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Tatiana Budtova, Stanislav Patlazhan, Sylvie Vervoort, Jan Weyts. Solvent release from highly swollen gels under compression: an important phenomenon that has to be taken into account. 38ème colloque annuel du Groupe Français de Rhéologie, Oct 2003, Brest, France. 4 p. hal-00579407

HAL Id: hal-00579407

<https://minesparis-psl.hal.science/hal-00579407>

Submitted on 23 Mar 2011

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Solvent release from highly swollen gels under compression: an important phenomenon that has to be taken into account

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Résumé : Nous avons étudié le comportement de gels fortement polyélectrolytiques sous compression uniaxiale. Il est observé que le gel se déforme et expulse de son solvant en même temps. Une analyse théorique prédit cette perte de solvant pour des gels faiblement chargés comme pour des gels neutres. Le phénomène est plus prononcé pour le cas du gel polyélectrolytique.

Mots-clés : gels, compression, déformation, expulsion de solvant.

Abstract The behavior of a strongly charged polyelectrolyte gel under a uniaxial compression was studied, demonstrating the evidence of gel deformation and volume loss at the same time. A theoretical approach shows that solvent release takes place for both weakly charged and neutral gels, being more pronounced for polyelectrolyte hydrogels.

1. Introduction

Hydrogels are highly swelling chemically cross-linked hydrophilic (polyelectrolyte) polymer networks. They swell/contract several hundred times and absorb/release solvent in response to changes in the surrounding medium or to the applied external fields. Hydrogels are widely used as superabsorbents and they are promising materials in food, cosmetics and pharmacological applications because of their intelligent absorption/release properties.

Even being swollen several hundred times, hydrogels keep their shape. In most of the applications and during processing gels are under a mechanical action. What should happen if such a gel is compressed or deformed? Only few publications consider the gel volume change caused by compression or try to perform experiments quicker than the solvent is released. Recently we showed that a hydrogel micro-particle based on a cross-linked poly(sodium acrylate-*co*-acrylic acid) and immersed in a silicon oil releases solvent under shear¹⁻³. However, aside of one example shown in

ref.1, there are no experimental or theoretical estimations of the importance of the gel volume loss caused by a mechanical action.

2. Materials and methods

2.1. Materials

Two types of strongly charged gels were used:

1. Stockosorb® 410K: it is a poly(potassium acrylate-*co*-acrylic acid) with a molar ratio of 0.7/0.3, chemically cross-linked by *N,N'*-methylenebisacrylamide, kindly provided by Stockhausen company. The gel was initially in the form of dry grains of size ~ 10-15 mm³ which were swollen in distilled water up to equilibrium (swelling degree being around 150 g/g). Gel disks with a diameter of about 12 mm and a height of about 1 mm were cut. Gels swollen less than at equilibrium were prepared using blotting paper to absorb water from the gel disks at 140 g/g.

2. A poly(sodium acrylate-*co*-acrylic acid) gel was synthesised by free-radical copolymerisation of partially neutralised acrylic acid crosslinked with *N,N'*-methylenebisacrylamide in a proportion of 300

mol to 1. The monomer concentration in the initial mixture was 25% (w/w). The equilibrium swelling degree in demineralised water was determined to be 200 g/g.

2.2. Methods

The compression experiments were performed with an RMS-800[®] rheometer, manufactured by Rheometrics, with plate-plate geometry. The plates were coated with a sandpaper to avoid sliding of wet gel samples. A gel disk was put on a fixed lower plate, the upper plate moved vertically down at a speed of 0.001 mm/s and the force exerted upon compression was measured. The changes in the gel disk sizes upon compression were monitored by a CCD camera. All data discussed here correspond to the gel samples before any breakage. The recorded sequences were analysed image by image with the help of image analysis software Visilog 5.3 from Noesis 2000.

3. Experimental results

3.1. Qualitative observations

During compression experiments, a gel disk of any swelling degree deforms and some solvent is released. The release of water can be easily noticed at the end of each compression experiment: droplets were left on the lower plate when the gap was opened and the gel disk removed. Another visual proof of the solvent release during compression is that a cylindrical gel sample seems to have a concave shape (see Fig.1).

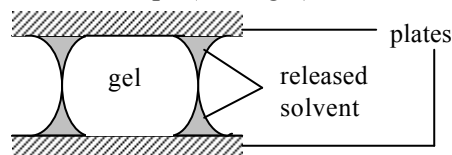


Fig.1. Schematic presentation of solvent release from a cylindrical gel under compression.

3.2. Deformation as a function of applied pressure

The dependence of a gel disk deformation $D(P)/D_0$ (D_0 being the initial disk diameter and $D(P)$ – disk diameter at a certain pressure P) on the applied pressure is presented in Fig.2 for different initial swelling degrees. The inset shows the beginning of the deformation-pressure curves for two gel disks of $Q_0 = 140$ g/g.

The deformation-pressure curves show the “s-shape”. The first region corresponds to the beginning of compression: the gel releases water immediately and thus pressure increase leads to small deformations. The slope changes when the force becomes higher than ~ 0.3 N (pressure of about 2000-3000 Pa). Then the deformation-pressure

dependencies are linear up to the moment when the diameter becomes extended in about 25%. The less the gel was swollen at the beginning, the higher pressures are needed to reach the same deformations as for the more swollen gels (compare, for example, curves 4 ($Q_0 = 20$ g/g) and 1 ($Q_0 = 140$ g/g) in Fig.2). This is an expected result, because the lower a gel is swollen, the higher is its elastic modulus. Above $D/D_0 \cong 1.25$, the deformation-pressure curves deviate from the linear regime, indicating the threshold of strain saturation of the gels.

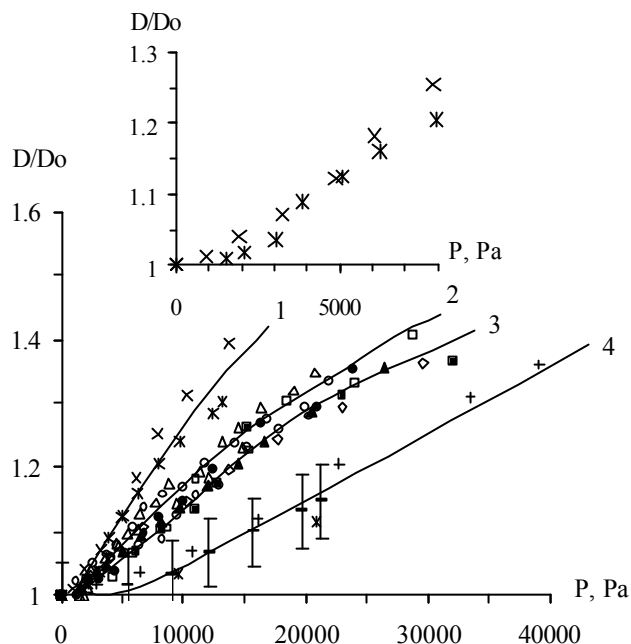


Fig.2. Deformation as a function of applied pressure for gels of the initial swelling degrees of 140 g/g (1), 100 g/g (2), 60 g/g (3) and 20 g/g (4). Lines are given to guide the eye.

Inset: beginning of deformation for two gel disks swollen at equilibrium (140 g/g).

3.3. Volume change as a function of applied pressure

In order to compare the data obtained for gels of different swelling degrees and of different sizes, a relative volume $V(P)/V_0$ (V_0 being the initial gel volume) was plotted as a function of pressure (Fig.3). All data fall together within the 10% experimental error. There is no significant influence of the gel initial swelling degree on its relative volume loss under compression. As well as for $V(P)$, the relative volume as a function of the applied pressure can be roughly described by two lines with the slopes differing in 6-7 times (see dashed lines in Fig.3). The lower the initial swelling degree, the higher is its shear modulus, thus the pressures it can sustain before breakage are higher and more water can be released.

We shall not speculate on the quantitative influence of the gel initial swelling degree on its behaviour under compression. The important features are i)

there is a significant volume loss due to the applied pressure and ii) there are two regions with different rates of solvent release. These two points will be compared with a qualitative theoretical prediction developed for uniaxially compressed hydrogels.

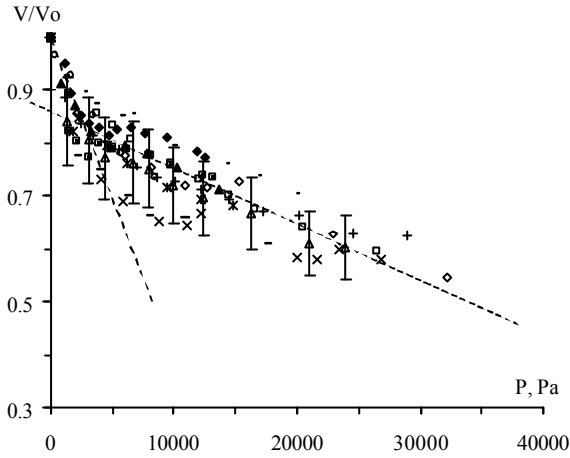


Fig.3. Dependence of the reduced volume on the applied pressure for all gel samples. Dashed lines show two regions with different slopes.

3.4. Theoretical predictions

The theory used is based on a thermodynamic approach developed for weakly charged hydrogels at equilibrium⁴. The hydrogel studied experimentally is strongly charged and far from equilibrium. However, it is important to check analytically in the first approximation if the theory developed for weakly charged gels predicts the gel volume loss under compression.

Let us consider a cylindrical sample of a hydrogel swollen at equilibrium in water. The average number of monomers in the chains connecting neighbouring cross-linking junction of the network is N . Each chain contains N/m charges separated by m monomers. The gel is assumed to be defectless and thus might be considered as a close packing of v coils, $v = v_z v_S$, v_z and v_S representing the numbers of chains per z -axis and per cross-section of the cylindrical sample respectively. The electrical neutrality of the system is provided by vN/m of counter-ions.

As far as the main goal is to examine whether the hydrogel volume changes under the uniaxial compression, the swelling degree of a gel before and after compression has to be calculated. The uniaxial symmetry of our problem results into two relevant swelling degrees: along the z -axis, α_z , and in the perpendicular (radial) direction, α_r . They are defined as $\alpha_z = L/L_{\text{ref}}$ and $\alpha_r = R/R_{\text{ref}}$ L and R being the lengths and radii of the cylindrical

sample under compression and L_{ref} and R_{ref} are the length and the radii at reference state, corresponding to a free non-swollen gel. As far as our samples were prepared in a large amount of solvent, the reference state corresponds to the Θ -condition with Gaussian internodal polymer chains of size $r_0 = dN^{1/2}$ (d being the persistent length), thus $L_{\text{ref}} = v_z r_0$ and $R_{\text{ref}} = v_S^{1/2} r_0$. At the stress free state the swelling degrees result into $\alpha_{0z} = L_0/L_{\text{ref}}$ and $\alpha_{0r} = R_0/R_{\text{ref}}$, where L_0 and R_0 represent sizes of the sample at room temperature and $P = 0$. (Generally speaking, α_{0z} and α_{0r} are not the same because of the anisotropic orientation of electric field around a cylindrical charged gel.)

The volume of a compressed and free gel can be expressed as $V = \alpha_z \alpha_r^2 V_{\text{ref}}$ and $V_0 = \alpha_{0z} \alpha_{0r}^2 V_{\text{ref}}$, respectively. The goal of the theoretical part is to estimate the relative volume change as a function of applied pressure:

$$\frac{V(P)}{V_0} = \frac{\alpha_z \alpha_r^2}{\alpha_{0z} \alpha_{0r}^2} \quad (1)$$

Because of the same reason of the axial symmetry, two components of the stress tensor, s_{zz} and s_{rr} have to be considered. They represent the uniaxial compression P and the lateral Laplace pressure $\Gamma = \gamma/R$ caused by the interfacial tension γ . Being equilibrated by gel elasticity, these stresses can be represented as:

$$P = \frac{1}{\alpha_r^2 V_0} \frac{\partial F}{\partial \alpha_z} \quad \text{and} \quad \Gamma = \frac{1}{2 \alpha_r \alpha_z V_0} \frac{\partial F}{\partial \alpha_r}, \quad (2)$$

where F is the free energy of the cylindrical sample. After substituting an expression for the free energy (see below) to Eq. (1), the dependence of swelling degrees α_z and α_r on P and Γ will be obtained.

The free energy of a weakly charged gel is expressed as a sum of the different contributions:

$$F = F_{el} + F_{\text{int}} + F_{el-st} + F_{tr} \quad (3)$$

The first term represents the elastic energy of the swollen gel:

$$F_{el} = \frac{1}{2} v k T \left[2 \alpha_r^2 + \alpha_z^2 - \frac{2}{f} \ln(\alpha_r^2 \alpha_z) \right] \quad (4)$$

where T is temperature, k is the Boltzmann constant and f is the functionality of crosslinks of the network.

The second term arises due to the Van der Waals interaction between polymer chains:

$$F_{int} = \nu N \left[\frac{B n_0}{\alpha_r^2 \alpha_z} + \frac{C n_0^2}{\alpha_r^4 \alpha_z^2} \right] \quad (5)$$

where B and C are the second and the third virial coefficients of pair and triple interactions between monomers of size d ($B \sim d^3 (T - \Theta)/T$ and $C \sim d^6$); $n_0 = d^{-3} N^{-1/2}$ is the concentration of monomers in the reference state.

The third term of Eq. (2) corresponds to the electrostatic energy of the system. It may play a significant role when a part of the counter-ions escapes from a polyelectrolyte gel into the surrounding solvent¹³. As a result, the volume fraction β of the counter-ions remaining in the gel is not sufficient to keep the condition of electrical neutrality satisfied, leading to charging of the gel by value $Q = q \nu N m^{-1} (1 - \beta)$ (q is the charge of the counter-ion). In our case the stored energy can be roughly estimated as the energy of a coaxial cylindrical capacitor with the radii of internal and external boundaries corresponding to the radii of the gel R and of the experimental cell $R_{out} = \xi R_0$, i.e.

$$F_{el-st} = \frac{Q^2}{\epsilon L} \ln \left(\frac{R_{out}}{R} \right), \text{ where } \epsilon \text{ is the dielectric}$$

constant of the solvent. Taking into account definitions of the swelling ratios of a free and compressed gel, we obtain the electrostatic contribution to the free energy of the cylindrical system:

$$F_{el-st} = kT \frac{l_B}{d} \frac{\nu^2 N^{3/2} (1 - \beta)^2}{m^2 \nu_z \alpha_z} \ln \left(\xi \frac{\alpha_{0r}}{\alpha_r} \right) \quad (6)$$

Here $l_B = \frac{q^2}{\epsilon kT}$ is the Bjerrum length. For the aqueous system under consideration $l_B = 0.7$ nm at room temperature, which is of the same order as the monomer size $d = 0.8$ nm of our hydrogel and thus we shall consider $l_B / d = 1$.

The last term of Eq. (3) corresponds to the translational entropy of counter-ions located inside and outside a polyelectrolyte gel:

$$F_{tr} = kT \frac{\nu N}{m} \left[\beta \ln \left(\frac{n_0 \beta}{m \alpha_r^2 \alpha_z} \right) + (1 - \beta) \ln \left(\frac{n_0 (1 - \beta)}{m (\xi^2 \alpha_{0r}^2 \alpha_{0z} - \alpha_r^2 \alpha_z)} \right) \right] \quad (7)$$

Substituting then Eqs. (4)-(7) into Eq. (3), and minimising the free energy for determination of the volume fraction of counter-ions, we obtain relationships between the swelling degrees of a polyelectrolyte gel and the applied stresses. For our case, we will neglect the contribution of the Laplace

pressure assuming that the interfacial tension γ between gel and water is about zero for highly swollen hydrogels.

These equations are non-linear and are solved numerically with the following parameters: $N = 100$, $m = 10$, $x = 20$, $y = 1$, $f = 3$, $L_{ref} = 10 R_{ref}$ and $\nu_S = 10^8$ (this value was calculated taking $R_{ref} = 100$ μ m). As a result the expression for the volume change as a function of the reduced applied pressure $V(P)/V_0 = f(P \frac{r_0^2}{kT})$ was obtained for polyelectrolyte gels (see Fig.4, curve 1).

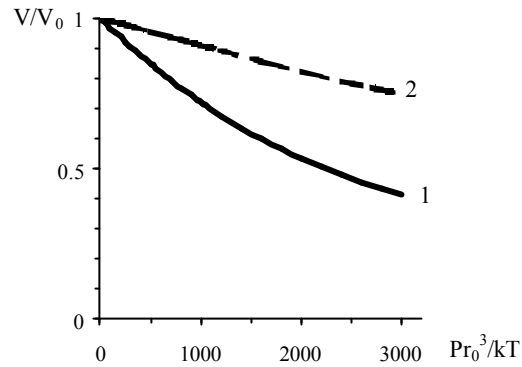


Fig.4. Dependence of the relative volume on the reduced pressure for a polyelectrolyte (1) and a neutral (2) gels.

In order to check if the obtained dependence has a general character, the same procedure was performed for neutral gels. The relative volume change of the neutral gel under uniaxial compression is shown in Fig.4, curve 2.

It is clear that whatever is the gel nature, solvent is released as soon as pressure is applied. The effect is more pronounced for a polyelectrolyte gel. It should be noted that even using a qualitative approach developed for weakly charged gels and substituting very general network characteristics, the trend of the theoretical curve for a polyelectrolyte gel is similar to the one observed in the experiment (compare Fig.4, curve 1 and Fig.3).

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