electrode–neural tissue interface. PVA/PAA hydrogel were used for coatings for poly-(dimethylsiloxane) (PDMS) based neural electrodes with the aid of plasma pretreatment. This study suggested that the hydrogel coating is feasible and favorable to neural electrode applications.

The major goal of our study was to examine whether enhanced tissue-biomaterial interface can be achieved by PVA/PAA hydrogel as a coating material for the implant at the tissue-implant interface. To achieve this goal, the specific aims for this study were: (1) to measure actuation force of the electric stimulus controlled PVA/PAA hydrogel, (2) to determine if the actuation force of the PVA/PAA hydrogel is affected by the swelling and shape characteristics of the hydrogel, and (3) to determine the optimal electric field for the hydrogel application as micro actuator or tissue-implant interface.

Materials and Methods

Specimen Preparation

Polyvinyl alcohol (PVA) and polyacrylic acid (PAA) were purchased from Sigma Aldrich and used without further purification. PVA was 89% hydrolyzed polyvinyl acetate and had a Mw of 146–186 kDa. PAA that contains less than 0.5% benzene having a Mw of 450 kDa and Tg of 106°C. The PVA/PAA hydrogel samples were prepared by dissolving PVA and PAA in deionized water at 4% and mixed together at a 1:1 ratio according to Quintero *et al.* [Quintero *et al.*, 2010]. The hydrogel was dehydrated in a custom made aluminium well plate in VWR iso-temperature oven (Sheldon Manufacturing Inc., Cornelius, OR) at 60°C for at least 24 hours.

Design and Manufacture of the Setup and Instrumentation

Two experiment setups were fabricated in this study, one of which was used for the measurement of swelling of the hydrogel; while the other for the measurement of shape and actuation characteristics of the hydrogel. Each setup used True Energy 9.6V/1600mAh Ni-MH RC car battery (purchased from RadioShack Corp.) for the supply of constant dc voltage. An electronic circuit having linear regulator was created to control the voltage supply. For swelling experiment as shown in Fig. 1, a bath was fabricated using dimension elite 3D printer (Dimension Inc., Eden Prairie, MN). The bath has two slots for platinum plated titanium mesh anode ($1/2'' \times 4''$ size with a $3''$ lug) and cathode ($2'' \times 6''$ size with $3''$ lug) electrodes. The electrodes were purchased from Rolling Thunder Pyro Corp., Rhinelander, WI. The dimension of the bath in the setup is suitable to fit a tissue culture 24 well plate (BD Falcon). Multiple swelling experiments can be conducted using this setup.

For shape characteristics experiments as shown in Fig. 2(a), two bath chambers with common slots for the platinum anode/cathode electro sets were fabricated using dimension elite 3D printer; one for height measurement and the other for width measurement. Each bath has a rectangular slot in the middle to latch a hydrogel holder as shown in Fig. 2 (b). The holder has serrated clamp to secure a rectangular shape hydrogel sample. Nikon SMZ stereomicroscope was used to measure the height and width changes. For actuation characteristics experiments, a plastic sheet that acted as a reference bar was glued with the holder by cyanoacrylate adhesive. The bath was placed on the XY stage for microscopic viewing purpose.

Measurement of Swelling Characteristics

For swelling studies, approximately $20 \text{ mm} \times 20 \text{ mm}$ size hydrogel samples were cut from the dried hydrogel films by a scissor. The samples were placed in at least 100 ml of phosphate buffer solution (PBS) in cell culture flask. The hydrogel was weighed before swelling and then pre-swollen for at least 24 hours. The swelling ratio was calculated by the swelling ratio equation as follows [Kim *et al.*, 2004]:

$$\frac{w_f \times 100\%}{w_i} \quad (1)$$

where w_f is the mass after the electric field and w_i is the initial mass before swelling.

Measurement of Shape Change Characteristics

A rectangular shape fully swallowed hydrogel sample with dimension of $10 \text{ mm} \times 5 \text{ mm}$ was cut out, secured in the specimen holder, and placed in a fabricated bath as shown in Fig. 2(a) at 10 V, 20 V, and 30 V for 2 hours. The dimensions of the height and width were measured every 10 minutes. Nikon SMZ 1000 stereo microscope was used to record the width and height changes in the hydrogel due to the electric field. Since the sample were secured using a clamp at the two ends, therefore, the length stayed constant. The dimension and shape changes of the samples from the recorded video were measured by Nikon NIS element basic research software as shown in Fig. 3 (a) and (b). The deformation ratio (contraction/expansion) of a sample was calculated from the following equation:

$$\text{Deformation ratio (\%)} = \frac{L_t - L_o}{L_o} \times 100 \quad (2)$$

where L_o and L_t are the initial and incremental height/width of the fully swollen sample in the various buffered solutions and length of the sample at a time, t , respectively.

Measurement of Actuation Characteristics

The recorded video from a shape change experiment was used for the measurement of the maximum deflection of the hydrogel membrane. The maximum deflection of hydrogel membrane due to electric field was measured from the nonconductive reference bar as shown in Fig. 4. Electrostatic pressure was measured by Maxwell's equation as follows [Shankar *et al.*, 2009]:

$$\text{Pressure, } P = \varepsilon \varepsilon_0 \left(\frac{v}{t} \right)^2, \quad (3)$$

with ε is the permittivity of medium, ε_0 is the dielectric constant of the hydrogel, v is the applied voltage and t is the thickness of the sample. The values of ε and ε_0 of an ionic hydrogel were assumed from literature [Luo *et al.*, 2007] as $\varepsilon = 80$ and $\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2}$.

Results and Discussion

Swelling Characteristics

Fig. 5 shows the swelling kinetics and time dependent swelling behaviour of the hydrogels in water at 10 V, 20 V, and 30 V. The hydrogels incrementally swelled for all 10 V, 20 V and 30 V electric fields. Although the increase of swelling ratios of all three samples tested under 10 V were higher than those sample under 20 V and 30 V. The swelling ratios of all three samples tested under 30 V were lower than those tested under 20 V. The sample at 10 V exhibited the highest rate of swelling ratio for the time dependent swelling behaviour, while the sample at 30 V exhibited the lowest rate of swelling ratio. The hydrogels also showed distinct voltage dependent swelling behaviour in pure water. The data of swelling ratio and time for all electric fields were fitted by a 3rd degree polynomial function. The polynomial function of swelling ratio versus time under 10 V and 30V electric field intensities was concave, whereas a convex polynomial function was found for the 20 V electric field intensity.

Shape Characteristics

Fig. 6(a) shows the discontinuous changes of heights for the rectangular shape hydrogels measured in a PBS solution in continuous applied electric field ranges from 0-30V values. The constant applied electric field across two the parallel platinum electrodes caused a contraction of the PVA-PAA hydrogels in the buffered solutions at higher voltages. The contraction increased proportionally with the increase of voltage. The contraction of the hydrogels showed a higher width change after 20 V. Fig. 6(b) shows the change of width for rectangular shape hydrogels measured in PBS solution in an applied electric field ranging

from 0-30V values. The constant applied electric field across the two parallel platinum electrodes caused an expansion of the PVA-PAA hydrogels in the buffered solutions at higher voltages. The expansion increased proportionally with the increase of voltage until 10 V. The expansion of the hydrogels showed a gradual decrease after 10 V. The ratio of expansion of width was significantly higher than the ratio of contraction of height. The resultant incremental shape changes occurred due to the increased swelling ratio behavior and ionic motion of the hydrogel at higher voltages. An increase in water absorption on one hand caused large swelling and mechanical instability of the coatings on the sample; on the other hand it enhanced electrical signal transfer across the electrode interface by offering high ionic conductivity near the electrodes [Lu *et. al.*, 2009].

Actuation Characteristics

Fig. 7 (a) shows the variation of maximum displacement under 10 V, 20 V, and 30V electric field intensities versus time. Uniform deformation after a specific threshold time interval (50 to 60 minutes) was observed due to electric stimulus. Results showed that the deflection of hydrogel under 10 V and 20V was higher compared to the deflection of those hydrogel under 30 V. Additionally, the deflection-time functions of hydrogel at 10 V and 20 V were significantly different compared to the deflection-time functions of those hydrogel samples at 30 V. Fig. 7(b) shows the calculated electrostatic actuator pressure versus deflection at the 50th minutes test time for 10 V, 20 V, and 30 V. Results showed that lower electrostatic pressure or internal stress and higher deflection or internal strain is generated in the hydrogel at higher voltages compared to the smaller voltages, when the samples were under a continuous electric field. The result also shows that the applied electric field produces negative stiffness to the hydrogel. This happens because of higher swelling ratios of hydrogel samples at higher voltages. The larger swelling expands the structure of the porous network in the hydrogel that leads to internal deformation.

Conclusions

Couple of experimental set ups were successfully designed and fabricated for determining the swelling ratio, shape change characteristics, and deflection due to electrostatic force. The purpose of characterizing the PVA/PAA hydrogel was to determine whether the volume change of the PVA/PAA hydrogel can be utilized as coating material for tissue-implant interface and to determine the optimum voltage for the application. The graphs show that with an increase of voltage, there is an increase in swelling and volume change. The increasing trend of swelling and volume of the hydrogel leads to higher deflection. The deflection of the hydrogel showed a decrease of electrostatic pressure with an increase in voltage. The PVA/PAA hydrogel generates incremental deflection with reduced internal stress due to the electrical stimulus. Further application of the PVA/PAA hydrogel for tissue-implant interface is currently undergoing.

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Fig. 1.
Experimental setup for swelling tests.

Fig. 2.
Experimental setup for shape change and actuation tests.

Fig. 3.
Microscopic image of dimensions of a pvp/paa sample: (a) height and (b) width

Fig 4.
Microscopic image for the measurement of maximum bending displacement of a pvp-paa sample from a reference bar.

Fig. 5.

The variation of swelling ratio under (a) 10 v, (b) 20v, and (c) 30v electric fields intensities versus time. A 3rd degree of polynomial function was fitted to the each set of data to show the variation.

Fig. 6. The variation of dimension changes of (a) height and (b) width from 0 to 30 v electric field intensities. A 3rd degree of polynomial function was fitted to the each set of data to show the variation.

Fig. 7.

(a) The variation of maximum displacement under 10 v, 20 v, and 30 v electric field intensities versus time. A 2nd degree of polynomial function was fitted to the data to show the variation. (b) The variation of electrostatic pressure versus maximum displacement calculated at the 50th minute of the experiment from a pvp-paa sample. A linear function was fitted to the data to show the variation.