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Deformation of ionic polymer gel films in electric fields

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Deformation of ionic polymer gel films in electrolyte solutions was studied under the influence of electric fields. The ionic polymer gel films used were poly(vinyl alcohol)–poly(sodium acrylate) composite gel films with a thickness of the order of submillimetres. The vibration of gel films in a.c. electric fields, has been observed for the first time. It was suggested that the vibration behaviour was based on a differential swelling. The vibration of the ionic gel films was roughly analysed as a mechanical bending of a uniform cantilever beam by sinusoidally varying forces.

1. Introduction

Ionic polymer hydrogels composed of a cross-linked polymer network, having ionizable groups and water swelling or shrinkage were studied in electrolyte solutions by the application of electric fields [1–3]. Such phenomena have recently attracted much attention because of their potential as electrically controlled biomimetic actuators or drug-delivery systems [4, 5]. They are also of scientific interest because they provide an opportunity to study how electric fields affect molecular motions of cross-linked polymer chains.

The electric field–associated volumeric changes are usually anisotropic or differential, and caused by the drift of mobile ions. The differential deformation leads to another deformation, bending, when applied to gel rods placed parallel to electrodes [6]. For instance, poly(sodium acrylate) gel in Na_2CO_3 aqueous solutions swells at the positive electrode side in d.c. electric fields and bends towards the negative one based on a bimetal principle (Fig. 1). The gel rod bends reversibly at a relatively high speed. A slender gel exhibits bending repeatedly under a.c. electric fields of low frequencies [7, 8]. The bending may be shown to be universal to all ionic polymer gels.

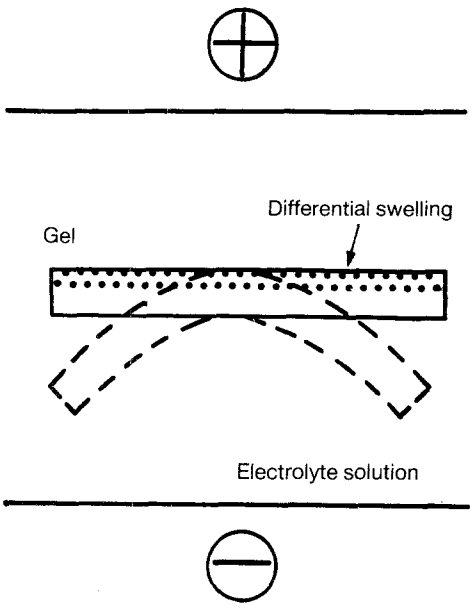

Figure 1 Bending mechanism of poly(sodium acrylate) gel rod induced by d.c. electric fields.

The purpose of this study was to investigate deformation of ionic gel films induced by electric fields. Because a microscopic conformational change of polymer chains near the surface of ionic gel produces macroscopic deflection, electric field-associated deformation behaviour is influenced strongly by the size or shape of the gels. It is expected that gel fibres or films will deform more quickly in electric fields. A new motion, vibration, of ionic gel film is reported for the first time.

2. Experimental procedure

2.1. Sample preparation

The ionic polymer hydrogel used experimentally was poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogel (PVA–PAA gel) prepared by repeatedly freezing and thawing aqueous solutions of PVA and PAA [9]. In a 100 ml beaker, 7.5 g PVA (Kuraray Co., Ltd, POVAL 124H) was dissolved in 50 ml mixed solvent of 30 vol % dimethyl sulphoxide–70 vol % water. The PVA solution was added to 7 g poly(sodium acrylate) (Waco Chemical Industries, Ltd). The mixture was sandwiched between two glass plates and frozen at −50 °C for 3 h. The frozen specimens were warmed slowly to room temperature at a rate of 5 °C h^{-1}. When this freezing and thawing process was performed, the mixture was changed into gel film. The freezing–thawing process was repeated three times to obtain a gel with high elasticity. The PVA–PAA gel consists of physically cross-linked PVA polymer network and linear PAA chains entangled with the PVA network. The water content in the PVA–PAA gel films was 93 wt %. Tensile strength and elongation at break were 0.23 MPa and 145%, respectively. The

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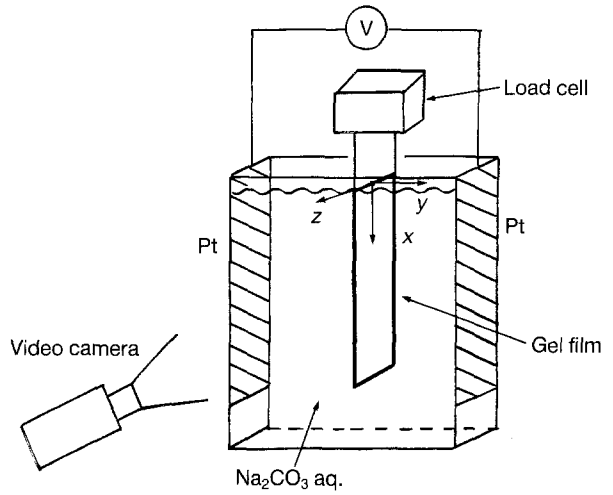

Figure 2 Schematic illustration of the test apparatus for electric field-applying measurements.

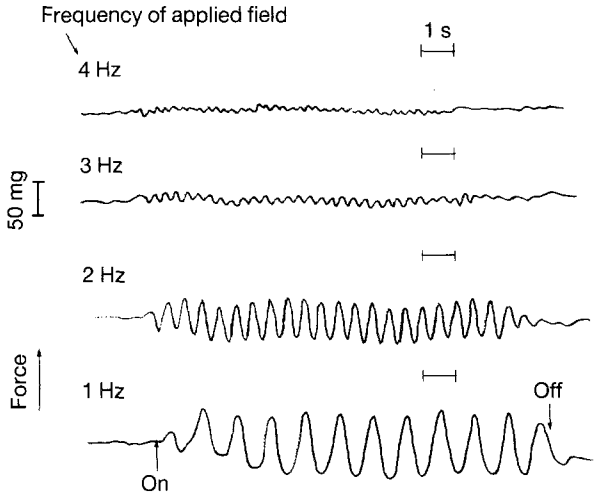

Figure 4 Vibration forces measured by the load cell.

thicknesses of the films were between 0.28 and 1.10 mm.

2.2. Measurement of deformation

Fig. 2 shows a schematic illustration of the test apparatus for electric field-applying measurements. The gel film fixed on a load cell (Orientec Ltd T7-15-240) was hung in 10 mM Na_2CO_3 aqueous solution. The length and width of the PVA–PAA gel film immersed in the solution were 40 and 10 mm, respectively. Then a.c. electric fields with 15 V cm^{-1} of 0.1–20 Hz were applied across the gel between platinum electrodes, with a separation of 6 cm.

3. Results and discussion

3.1. Vibration behaviour

Fig. 3 indicates deflection curves of the PVA–PAA gel film in a.c. electric fields. Like polyelectrolyte gels, the gel film showed a bending–straightening motion when subjected to electric fields of less than 1 Hz. It has, however, begun to wave or vibrate under signals from 2–5 Hz. At higher frequencies, the gel film did not respond to the electric signals. In a 2 Hz signal, two nodes were observed at a point $x = 0$ and at $x = 0.75L$ (L is the length of the film). There are two antinodes with a deflection of 2 mm at $x = 0.52L$ and $x = 1.0L$. The number of the node in the deflection curve increases with the frequency of the applied field. The thickness of the gel film greatly affects how the vibrational motion occurs. It has not been observed in the 1.10 mm thick film. The highest frequency to which the gel film can respond also depended on the thickness of the gel film. The 0.28 mm thick gel film responded to a 12 Hz signal. This indicates that the PVA–PAA gel has a response time of the order of at least 100 ms. The forces measured by the load cell are shown in Fig. 4: they changed like sinusoidally varying waves. It was found that the frequency of the force was harmonized with that of the applied field.

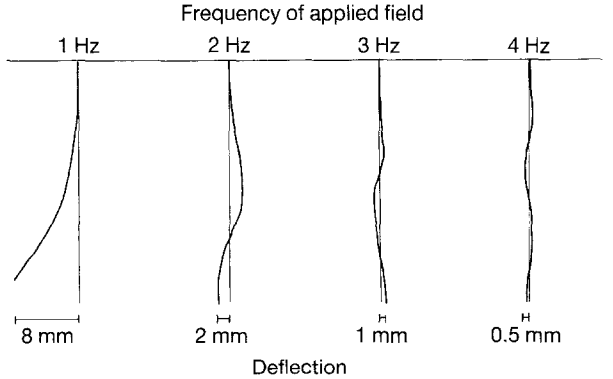

Figure 3 Deflection curves of poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogel films in electric fields of various frequencies. In Figs 3 and 4, the thickness of the specimen is 0.41 mm.

3.2. Analysis

The experimental results suggest that the vibration of the PVA–PAA gel films in a.c. electric fields derives from the bending. The PVA–PAA gel first bends due to a differential swelling. When the polarity of the applied field is changed, the swollen gel begins to shrink and straightens again. According to a previous study [8], it has already been demonstrated that the differential swelling on the bending under electric signals of less than 1 Hz was caused mainly by the osmotic pressure effect rather than by the solvent polarization effect. The osmotic pressure was determined by differences of mobile-ion concentrations between the inside and the outside of the gel.

Attempts were made to analyse the vibration of gel films supposing that it is caused by a differential swelling. As already mentioned, the bending deformation is regarded as a mechanical bending of a uniform beam based upon a bimetal principle. Thus it seems that the vibration of ionic gel films in a.c. electric fields is also a mechanical bending vibration of a uniform cantilever beam by sinusoidally varying forces. We begin from the partial differential equation for the deflection of bending vibration of a uniform cantilever beam [10]. If the effects of shear deformation and rotatory

inertia are neglected, the differential equation is given by

$$EI(d^4w/dx^4) + m(d^2w/dt^2) = F(x, t) \quad (1)$$

where E is the Young's modulus of gel, I the moment of inertia of the beam cross-section, m the beam mass per unit length, and $F(x, t)$ the external force $\{F(x, t) = C\sin 2\pi ft\}$.

The solution to Equation 1 is generally expressed by $W(x, t) = \Sigma w(x)q(t)$, and so $w(x)$ can be calculated from Equation 1 at $F(x, t) = 0$.

$$EI(d^4w/dx^4) + m(d^2w/dt^2) = 0 \quad (2)$$

Equation 2 is the so-called Bernoulli–Euler beam equation. The solution to this fourth-order equation contains four constants and is written in the form

$$w(x) = C_1\cosh\beta x + C_2\sinh\beta x + C_3\cos\beta x + C_4\sin\beta x \quad (3a)$$

$$(*)\beta^4 = \omega^2 m/EI \quad (3b)$$

For a cantilever beam with x separated from the fixed end, the boundary conditions are $w(0) = 0$, $w''(0) = 0$ and $w''(L) = 0$, $w'''(L) = 0$. Using the boundary conditions, we obtain the frequency equation

$$\cosh\lambda\cos\lambda = -1, \quad *\lambda = \beta L \quad (4)$$

where $\lambda_1 = 1.8751$, $\lambda_2 = 4.6941$, and $\lambda_i = (2i - 1)\pi/2$ $(i \geqslant 3)$. Using the eigenvalues λ, the natural frequency is determined from Equation 4

$$\omega = \lambda^2(EI/m)^{1/2}/L^2 \quad (5)$$

So Equation 3 is reduced to Equation 6

$$w_n(x) = C\{(\cosh\lambda_n + \cos\lambda_n) \times [\cosh(\lambda_n x/L) - \cos(\lambda_n x/L)] + (\sinh\lambda_n - \sin\lambda_n) \times [\sinh(\lambda_n x/L) - \sin(\lambda_n x/L)]\} \quad (6)$$

In the mechanical bending, when $n = 2$, there are two nodes at $x = 0$ and $x = 0.774L$ and two antinodes at $x = 0.475L$, and $x = 1.0L$ in the deflection curve $w_2(x)$ of Equation 6. As shown in Fig. 3, in a 2 Hz signal, the second node has been located at $x = 0.75L$. There is the second antinode at $x = 0.52L$. So the deflection curve of the gel film in a 2 Hz signal is similar to $w_2(x)$.

The cross-section of the PVA–PAA gel film is a rectangular plate with the dimension of bt. Here b and t represent the width and thickness of the gel film, respectively. So the moment of inertia of the beam cross-section, I, is given by [11]

$$I = \int_{-t/2}^{t/2} y^2 b\,dy = bt^3/12 \quad (7)$$

Because the beam mass per unit length, m, is calculated from $m = \rho bt$ (ρ is the density of the gel), inserting Equation 7 into Equation 5 results in

$$\omega_n = 2\pi f = \lambda_n^2 t(E/12\rho)^{1/2}/L^2 \quad (8)$$

If the vibration of the gel film is regarded as the mechanical bending vibration of a cantilever beam, the resonance frequency of gel vibration is proportional to thickness, t, or λ^2 as predicted from Equation 8. Fig. 5 indicates the first resonance frequency for gel films with various thicknesses. The open circles and the dotted line represent experimental results. The solid line ($f = 0.29t$, t in mm) shows values calculated from Equation 8 using $\rho = 0.02\ \mathrm{g\,cm^{-3}}$, $\lambda_1 = 1.8751$, $L = 4$ cm, and $E = 1.61 \times 10^6\ \mathrm{dyn\,cm^{-2}}$. In calculating the value of ρ, the effect of buoyancy has been subtracted. Both the experimental and calculated results are qualitatively proportional to the thickness of

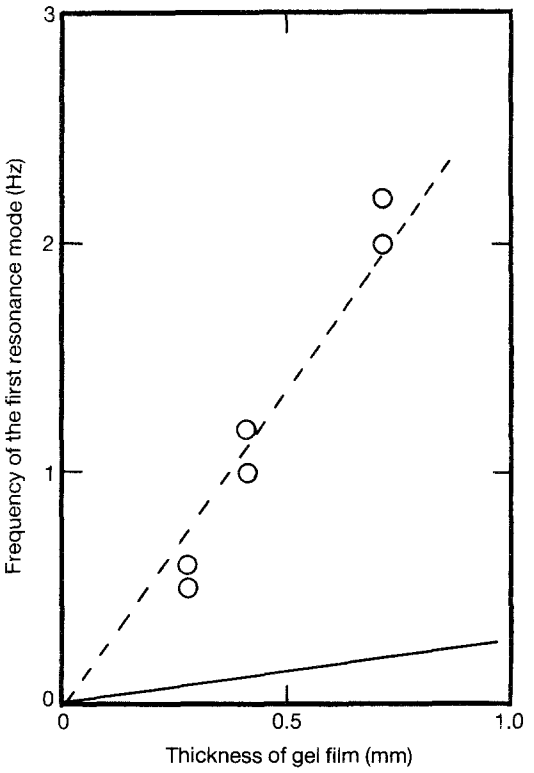

Figure 5 The frequency of the applied field to show the first resonance mode in gels with various thicknesses. (○) Experimental results, (——) $f = 0.29t$, calculated from $f = \lambda^2 t(E/12\rho)^{1/2}/2\pi L^2$, using $\lambda = 1.8751$, $L = 4$ cm, $E = 1.61 \times 10^6\ \mathrm{dyn\,cm^{-2}}$, and $\rho = 0.02\ \mathrm{g\,cm^{-3}}$.

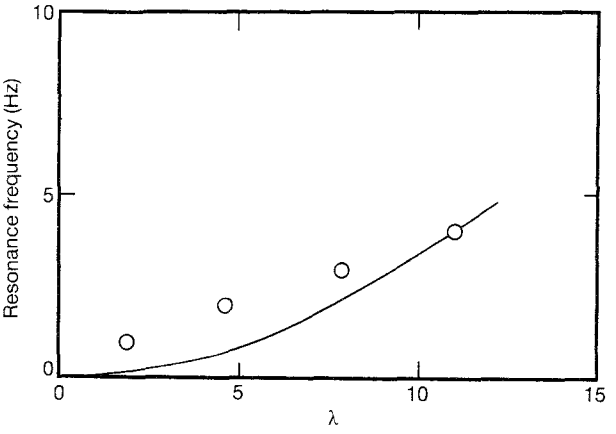

Figure 6 Relationship between the resonance frequency of the vibration and λ. (○) Experimental results, (——) $f = 0.034\lambda^2$ calculated from the equation in Fig. 5, using $t = 0.41$ mm, $L = 4$ cm, $E = 1.61 \times 10^6\ \mathrm{dyn\,cm^{-2}}$, and $\rho = 0.02\ \mathrm{g\,cm^{-3}}$.

the gel film. When the buoyancy is not affected, the relationship between f and t is given by $f = 0.04t$ using $\rho = 1.02\,g\,cm^{-3}$. The equation, $f = 0.04t$, cannot explain experimental results adequately. In Fig. 6, the resonance frequency for the 0.41 mm thick gel film is plotted as a function of λ. The solid line represents $f = 0.034\lambda^2$ calculated from Equation 8 using $\rho = 0.02\,g\,cm^{-3}$. The experimental results are in agreement with the calculated values. When $\rho = 1.02\,g\,cm^{-3}$, the equation is given by $f = 0.0047\lambda^2$. The experimental results can hardly follow the equation. From comparisons with the calculated and experimental results, the vibration of gel films in a.c. electric fields seems to be roughly analysed as a mechanical bending vibration of a uniform cantilever beam by sinusoidally varying forces. It is suggested that the buoyancy has played an important role in the occurrence of the vibration of gel films.

4. Conclusion

To open a door to the application of biomimetic energy-transducing devices using polymer gels we require more complicated motions of gels induced by electric fields. Translational or rotational motions have already been designed using the bending deformation [8]. A new motion, vibration of the PVA–PAA gel films in a.c. electric fields, has been presented. The vibration of gel films seems to be based on a differential swelling and has been roughly analysed as a mechanical bending vibration of a uniform cantilever beam. The bending of the soft materials is thus a flexible and dexterous deformation similar to biological motions. The next objective of this study is to confirm whether or not the differential swelling in gel films occurs.

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