Electromechanical nonionic gels

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New Journal of Physics 10 (2008) 023016 (9pp)
Received 1 October 2007
Published 13 February 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/2/023016

Abstract. The electrically induced bending of nonionic polyvinyl alcohol gels, bending over 90° within 100 ms, is the fastest motion in the field of electroactuation of polymers. This rapid bending produces initial mechanical vibrations followed by a durable displacement that contrasts highly with the relaxation observed with elastomer- and polyelectrolyte-based actuators. Here, we characterize the bending process using video imaging and laser detecting technology and establish a physical model for the electromechanical conversion, based on our observation of an induced solvent migration. Our results show excellent agreement between the measurements and calculations. This study provides general rules for understanding the electrically induced bending of isotropic dielectrics and may also shed light on nonmuscular biological engines.

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1. Introduction

Electroactive polymers are known for their ability to convert electricity into mechanical energy and have been exploited for various applications. A number of polymers classified as isotropic elastomers [1, 2], polyelectrolytes [3, 4], conducting polymers [5] and nonionic gels [6] have been electrically induced to bend into a similar mechanical deformation. However, their performance, together with their driving conditions, varies noticeably, depending heavily on the electrical properties of the materials.

Interpreting the stresses and strains induced in isotropic materials by electrostatic fields is technically difficult and often improper, as pointed out by Krakovsky et al [7]. This becomes even more complicated as the electroactive materials are wetted with aqueous solutions [8] or embedded with salt additives [9]. In Maxwell’s theory, a space charge distribution that reflects in a distorted electric field in the materials is required to produce distorted stresses and strains for bending deformation. The space charge can be induced by an electric field in a number of ways, including corona discharge and ion dissociation. On the other hand, such physical events as solvent diffusion can also significantly contribute to the induced stresses and strains [8]. It is not surprising that most of the reported studies of the electroactuation of polymers were carried out qualitatively rather than quantitatively.

Nonionic gels, consisting of a fixed nonionic polymer network and a mobile dielectric solvent, have shown an ability for electroactuation [6, 10]. In particular, polyvinyl alcohol dimethylsulfoxide (PVA/DMSO) gels with low polymer concentrations (<3%, w/w) have demonstrated their outstanding performance—a large bending of over 90° can be induced/restored in a fraction of a second by the application/removal of an electric field, and during the application of an electric field the induced deformation can remain steady [6]. This performance was in sharp contrast to that of other types of electroactive polymers [3, 8], providing exclusive information for understanding the electromechanical conversion. Dielectric solvent has been suggested to play a key role in the electroactuation of the gels; however, the real mechanism still remains unclear [11].

In this paper, we will characterize the electrically induced bending deformation of the PVA/DMSO gels and build a simple physical model based on the electrical properties of dielectric solvents. Finally, we will also evaluate the proposed model against the experimental measurements.

2. Materials and methods

PVA/DMSO gels, prepared as previously reported [6], were cut into strips whose dimensions were approximately 20 × 8 × 1.5 mm³. The set-up for the experiment included the following steps. First, a gel sample was sandwiched between a pair of parallel rectangular platinum plates roughly half the length of the sample; this was done gently to avoid causing significant mechanical deformation. Then, both sides of the exposed portion of the gel were fully covered with gold sheets of 0.1 µm in thickness, which were used as the compliant electrodes and laser reflectors; these were assumed to store negligible elastic energy during mechanical deformation. Next, a dc power supply was connected to the platinum plates to conduct electricity to the compliant electrodes by physical attachment. Finally, the gel was rotated about a position with the sample standing vertically on its side edge so as to minimize gravitational influence on the deformation.
Mechanical deformation was measured either by using a CCD-camera-equipped microscope at low magnification or by using laser distance-detecting technology [11]. Analyses were carried out on personal computers running conventional software.

3. Results

Figure 1(a) is a schematic illustration of the gel samples used in the experiments, where the arrow refers to a primary solvent flow induced running towards the cathode [11]. The effective dimensions of the gel were measured carefully with calipers. Figure 1(b) shows a typical image of the electrically induced bending deformation, where the gel was chemically crosslinked for 80 min and 800 V was applied. The grid squares in the picture are 1 mm² in area. The bending process was video-recorded at the rate of 30 frames per second, and the image shown is the third frame from the very beginning of the bending deformation. In other words, it took 60 ms for the gel to bend more than 90°. The bending direction indicates that the gel was subjected to more stresses on the cathode side than on the anode side, and the formed arc shape implies that an electric field was applied uniformly through the length of the gel.

A detailed measurement of the induced bending at relatively low voltages was carried out by using laser detecting technology, illustrated in figure 2(a), where the parameters \( r, h, \) and \( s \) are geometrically related, as described in section 4. It should be mentioned here that any displacement bending towards the incoming laser beam will appear in the measurement as positive and otherwise as negative. The conducting current was also synchronously collected as a reference to the application of an electric field.

Figure 2(b) reveals the time course of the induced displacement and the conducting current at a series of applied voltages. The voltage was pulsed on for about 15 s and then off for 15 s by turning the power on and off; its magnitude was increased from 100 to 600 V in 100 V increments. As shown in the plot, both the detected mechanical displacement and conducting current show sharp responses to all the applied square-wave voltages except 100 V. On one hand, the induced displacements showed slight increases with time, except at the ends of the pulses, where abrupt peaks were observed. We attribute this increasing trend to the baseline
slightly shifting upward. Overall, the induced displacements over time seemed to increase quadratically as the applied voltage increased. On the other hand, the conducting currents varied in pattern from the displacements measured, showing significant decay during the application of an electric field. This is partially attributed to the impurities existing in the gel. On average, the current over time seems to increase linearly with the increase of the applied voltage.

The inset of figure 2(b), which presents an enlarged view of the plot at an applied voltage of 400 V, reveals the details of the electroactuation. The induced displacements were divided into four consecutive portions: (i) a sudden shrinkage that appears negative, (ii) a rapid bending defined as between the bottom and the first peak, (iii) a harmonic vibration that damps within about 1 s, and (iv) a final steady bending displacement. We attribute the sudden contraction to the electrostatic attraction between the two electrodes, due to the fact that it happens before the conducting current reaches a plateau; we attribute the harmonic vibration to the rapid bending motion and good elasticity of the gel. If we here define the response time for the electroactuation as the time between the lowest and highest points of the detected deformation, it is of the order of 100 ms at a time resolution of 10 ms.

Induced vibrations were consistently observed as the electric field was suddenly turned on or off. Our preliminary analysis found that the vibrating frequencies were identical regardless of the triggering conditions. This implies that the gel behaves mechanically as a perfect elastic body oscillating at its own resonant frequency. The elastic properties of highly swollen PVA/DMSO gels were also confirmed previously in stress–strain experiments.

With the known resonant frequency \((f)\), the bending Young’s modulus \((Y)\) of a gel can then be simply estimated from the classic formula \([12]\),

\[
Y = \frac{48\pi^2 l^2 f^2 \rho'}{\lambda^4 d^2},
\]  

\(1\)
Table 1. Measured moduli of PVA/DMSO gels

| Sample | Crosslinking time (min) | Polymer content (%) | Bending modulus (N m$^{-2}$) |
|--------|------------------------|---------------------|-----------------------------|
| Gel (1) | 60                     | 1.3                 | 980                         |
| Gel (2) | 80                     | 2.0                 | 2940                        |
| Gel (3) | 100                    | 2.7                 | 7970                        |

where $l$ (m) is the effective length of the gel; $d$ (m) is the thickness; $\rho'$ (kg m$^{-3}$) is the density; and $\lambda = 1.859$ for rectangular cantilever beams.

Table 1 presents the measured moduli of PVA/DMSO gels crosslinked for varied times, where the mean value of five measurements is presented and where the standard deviations were estimated to be less than 10%. All gels used here were prepared from an identical precursor gel and measured when they were fully swollen with DMSO. As shown in the table, with the increase of chemical crosslinking time, the obtained gels show an increase in polymer ratio (corresponding to less expansion) and in Young’s modulus.

4. Discussion

The structural stability of a polymer gel is known to be governed by pressures that include the osmotic pressure and other pressures resulting from polymer elasticity, electrostatic interactions and entropy change. Any change in the pressures leads to continuous structural deformation of gels and even an abrupt structural collapse known as a volume phase transition [13]. When a gel is subjected to the influence of an external electric field, the electro-osmotic pressure should be taken into account.

It is known that corona discharge from electrodes can produce unipolar charges and generate mechanical forces in dielectric solvents [14, 15]. Between two ideal parallel plate electrodes filled with dielectric solvent, the spatial electric field $E(x)$ was approximately given in the 1960s by Stuetzer [16]:

$$E(x) = \frac{3}{2} \left( \frac{U - U'}{d} \right) \sqrt{\frac{x}{d}},$$

(2)

where $d$ is the distance between the electrodes; $x$ is the position from the emitting electrode surface; $U$ is the voltage applied; and $U'$ is a parameter originally designed for improving the approximation and appearing here as a cut-off voltage.

Since the nonionic PVA/DMSO gels used in our experiments contain more than 97% (w/w) of the dielectric solvent, equation (2) may be validly applied to the electroactuation of the gels. Thus, under the influence of the electric field, the polymer network of a gel is subjected to the Maxwell stress $\sigma(x) = \varepsilon_0 \varepsilon_r E^2(x)/2$. Combining with equation (2), the equation is then given as

$$\sigma_p(x) = \frac{9\varepsilon_0\varepsilon_r p}{8} \left( \frac{U - U'}{d} \right)^2 \frac{x}{d},$$

(3)

where the subscript ‘p’ represents ‘polymer’ (subscript ‘s’ will represent ‘solvent’, below). This distorted stress $\sigma_p(x)$ contributes directly to the induced bending stresses of the gels.
On the other hand, the dielectric solvent is also subjected to the ‘Maxwell stress,’ which is given in a similar form:

$$\sigma_s(x) = \frac{9\varepsilon_0\varepsilon_r}{8} \left( \frac{U - U'}{d} \right)^2 \frac{x}{d}. \quad (4)$$

For this stress $\sigma_s(x)$, corresponding to a solvent pressure gradient, which causes the fluid solvent to flow, we here need to know the answer to the following question: can this ‘solvent stress’ simply convert into gel stresses? If yes, how much may it contribute to the total bending stresses of the gel?

To reveal the role of the solvent in electroactuation, we demonstrated here the electroactive behavior of the pure DMSO solvent as well as of a diluted PVA/DMSO solution. Experiments were carried out in a similar configuration as for the gel electroactuation, with a distance of 1.5 mm between a pair of parallel gold-plated electrodes. The capacitor was partially immersed in a solution before an electric field was applied across it.

Figure 3(a) shows an image with an illustration of the pure DMSO solvent rising up between the electrodes at an applied voltage of 400 V. The phenomenon of the solvent rising under the influence of an electric field is known as electrostriction, and the climbing height ($h$) can be predicted by using the formula $h = (\varepsilon_{\text{solvent}} - \varepsilon_{\text{air}})E^2/(2\rho g)$, where $\rho$ is the mass density of the solvent. We verified the validity of the formula for the pure DMSO solvent over a wide range of applied voltages up to 1000 V \cite{11}. This indicates that the DMSO solvent used in our experiments was not changed in its dielectric property by the application of an electric field. Unfortunately, the predicted ‘solvent stress’ in equation (4), which would appear in pressure gradient, was not observed.

When the pure DMSO solvent was replaced with a diluted 0.5% (w/w) PVA/DMSO solution, the situation changed dramatically, as shown in figure 3(b). Apparently, the solution climbed significantly higher on the cathode side than on the anode side, in accordance with the electrically induced bending direction of the gels during electroactuation. This implies that equation (4) might be valid for the presence of polymers in such an experimental arrangement. We speculate that polymers play a key role in increasing the viscosity of the solution, thus reducing possible occurrences of fluid convection and turbulence caused by directional charge movement \cite{11} and, in return, stabilize the space charge distribution that builds up the electric field expressed in equation (2).
Such a ‘solvent stress’ is expected to be more effective in polymer gels than in corresponding solutions, due to polymers in the former having less mobility than in the latter. We introduce here a parameter, \( \eta \), to describe the converting efficiency of the ‘solvent stress’ \( \sigma_s(x) \) into the gel stress \( \sigma^*_s(x) \), and they are linked as

\[
\sigma^*_s(x) = \eta \sigma_s(x)
\]  
(5)

By adding equations (3) to (5), the resultant stresses \( \sigma(x) \), which are responsible for the induced bending deformation of the gels, are obtained:

\[
\sigma(x) = \sigma_p(x) + \sigma^*_s(x) = \frac{9 \varepsilon_0 (\varepsilon_{rp} + \eta \varepsilon_{rs})}{8} \left( \frac{U - U'}{d} \right)^2 \frac{x}{d^2}.
\]  
(6)

Apparently, \( \sigma(x) \) is a linear function of position \( x \) and a quadratic function of the applied voltage \( U \). Such stresses would cause an unconstrained gel to bend into a dome-like shape. In our experiments, gels were clamped between a pair of parallel platinum plates; they could bend freely only in the direction perpendicular to the clamping edges. When the gel is short enough compared with its width, it may be treated as a classic cantilever beam for calculating the bending displacement. It should be mentioned here that the neutral plane of zero stress for the bending gels is located at \( x = 0 \) rather than at \( x = d/2 \) for the classic model.

Thus, the stresses in equation (6) are linked with the geometrical deformation of the gel as

\[
\int_0^d a \sigma(x)x \, dx = \frac{YI}{r},
\]  
(7)

where \( I = a \cdot d^3/12 \), the second moment for a rectangular beam.

Replacing \( \sigma(x) \) with equation (6) and integrating equation (7) yields the final form for the electromechanical conversion of gels, giving

\[
\frac{1}{r} = \frac{9 \varepsilon_0 (\eta \varepsilon_{rs} + \varepsilon_{rp})}{2 E'd} \left( \frac{U - U'}{d} \right)^2.
\]  
(8)

In this formula, \( \eta \) and \( U' \) are the only two uncertain parameters. The bending curvature \( (1/r) \) of gels can be obtained from the measured displacement \( s \) by using the formula (see the geometric relationship in figure 2)

\[
\frac{1}{r} = \frac{2s}{h^2 + \delta^2}.
\]  
(9)

Now, we are able to compare our measurements with equation (8). Figure 4 presents the measured curvatures of the gel, induced at a series of electric field strengths, together with the fitted curves using equation (8). In the fitting, \( \varepsilon_{rp} = 3.5 \) for PVA polymer, \( \varepsilon_{rp} = 40 \) for DMSO solvent, and the gel moduli measured in table 1 were used. As a result, we extrapolated \( \eta = 99.5\% \) and \( U' = -72.2 \) V for the gels crosslinked for 80 min, \( \eta = 80.0\% \) and \( U' = 21.7 \) V for the gels crosslinked for 100 min. As mentioned above, the physical meaning of \( U' \) is ambiguous. The significantly lower \( \eta \) obtained from a longer chemically crosslinking gel (corresponding to a higher polymer ratio) seems to contradict our expectation. We attribute the discrepancy of \( \eta \) to the variation of the molecular interaction between the polymer and solvent in the gels, rather than to the polymer concentration.

Chemical crosslinking could weaken the polymer–solvent interactions by consuming the polar hydroxyl groups on the PVA molecular chains, with which the polar DMSO solvents...
Figure 4. Measured curvatures of the bending gels as a function of the strength of the applied electric field, together with the fitted curves using equation (8).

Figure 5. The DMSO evaporation ratio from PVA/DMSO gel surfaces as a function of time under a vacuum condition of 40 kPa.

strongly interact. This speculation was verified by measuring the solvent activity of the gels crosslinked at varied times. The higher activity of the solvent means a weaker interaction between the polymer and the solvent. Figure 5 shows the DMSO evaporation ratio from the PVA/DMSO gel surfaces in a vacuum chamber of 40 kPa, where all the gels had an identical surface area of $2 \times 2 \text{ cm}^2$. The solvent evaporation ratio is defined as the weight loss of a gel over its initial weight in fully swollen state. The results clearly show that a longer crosslinking time leads to a higher solvent evaporation ratio of the gels. In other words, chemical crosslinking
increases the solvent activity of the gels due to a weakened molecular interaction between the polymer and the solvent.

5. Conclusion

Nonionic polymer gels were electrically actuated in a rapid, durable bending deformation using an electric field of moderate strength. Unipolar free charges induced by an electric field are considered responsible for the rapid bending of the nonionic gels.

Our established model, based on the electrical properties of a dielectric solvent, was experimentally verified, indicating that both the polymer and the solvent contribute to the induced stresses and strains of the nonionic gels and that the performance depends proportionally on the dielectric constants of polymer and solvent. However, molecular interaction between the polymer and the solvent in the gels may affect the performance of electroactuation.

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