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# Crazing dynamics in the swelling of thermally crosslinked poly(vinyl alcohol)–poly(acrylic acid) films

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A continuum kinetic model is used to describe the dynamics of crazing in a reticulated polymer film that is exposed to sudden hydration in order to form a hydrogel. The appearance of microfractures in a thermally crosslinked 80 wt% poly(vinyl alcohol)–20 wt% poly(acrylic acid) strip can be related to the internal strain of the polymer network and the thickness of the film. It is proposed that fractures are precipitated by the swelling of superficial layers of the polymeric matrix, which causes the drier middle layer to fail in tension when its yield stress is exceeded.

## 1. Introduction

A hydrogel is a hydrated polymer network which, because it is part solid and part fluid, displays a wide range of rheological and physical properties [1]. Polyelectrolyte hydrogels also possess many properties typical of biological tissues, which in themselves consist of a liquid phase retained in a solid polymeric matrix [1–5]. For instance, some gels exhibit softness, elasticity, strength [6], permeability to gas [7] and to a wide class of solutes, and other complex functions that are similar to muscle, cartilage and skin [1, 8].

The attributes of hydrogels render them suitable in biomedicine as soft contact lenses and for other promising applications, including drug delivery systems, tissue expanders, vascular prostheses, controllable perm-selective membranes [9] and stand membranes for the immobilization of enzymes or cellular cultures [10].

Moreover, gel materials have also aroused great interest in other fields ranging from the agricultural and food industries to life sciences [4], attracting researchers in different disciplines to study and characterize them.

With the aim of achieving a better basic understanding of gels, the work described in this paper was devoted to illustrating a phenomenon, namely crazing, which under certain conditions can be observed during hydration of thin polyelectrolyte strips. While undergoing this process, the material loses its characteristic transparency and a network of opalescent filaments appears in the bulk of the sample, which then vanish when equilibrium is reached. A microscopic examination can sometimes reveal a network of fractures within the sample, demonstrating a loss of mechanical strength.

In particular, the purpose of this work was to comprehend why crazing occurs in polyelectrolyte dry films during sudden hydration, and the role of physical parameters (the thickness of the film, the elastic modulus and yield stress of the gel matrix, the degree of swelling induced by hydration, the distance between the crazing lines, etc.) influencing this process [11, 12].

A simplified kinetic model derived from a poroelastic theory developed by Biot [13] in the mid-1950s is used. The model was first applied to the consolidation of porous rocks filled by fluids, and was then extended to the dynamics of gels by Johnson [14]. The stationary fluid approximation used here is the version developed by Tanaka and Fillmore for hydrogels with large amounts of water [15] and has been successfully applied to the case of gels with a polymer content upto 50 vol % [16].

## 2. Materials and methods

The thermally crosslinked poly(vinyl alcohol) (PVA; 80 wt %, molecular weight 14 000, AnalytiCals, Carlo Erba, Milan, Italy)–poly(acrylic acid) (PAA; 20 wt %, molecular weight 250 000, Aldrich Chemical Co., Milwaukee, Wisconsin, USA) hydrogel was prepared following the method of Kuhn and Hargitay [17]. Small strips were cut from the thin sheets, which were obtained by casting aqueous PVA–PAA solution and curing at 130 °C for 45 min. Some strips were completely dehydrated in an oven at 40 °C in the presence of desiccant (silica gel) under a mild vacuum. Other strips, opportunely hydrated to form a hydrogel (typically 0.5 cm wide, 0.5–1 cm long and 0.02–0.05 cm thick) were dried until their linear dimensions were reduced by 8%. This type of sample is referred to here as partially dried. At time $t_0 = 0$ samples of both states of dryness were immersed in distilled water at 20 °C and allowed to swell freely. The lengths of the gels were recorded as a function of time using a stereomicroscope (Wild M3, Carl Zeiss, Oberkochen, FRG) and a graduated eyepiece.

Measurement of the elastic Young's modulus of the material was performed by a low-frequency (10 Hz)

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dynamic tensile test, using a Rheolograph Piezo (ToyoSeiki, Tokyo, Japan). The experiment was carried out by gradually increasing the water content of the vacuum-dehydrated gel and measuring the hydrogel volume dilatation by recording the linear dimension of the sample at zero tension (the sample was isotropic).

The shear elastic modulus of the gel as a function of the gel water content was determined indirectly using [18]

$$\mu = E\left(\frac{3k}{\mu} + 1\right)\Big/\frac{9k}{\mu} \approx 0.377E$$

as a function of the Young's modulus, $E$, and the ratio between the bulk and the shear elastic moduli, $k/\mu$, which is taken to be 2.5 for this material [16]. A stress–strain relationship for dehydrated samples was obtained by tensile tests under ambient conditions. Dumbbell-shaped thin strips of dehydrated gel, about 3.0 cm long, 0.007 cm thick and 0.5 cm wide at the centre, clamped in hydraulic jaws, were stretched to breaking at a rate of 0.5 cm min$^{-1}$ using a model 4302 testing machine (Instron Ltd, High Wycombe, UK). Stress versus strain curves were obtained by plotting the outputs of the load cell and the extensometer on an $X$–$Y$ recorder.

The equations describing the swelling process of dry polymer films were solved by a numeric algorithm. Calculations were performed by adopting an implicit finite-differences method and solving the resultant non-linear algebraic system with the Newton–Raphson technique. Using an appropriate choice of the spatial and temporal increments (1/20 of the film thickness and 1/2000 of the characteristic time of the process) the convergence was optimized.

## 3. Theoretical model

The kinetics of free swelling of dilute hydrogels has already been analysed for a thin gel strip using an analytical model [16, 19]. Neglecting inertial effects, the equation of polymeric network motion for dilute gels is formulated [13, 15, 20] as

$$f\frac{\partial U_i}{\partial t} = \frac{\partial \sigma_{ij}^{\mathrm{gel}}}{\partial j} \qquad i, j = x, y, z \tag{1}$$

where $\sigma_{ij}^{\mathrm{gel}}$ is the stress tensor of the gel polymeric matrix, $U_i$ is the displacement vector of a gel element from the reference position in the final swollen state and $f$ is the frictional coefficient between the polymer network and the interstitial fluid [15].

For a gel, the linear stress–strain relationship

$$\sigma_{ij} = k\varepsilon_{\alpha\alpha}\delta_{ij} + 2\mu(\varepsilon_{ij} - \varepsilon_{\alpha\alpha}\delta_{ij}/3) + \beta\delta_{ij} \tag{2}$$

is assumed [13, 20], where the strain

$$\varepsilon_{ij} = \left(\frac{\partial U_i}{\partial j} + \frac{\partial U_j}{\partial i}\right)\Big/2$$

$k$ and $\mu$ are, respectively, the bulk and shear elastic moduli of the gel, $\beta$ is the chemically induced stress at zero strain, $\varepsilon_{\alpha\alpha}$ is the trace of the strain matrix $\varepsilon_{ij}$ (corresponding to the gel dilatation) and $\delta_{ij}$ is the Kroneker delta. The material parameters in Equations 1 and 2 are, in general, functions of the pH, the ionic strength of the solution permeating the gel, the solvent–polymer affinity and the temperature.

In the free swelling of partially dried gels in distilled water, the gel water content, $\phi_w$, defined as the ratio between the volume of water and the total volume of gel and also known as the gel hydration, remains practically constant. Therefore $\mu$, $k$, $\beta$ and $f$ can be considered constants ($\beta$ can be set equal to zero). Moreover, in the case of a thin gel film, for which the length is much greater than the thickness, it is possible to obtain the following equations [16] [where the $z$-axis is chosen perpendicular to the flat surface of the thin gel sheet (Fig. 1)]:

$$\partial\varepsilon_{xx}/\partial t = D\,\partial^2\varepsilon_{xx}/\partial z^2 \tag{3a}$$

$$\partial\varepsilon_{yy}/\partial t = D\,\partial^2\varepsilon_{yy}/\partial z^2 \tag{3b}$$

$$\partial\varepsilon_{\alpha\alpha}/\partial t = D_s\,\partial^2\varepsilon_{\alpha\alpha}/\partial z^2 \tag{3c}$$

where $D$ is a diffusion coefficient equal to $\mu/f$ and $D_s = (k + 4\mu/3)/f$.

An analytical solution for the strain $\varepsilon_{xx}$ and $\varepsilon_{zz}$, as a function of the $z$ co-ordinate, is obtained from Equations 3 [16]

$$\varepsilon_{xx} = \frac{4\varepsilon_0}{\pi}\sum_n\left(\frac{(-1)^n}{2n+1}\right)\exp\left(-\frac{(2n+1)^2 t}{\tau}\right) \times \cos\left(\frac{(2n+1)z\pi}{a}\right) \tag{4a}$$

$$\begin{aligned}\varepsilon_{zz} &= \varepsilon_{\alpha\alpha} - 2\varepsilon_{xx}\\ &= \frac{4\varepsilon_0}{\pi}\sum_n\left(\frac{(-1)^n}{2n+1}\right)\left[3\exp\left(-\frac{(2n+1)^2 t}{\tau_s}\right) - 2\exp\left(-\frac{(2n+1)^2 t}{\tau}\right)\right]\cos\left(\frac{(2n+1)z\pi}{a}\right)\end{aligned} \tag{4b}$$

where $\varepsilon_0$ is the gel initial (negative) strain of the sample, taking as the reference ($\varepsilon = 0$) the fully swollen-gel film with thickness $a$ and length $L$ at $t = \infty$. $\tau$ and $\tau_s$ are the characteristic time constants of the gel network readjustment.

The length $L(t)$ and the thickness $a(t)$ of the gel strip can be calculated from Equations 4 as

$$\begin{aligned}L(t) &= L(1 + \varepsilon_{xx}(z = 0))\\ &= L\left[1 + \frac{4\varepsilon_0}{\pi}\sum_n\left(\frac{(-1)^n}{2n+1}\right)\exp\left(-\frac{(2n+1)^2 t}{\tau}\right)\right]\end{aligned} \tag{5a}$$

$$\begin{aligned}a(t) &= a + 2\int_0^{a/2}\varepsilon_{zz}\,\mathrm{d}z\\ &= a\left\{1 + \frac{8\varepsilon_0}{\pi^2}\sum_n(2n+1)^{-2}\left[3\exp\left(-\frac{(2n+1)^2 t}{\tau_s}\right) - 2\exp\left(-\frac{(2n+1)^2 t}{\tau}\right)\right]\right\}\end{aligned} \tag{5b}$$

Fig. 2 shows the strain inside a partially dried gel, undergoing free swelling in distilled water, as a

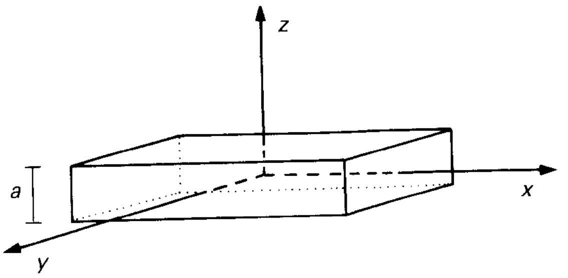

*Figure 1* Schematic diagram of the reference co-ordinate system of the sample.

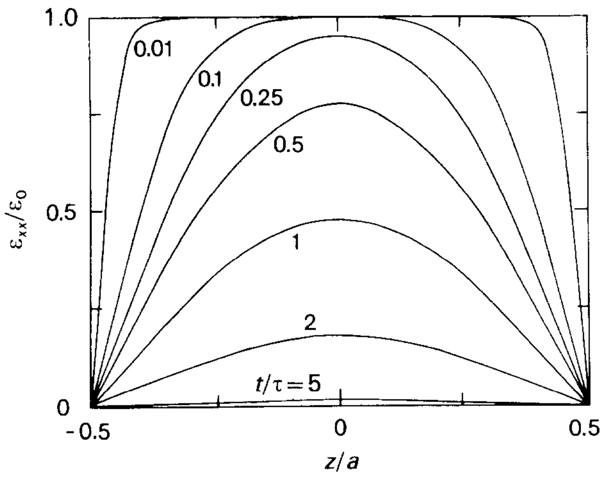

*Figure 2* Calculated strain, $\varepsilon_{xx}/\varepsilon_0$, in a partially dried hydrogel strip undergoing free swelling, as a function of the reduced variable $z/a$ at various normalized times, $t/\tau$, using Equation 4a.

function of the variable $z/a$, and at different times, as calculated from Equation 4a. The temporal parameter is normalized with respect to the characteristic time $\tau = a^2/\pi^2 D$, obtained by substituting Equation 4a into Equation 3a.

A peculiar characteristic of film swelling, as can be noted from Equation 3c, is that the network has two readjustment time constants, $\tau = a^2/\pi^2 D$ and $\tau_s = a^2/\pi^2 D_s$. The former is related to the slower shear elongation along the $x$- and $y$-axes, and the latter to the faster dilatation motion of the gel polymeric matrix. The coupling of these two aspects forces the normalized strain $\varepsilon_{zz}/\varepsilon_0$ to become negative (Fig. 3) and the film thickness to behave as reported in Fig. 4. From these calculations, the gel strip first increases its thickness (even beyond its equilibrium value) and then its length.

The continuum model developed so far describes the behaviour of partially dried gels quite well, whereas it is not directly applicable to the swelling of completely dehydrated samples. In fact, when gel hydration, $\phi_w$, undergoes a large change during the swelling process (i.e. free swelling of dehydrated samples, where $\phi_w$ ranges from zero to the value of maximum hydration), the elastic parameters $\mu$ and $k$ of the gel, the chemical stress $\beta$ and the gel hydraulic permeability $1/f$ [21] cannot be considered constants in Equation 1 [13, 22]. The range of validity of Equation 1 has been empirically determined to extend over a large range of degrees of hydration [14, 16, 20, 23].

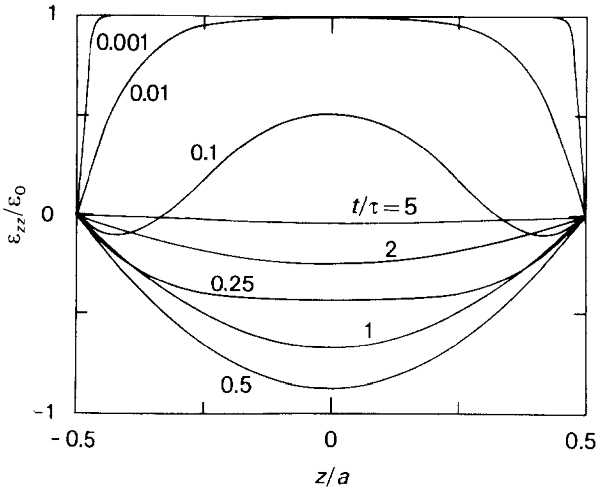

*Figure 3* Calculated strain, $\varepsilon_{zz}/\varepsilon_0$, in a partially dried hydrogel strip undergoing free swelling, as a function of the reduced variable $z/a$ at various normalized times, $t/\tau$, using Equation 4b.

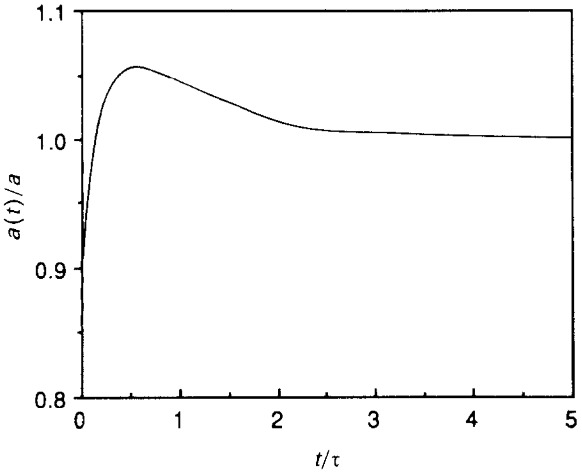

*Figure 4* Normalized thickness of the gel film versus the reduced time $t/\tau$ calculated from Equation 5b.

Considering $\mu$, $k$ and $f$ as functions of the gel hydration degree, Equation 1 combined with Equation 2 leads to

$$\frac{\partial U_x}{\partial t} = D\frac{\partial^2 U_x}{\partial z^2} + \frac{1}{f}\frac{\partial \mu}{\partial z}\frac{\partial U_x}{\partial z} \tag{6a}$$

$$\frac{\partial U_y}{\partial t} = D\frac{\partial^2 U_y}{\partial z^2} + \frac{1}{f}\frac{\partial \mu}{\partial z}\frac{\partial U_y}{\partial z} \tag{6b}$$

$$\frac{\partial U_z}{\partial t} = D\frac{\partial^2 U_z}{\partial z^2} + \frac{1}{f}\frac{\partial \mu}{\partial z}\frac{\partial U_z}{\partial z} + (D_s - D)\frac{\partial \varepsilon_{\alpha\alpha}}{\partial z} + \frac{\varepsilon_{\alpha\alpha}}{f}\frac{\partial (k + \mu/3)}{\partial z} \tag{6c}$$

The dependence of the shear elastic modulus, $\mu$, on the gel water content in Equations 6 has been experimentally determined and the bulk elastic modulus, $k$, is assumed proportional to $\mu$ as a first approximation.

Equations 6 have been solved numerically by assuming a linear dependence of $D$ on the gel water content, $\phi_w$ (and ultimately on the gel dilatation $\varepsilon_{\alpha\alpha}$)

$$D = D_\infty(1 - \varepsilon_r + m\varepsilon_r) \tag{7}$$

where $\varepsilon_r$ is the gel dilatation, $\varepsilon_{\alpha\alpha}$, normalized with respect to the initial dilatation, $\varepsilon_{\alpha\alpha_0}$, $D_\infty$ is the limiting value of the gel network diffusion coefficient in the fully hydrated state (at $t = \infty$, when $\varepsilon_r = 0$) and $m$ is a coefficient available from the experimental data.

The normalized strain $\varepsilon_{xx}/\varepsilon_0$ inside a dehydrated gel strip submitted to a stepwise hydration in distilled water is shown in Fig. 5a, in which the curves have been calculated for various values of time preceding the crazing ($t \leq 0.652\tau$). Profiles of the normalized gel dilatation, $\varepsilon_{\alpha\alpha}/3\varepsilon_0$, for these times are shown in Fig. 5b. Fig. 5a and b was obtained by a numerical solution of the respective diffusion equations (Equations 6a and c), in which $D_\infty = 9.6 \times 10^{-12}\ \mathrm{m^2\,s^{-1}}$, $\varepsilon_{\alpha\alpha_0} = 3\varepsilon_0 = -1.401$, $m = 2.1 \times 10^{-2}$ and $k(\varepsilon_{\alpha\alpha}) \approx \mu(\varepsilon_{\alpha\alpha})$ have been used. For the same values for the parameters as above, the normalized $\varepsilon_{zz}/\varepsilon_0$ strain profiles before crazing are shown in Fig. 5c.

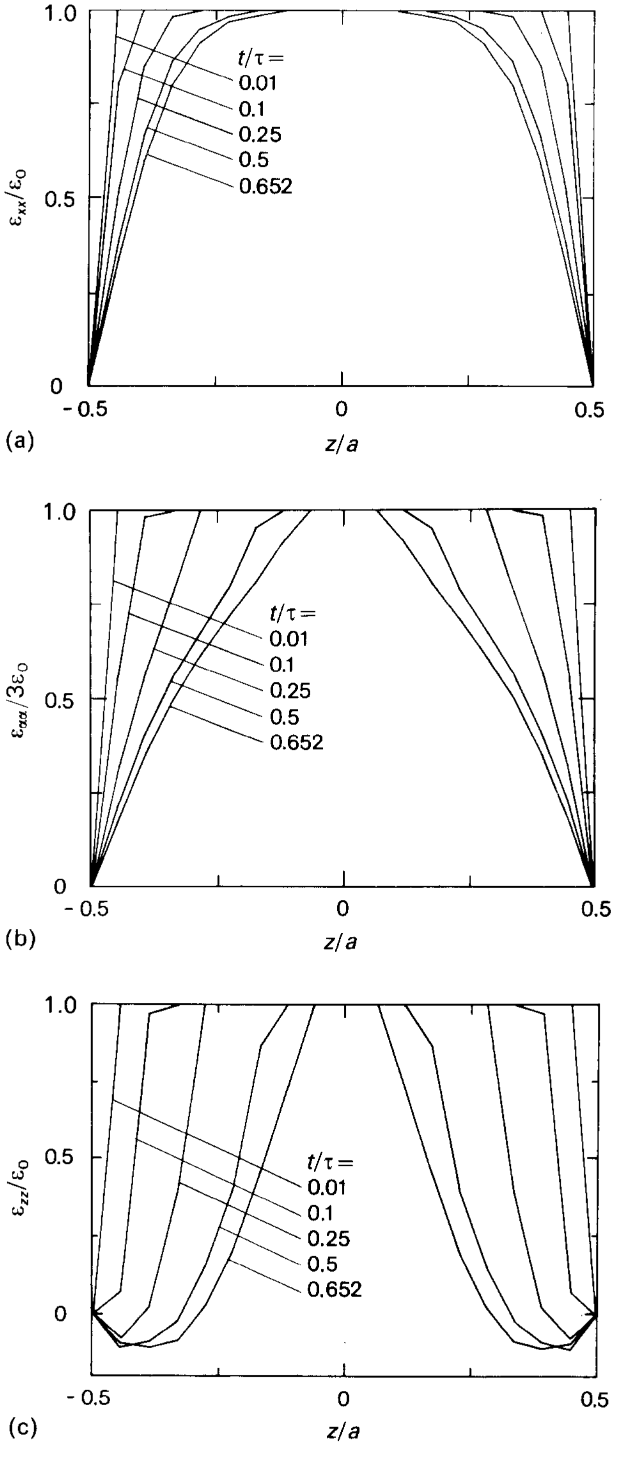

*Figure 5* The profiles of (a) the normalized strain $\varepsilon_{xx}/\varepsilon_0$, (b) the normalized dilatation $\varepsilon_{\alpha\alpha}/3\varepsilon_0$ and (c) the normalized strain $\varepsilon_{zz}/\varepsilon_0$ of a dehydrated PVA–PAA strip left to swell freely in distilled water. The curves, obtained by solving numerically the system of Equations 6, are depicted at various reduced times.

## 4. Experimental

The propagation of free swelling of a thin polyelectrolyte strip differs according to whether its starting state is dehydrated or partially dried. In Fig. 6 the normalized length change, $[L - L(t)]/[L - L(0)]$, of a gel strip undergoing free swelling, starting from a partially dried state, is plotted as a function of normalized time, $t/\tau$. The full line represents the theoretical behaviour calculated from Equation 5a.

The normalized change in length of a completely dehydrated sample undergoing swelling is shown in Fig. 7. Comparing Figs 6 and 7, it can be noted that the swelling of the sample starting from the dehydrated state shows an initial slow expansion, and then commences exponential decay by a length jump which is contemporary to the formation of crazes.

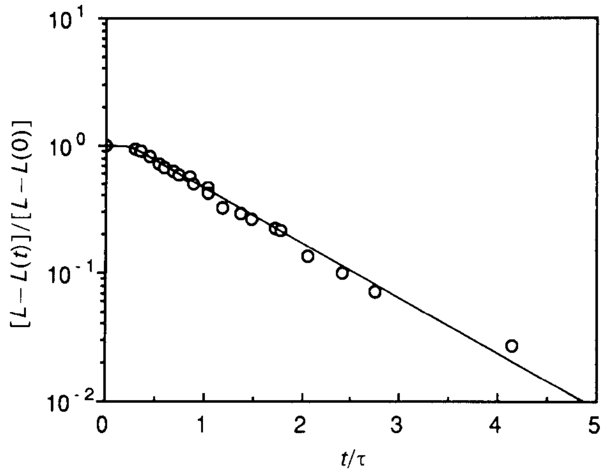

*Figure 6* (○) Measured length change of a gel strip $[L - L(t)]/[L - L(0)]$ as a function of the reduced time, $t/\tau$, when partially dried. The full line is that calculated from Equation 5a.

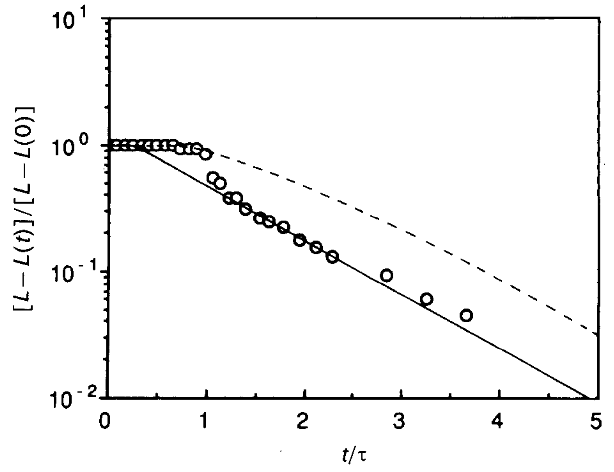

*Figure 7* (○) Measured length change of dehydrated polyelectrolyte strip as a function of the reduced time, $t/\tau$. The broken curve, obtained by inserting the numerical solution of Equations 6 into Equation 5a, is compared with the behaviour calculated for a partially dried gel (full line).

Gel samples were analysed to evaluate their material parameters at various degrees of hydration. The shear elastic modulus of PVA–PAA gel as a function of the hydration-induced strain, $\varepsilon = \varepsilon_{\alpha\alpha}/3$, is shown in Fig. 8. Fig. 9 is a typical stress–strain curve for a PVA–PAA dehydrated sample under ambient conditions. Here the stress is normalized to the initial sample cross-sectional area. On an average of five measurements, the value of the yield stress, $\sigma_y$, was calculated to be $\sigma_y = (1.00 \pm 0.04) \times 10^8$ Pa.

Using a value of $m = 2.1 \times 10^{-2}$, obtained from a least-squares fit of the experimental data, the diffusion coefficient and the friction coefficient of the gel in the dry state gave $D_d = 2.0 \times 10^{-13}\ \mathrm{m^2\,s^{-1}}$ and $f_d = \mu/D_d = 2.0 \times 10^{22}\ \mathrm{N\,s\,m^{-4}}$, respectively.

## 5. Discussion

When a dehydrated gel strip is immersed in distilled water, the sample has two expanding swollen peripheral layers and an internal one still in the initial state, as can be deduced from Fig. 5. The dehydrated polymer layer has an elastic shear modulus $\mu \approx 4 \times 10^9$ Pa, three orders of magnitude larger than that of the completely hydrated state. As time progresses the internal rigid layer (Fig. 5b) becomes thinner and the dilatation force of the swollen peripheral layers gets stronger. This leads to an enormous increase in the force per unit cross-sectional area in the internal polymeric layer of the sample. When the stress reaches the yield value, the internal layer suddenly elongates or even breaks and the gel length changes abruptly (Fig. 7). It is therefore possible to correlate the value of the yield stress of PVA–PAA gel with some quantitative crazing features.

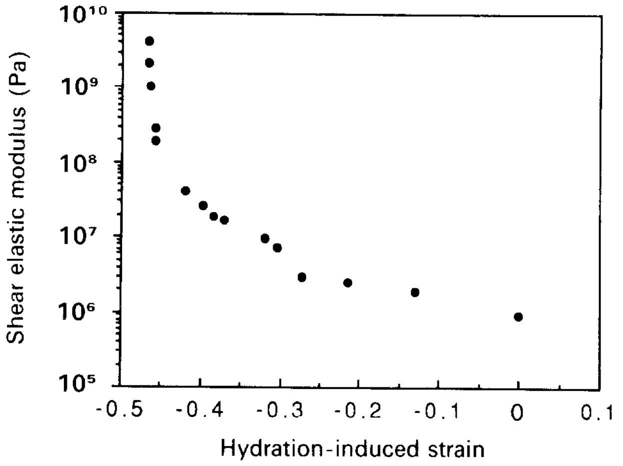

*Figure 8* Shear elastic modulus of a PVA–PAA gel measured as a function of the hydration-induced strain $\varepsilon_{\alpha\alpha}/3$. The reference zero strain is the fully swollen gel state.

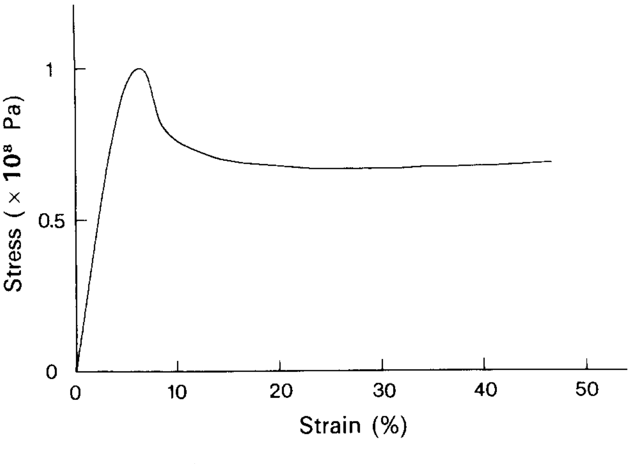

*Figure 9* Stress–strain curve for dry PVA–PAA sample under ambient conditions until the breaking point. The stress is referred to the initial cross-sectional area of the sample.

In the event of crazing, the stress in the internal dry layer of gel can be evaluated from its cross-sectional area and the external shear forces acting on it.

The tension, $\Delta F$, on an elemental volume of gel strip can be calculated from the total shear forces acting on it (Fig. 10) as

$$\Delta F = \mathrm{d}A \sum_{i=1}^{2} [\sigma_{zx}(x + \mathrm{d}x, z_i) - \sigma_{zx}(x, z_i)]$$

where $\mathrm{d}A$ is the surface area of the elements on which the shear stresses act, and $z_i$ are the co-ordinates delimiting the dry internal layer when crazing is forming. Since, for planar symmetry conditions, $\partial U_z/\partial x = 0$ and $\sigma_{zx} = 2\mu\varepsilon_{xz}$, $\sigma_{zx} = \mu\partial U_x/\partial z$, the total force is

$$\Delta F = \mathrm{d}A\mu \sum_{i=1}^{2} (-1)^i (\partial U_x/\partial z|_{(x+\mathrm{d}x,\, z_i)} - \partial U_x/\partial z|_{(x,\, z_i)}) \tag{8}$$

or, equivalently,

$$\Delta F = \left[\sum_{i=1}^{2} (-1)^i (\mu\partial^2 U_x)|_{z=z_i}\,\mathrm{d}x\right]\mathrm{d}A \tag{9}$$

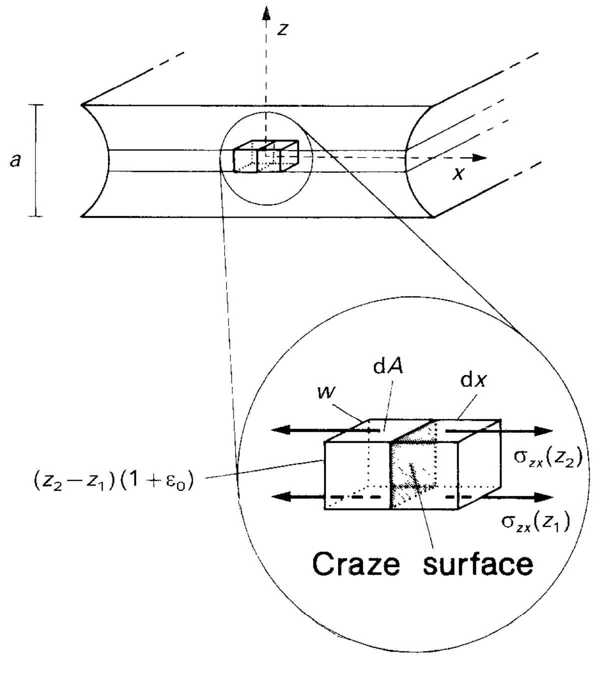

*Figure 10* Schematic representation of the swelling geometry of a polyelectrolyte thin strip. The inset shows the shear forces acting on an elemental volume of material.

When the gel crazing appears (at $t = t_c$) the stress $\sigma_{xx} = \Delta F/S$ equals the gel yield stress $\sigma_y$

$$\begin{aligned}\sigma_y &= \Delta F/S \\ &= \frac{\left[\sum_{i=1}^{2} (-1)^i (\mu \partial^2 U_x/\partial z\,\partial x)|_{z=z_i}\,\mathrm{d}x\right]\mathrm{d}x}{(z_2 - z_1)(1 + \varepsilon_0)}\end{aligned} \tag{10}$$

where $S = w(z_2 - z_1)(1 + \varepsilon_0)$ is the cross-sectional area of the internal dry polyelectrolyte layer at the initiation of crazing, $w$ is the elemental sample width (along the $y$-axis) and $\mathrm{d}A = w\,\mathrm{d}x$.

The values of $z_i$ are obtained by finding the maximum of the force per unit cross-section of Equation 10, satisfying

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\mu(\partial^2 U_x/\partial z\,\partial x)}{z(1 + \varepsilon_0)}\right) = 0 \tag{11}$$

Equating the distance $\mathrm{d}x$ on which the shear forces act with the distance between two adjacent lines of crazing, $\Delta x_c$, and summing over $i$ (considering a symmetrical system in which $z_1 = -z_2$) gives

$$\Delta x_c = \left(\frac{z_2(1 + \varepsilon_0)\sigma_y}{(\mu \partial^2 U_x/\partial z\,\partial x)|_{z=z_2}}\right)^{1/2} \tag{12}$$

By using the measured values of the yield stress of PVA–PAA films ($\sigma_y = 1.0 \times 10^8$ Pa) and the gel fractional length variation ($\varepsilon_0 \approx -0.50$), and taking the value of the function $z_2/[(\mu \partial^2 U_x/\partial z\,\partial x)|_{z=z_2}] = 4.32 \times 10^{-15}\ \mathrm{m^4\,N^{-1}}$ (obtained by the strain profiles), $\Delta x_c$ is estimated to be 465 μm. The spacing between two crazing lines has been measured by a microscope and found to be 450 ± 25 μm, in agreement with the value deduced above.

If the craze spacing, $\Delta x_c$, is of the same order of magnitude as or larger than the sample size, crazing does not form. This can be achieved either by increasing the film thickness (by substituting $Z = z/a$ in Equation 12, then $\Delta x_c$ is proportional to $a$) or its yield stress in the dry state, or by reducing the shear elastic modulus of the inner layer, or even by reducing the total fractional length change, $\varepsilon_0$. The last two conditions apply to partially dried gel films with $\mu \approx 10^6$ Pa and $\varepsilon_0 \approx -0.08$. Moreover, in this case it must be noted that the strain profiles during the free swelling of partially dried samples in Figs 2 and 3 are quite different from those of dehydrated samples in Fig. 5a and c, so Equation 10 does not have a maximum leading to the distribution of the shear stress on to the whole section of the film. Therefore, the crazing does not appear and the gel length time course does not have a discontinuity (see Fig. 6).

Finally, it is of interest to note that, from our results, the evaluation of certain material parameters of the gel in the dehydrated state is possible. In fact, Equation 7 permits the extrapolation of the value of the gel diffusion coefficients, $D$, in dehydrated conditions. From this parameter the fluid–matrix friction coefficient, $f = \mu/D$, can be derived. This value undergoes a remarkable increase from $10^{16}$ to $10^{22}\ \mathrm{N\,s\,m^{-4}}$ in going from wet to dry conditions.

## 6. Conclusions

The continuum model proposed describes in a satisfactory manner the kinetic behaviour of the swelling and crazing of dry PVA–PAA polyelectrolyte films. The description of the swelling process arising from the numerical simulation has been very helpful in its understanding, even allowing the recognition of particular aspects such as the fractal structure of the system which is illustrated by the repetition of the phenomenon on a reduced scale (closely spaced crazing lines in the internal dry polymer subsystem in between two primary ones).

It must be noted, however, that the non-linearity of the differential equations and the approximated linear dependence of the diffusion coefficient, $D$, on the gel dilatation, $\varepsilon_{\alpha\alpha}$, affect the accuracy of the strain profiles, and the observed buckling patterns, which would help to relieve the interfacial stress that builds up at the interface between the crystalline and swollen polymer, are not included in the theory [24].

In conclusion, the model has shown that the hydration of crosslinked polyelectrolytes can enhance an unwelcome phenomenon in very thin and dry films. The most easily controllable parameter among all those that influence the appearance of crazing, as defined by the model, is the fractional length change, $\varepsilon_0$. To avoid craze formation, very gentle step changes in the hydration process, keeping the parameter $\varepsilon_0$ as small as possible, are advisable.

Further work is being carried out to improve the model by establishing a more realistic dependence of the gel diffusion coefficient on the degree of hydration.

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