Notes

Hydrogel under Shear: A Rheo-optical Study of the Particle Deformation and Solvent Release

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Introduction

Hydrogels are chemically cross-linked charged polymer networks that swell in aqueous solutions several hundred times. One of the most striking properties of hydrogels is that they can keep their shape even when polymer concentration inside the gel is very low, less than 1%. In most publications dealing with gel deformation, the hydrogel is deformed less than 10−15% (see, for example, refs 1−4), and experimental results are interpreted either by classical network elasticity theory or using a scaling approach.[5] In rheological and/or compression experiments, it is assumed that there is no solvent release from the deformed gel.

In this paper we report the first results on a rheo-optical study of the hydrogel behavior under shear. A swollen hydrogel particle was immersed in silicon oil and sheared. High gel deformations (>30%) and water release from the particles were observed, both effects being far from the classical hypothesis used to describe gel deformation. It does not seem possible to apply here theories used to interpret either the deformation of a liquid droplet in an immiscible fluid or the behavior of a rigid particle under shear. Solvent release from a gel under simple shear has never been seriously considered and measured. Rheo-optics gives this opportunity and shows that these effects are not negligible. What we demonstrate here are several phenomena that are of a fundamental interest (for example, in the understanding of drug delivery systems) and that can lead to practical applications as well (in food and cosmetics industries).

Materials and Methods

The hydrogel spherical particles used in this study were poly(0.75 sodium acrylate−0.25 acrylic acid), cross-linked by *N*,*N*′-methylenebis(acrylamide), kindly provided by Kobo Products Inc. ("Aqua Keep 10SH-NF"). The maximal swelling degree in water was 280 g/g. Gel particles swollen to different extents (from 10 to 280 g/g, diameter from 70 to 250 μm) were prepared by mixing dry gel powder with a certain amount of distilled water. Here we present results only for particles of 140 μm diameter of two swelling degrees, 110 and 280 g/g.

A small amount of swollen gel particles was immersed into the silicon oil RHODORSIL 47V and gently mixed by hand in order to separate one particle from another. A counterrotating rheo-optical system was used for in situ study of the gel behavior under shear.[6] First, we fixed shear rate and measured the development of the gel size as a function of time. Then, when the gel dimensions were not changing in time any more (this case was considered as a steady state), the shear rate was changed, and the procedure was repeated. As a comparison, we performed the same experiments for a water droplet of the same diameter. The experimental error in the particle size measurements is ±5 μm, which gives less than 10% relative error in deformation calculation.

Results and Discussion

Visual Observations. An example of the hydrogel behavior under shear is presented in Figure 1. It is qualitatively the same for any gel swelling degree and any particle size. The initial state of the gel before shearing is a sphere (Figure 1a).

At low stresses the gel deforms and becomes an ellipsoid. In this setup we measure two particle dimensions: the long axis L and one of the short axes D. The second short axis can be easily calculated from the particle volume conservation. We obtained that it was smaller than D, which means that the gel becomes elongated and flat. We shall use L/D as a measure of a particle deformation.

The increase in the shear stress leads to a solvent release from the swollen hydrogel (see Figure 1b). Two cones of water appear symmetrically at the particle edges in the flow direction. In this case, we shall characterize the gel by two parameters: the deformation of the particle itself L/D (without the water cones) and the deformation of the particle + water L_{g+w}/D (Figure 1c). Both gel deformation and water release under shear are reversible phenomena: if stopping to shear, water is absorbed back by the gel and the particle becomes spherical again.

At high shear stresses ($\sigma > 1500$ Pa), water can be detached from the edges of the cones, and very tiny water droplets are produced which flow separately from the gel. This phenomenon opens new perspectives in the hydrogel applications. The detachment looks similar to what happens when a low-viscosity droplet is sheared in a high-viscosity matrix. Because of interfacial tension effects (like Rayleigh instabilities; see, for example, ref 7), the drop elongates slightly and breaks down. When gel was swollen in water, the loss of solvent was too small to be measured. One way to make solvent detachment easier is to decrease the interfacial tension between solvent and oil. We obtained easy solvent detachment when the same gel was swollen in an aqueous solution of a surfactant (synperonic F127: a triblock poly(ethylene oxide)−poly(propylene oxide) copolymer). However, in this article we shall concentrate only on the general behavior of a swollen-in-water hydrogel under shear.

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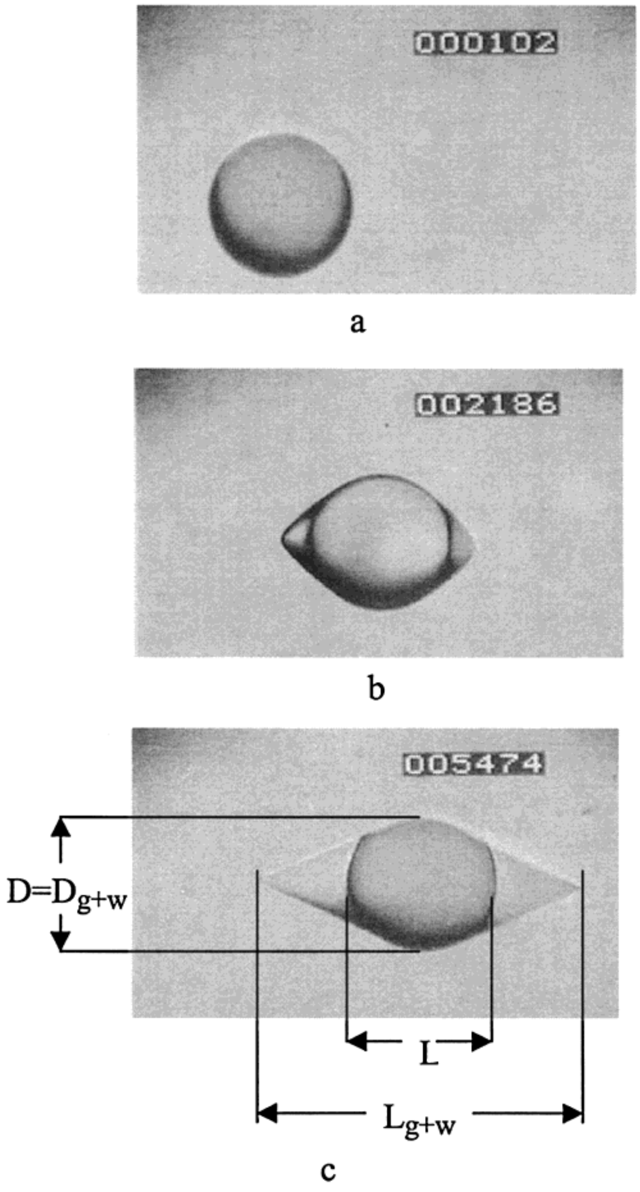

Figure 1. Optical micrographs of a swollen-in-water gel particle in silicon oil between two transparent plates: initial state (no shear) (a), beginning of water release (about 250 Pa) (b), and strong water release (about 800 Pa) (c).

From visual observations, it was clear that the particle and gel + water long axes are not parallel to the transparent plates. In this setup it is not possible to measure the particle orientation with respect to the transparent plates. Thus, an orientation angle had to be imposed in order to calculate the real value of the long axis. For a water droplet in a silicon oil, Cox equations give an orientation angle of 45°, the ratio of water-to-oil viscosity being very small, 10^{-5}. It is not possible to calculate the same viscosity ratio for a gel particle in silicon oil. However, as far as the water cones around the gel visually behave as a low-viscosity droplet in a high-viscosity matrix, we used 45° as the orientation angle and the deformation values L/D and L_{g+w}/D were calculated taking this angle into account. Such an approximation being very rough does not influence the phenomena discussed in this paper.

Hydrogel Deformation and Water Release: Kinetics and Steady-State Results. An example of the kinetics of a deformation of a gel particle swollen to its maximal degree and of gel + released water under shear is presented in Figure 2 together with the deformation of a water droplet of the same initial diameter at 573 Pa. Similar results were obtained for gel particles of other swelling degrees and sizes.

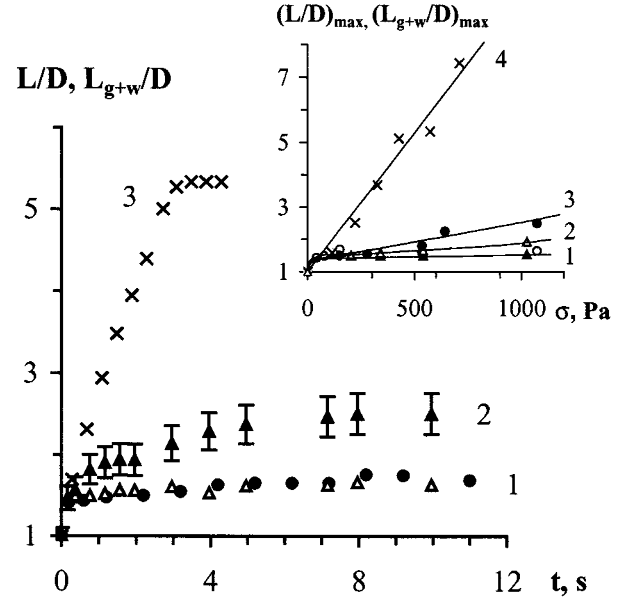

Figure 2. Kinetics of a gel particle of $Q = 280$ g/g deformation (1: $\sigma = 146$ Pa (opened symbols) and 1074 Pa (dark symbols)), gel + water (2), and water droplet (3). Inset: steady-state deformation as a function of shear stress for a gel particle (1: $Q = 110$ g/g (dark symbols) and 280 g/g (opened symbols)), gel + water for gel with $Q = 110$ g/g (2) and 280 g/g (3), water droplet (4). Lines are given to guide the eye.

After the beginning of shear, the gel particle starts to deform, and in a few seconds the deformation reaches its maximal value of about 1.7. At high stresses, water starts to release from the gel, L_{g+w}/D being obviously greater than L/D and also reaching its maximal value in a few seconds. As long as the shear stress is then not changed, the gel particle with two water cones around it flows without changes (steady state). The kinetic curves of gel, gel + water, and water droplet have the same trend. As soon as water is released, the ratio L/D for the particle remains constant in time, but the absolute values of the gel dimensions decrease.

The dependence of the maximal deformation of a particle $(L/D)_{max}$ and of gel + water $(L_{g+w}/D)_{max}$ on the shear stress σ is shown in the inset of Figure 2. A remarkable feature is that the gel deformation in the steady state practically does not depend on the applied shear stress. For the same shear stress, more water is released from a higher swollen gel, and as far as water droplets can be easily deformed in many times (see curve 4), $(L_{g+w}/D)_{max}$ depends on the shear stress and the values of $(L_{g+w}/D)_{max}$ for 280 g/g are higher than that for 110 g/g.

The parameter characterizing the moment of reaching a steady state for a gel and gel + water particles is time, because it turned out to be independent of the shear stress and it is practically the same for a gel and gel + water particle: 7.5 ± 1.5 s for a gel at $Q = 280$ g/g and 10 ± 2 s for a gel at $Q = 110$ g/g. These values are 1.5−2 times higher than that for a droplet of water (5.5 ± 1 s). Since the time to reach equilibrium is independent of shear stress, it must be controlled only by the internal relaxation time of the gel deformation.

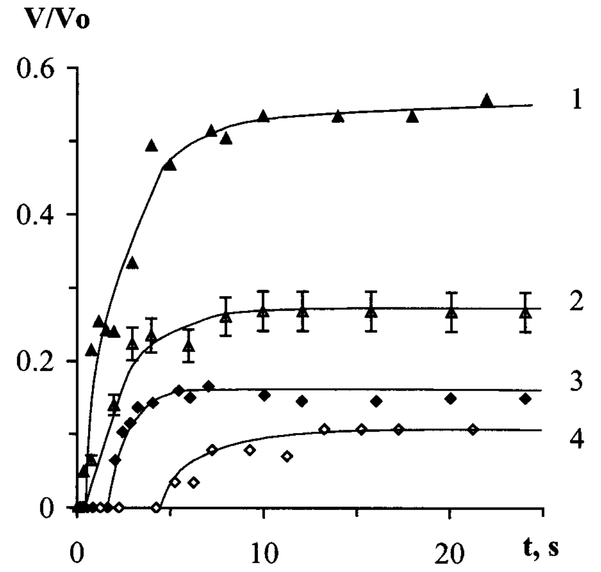

Figure 3. Development of the relative volume of released water in time for a gel swollen at 280 g/g (shear stress of 1074 Pa (1) and 535 Pa (3)) and at 110 g/g (shear stress of 1026 Pa (2) and 540 Pa (4)). Lines are given to guide the eye.

The volume *V* of released water was estimated as a sum of the volumes of two equal cones (see Figure 1b,c). The development of the released water volume as a function of time for several shear stresses is presented in Figure 3 for both swelling degrees, expressed as the relative volume V/V_0, V_0 being the volume of the spherical gel particle at rest.

After starting to shear, it takes some time before water releases from the gel. Then the amount of released solvent increases in time and reaches a certain maximal value. At any time of shearing, the higher are shear stress and degree of swelling, the more solvent is released. Its amount can be very high, up to 50% of the initial gel size (Figure 3, curve 1).

A criterion reflecting the moment of solvent release that is independent of shear stress was found. It is a certain deformation value $L/D \approx 1.5$ that is needed to be reached when the reaction of the gel to shear increase (above 200–250 Pa) is not to increase its deformation, but to release water. This value does not depend on gel degree of swelling within the studied region.

The fact that above a certain shear stress the gel releases solvent as a reaction to further stress increase means that the hydrogel thermodynamic equilibrium (balance between swelling and elastic forces) is broken, and under stress the gel reaches a new swelling degree. The applied stress is acting in the same way as if the gel elastic modulus is increased or if the solvent quality and/or degree of ionization are decreased. Thus, the moment of solvent release is an important factor, which reflects gel intrinsic properties. It can be taken as a measure of a gel swelling pressure and studied by rheo-optics.

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