

Electronic Supplementary Information 2

Hydrogel pore diameter from mechanical testing

Context

The aim of this supporting information section is to provide the detailed theory for evaluation of the average pore size from mechanical testing of hydrogel samples. This provides the derivation of eq. 13 in the main text.

Water flow in hydrogels

Covalently crosslinked alginate hydrogels show stress relaxation which has been linked to the migration of pore water under pressure gradients.¹ Pore water migration in hydrogels, in turn, is tightly linked to the pore radius in the framework of the Darcy hydraulic conductivity theory of porous media.² Indeed, the flow speed of pore water in a porous medium is proportional to the pressure gradient, according to²:

$$v = -\frac{K_s}{\eta} \cdot \frac{\partial P}{\partial x} \quad (\text{S8})$$

where K_s is the Darcy permeability coefficient, η the pore fluid's viscosity, P the pressure and x a spatial coordinate along which the pressure gradient and flow are measured. The Darcy permeability K_s is directly linked to the pore radius³:

$$r_{\text{pore}} = \sqrt{8K_s} \quad (\text{S9})$$

where we have assumed a fraction pore volume of $\varepsilon \approx 1$ (cf. eq. 2 in ³).

Stress relaxation

In stress relaxation, the origin of the pore pressure gradient is the mechanical compression. Indeed, upon rapid uniaxial compression, the hydrogel will behave nearly incompressibly, leading to an apparent Poisson ratio of 0.5; as water loss leads to volume loss, the gel tends towards a purely uniaxial compression state with a Poisson ratio of 0, as suggested by a decrease of quite exactly 50% of the stress observed in a typical stress relaxation experiment¹. The physics of the compression process and stress relaxation experiment is outlined in Fig. S10:

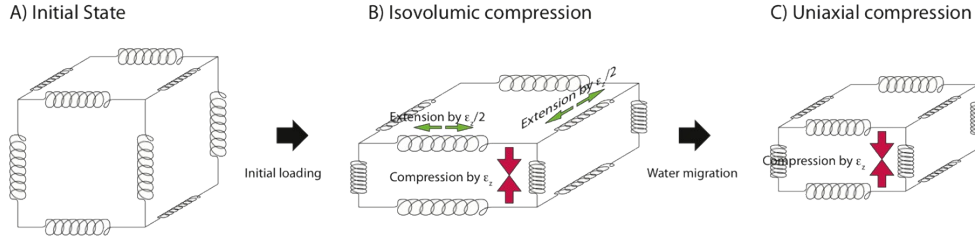


Figure S10. Schematic view of the stress relaxation in covalently crosslinked hydrogels. The initial compression is isovolumetric, due to the intrinsic incompressibility or wall material and pore water, so when applying rapid initial loading (from A to B), lateral expansion compensates volume loss from uniaxial compression. Only upon stress relaxation the pore water is lost, and with it the associated lateral expansion (from B to C).

Taking the relaxation as being a transition from Poisson's ratio of 0.5 to 0, the pressure in the pores can be seen as being responsible for the initial lateral extension, it therefore is given by:

$$P = E^*(\epsilon_x + \epsilon_y) \quad (\text{S11})$$

Where E is the Young modulus of the polymer network, and the strains ϵ_x and ϵ_y represent the expansion perpendicular to the compression force (initial volume conservation at a Poisson ratio of 0.5 implies $\epsilon_x + \epsilon_y = -\epsilon_z$, z being the direction of mechanical compression). The lateral strain ϵ_x and ϵ_y represents excess pore water that needs to be evicted from the pores before achieving $P=0$, hence we can also write

$$P = \frac{\Delta V}{V} E \quad (\text{S12})$$

where $\frac{\Delta V}{V}$ is the relative excess water; immediately after compression, we have $\frac{\Delta V}{V} = -\epsilon_z$, while after stress relaxation, $\frac{\Delta V}{V} = 0$.

In microscopic terms, excess pore water volume is lost over time due to gradients of the flow speed v throughout the gel:

$$\frac{\partial}{\partial t} \left[\frac{\Delta V}{V} \right] = -\frac{\partial v}{\partial x} = \frac{K_s}{\eta} \frac{\partial^2 P}{\partial x^2} = \frac{EK_s}{\eta} \frac{\partial^2}{\partial x^2} \left[\frac{\Delta V}{V} \right] \quad (\text{S13})$$

By comparison with Fick's law of diffusion under mass conservation, the excess pore water volume $\frac{\Delta V}{V}$ follows a diffusion equation:

$$\frac{\partial}{\partial t} \left[\frac{\Delta V}{V} \right] = D_{app} \frac{\partial^2}{\partial x^2} \left[\frac{\Delta V}{V} \right] \quad (\text{S14})$$

where the apparent “diffusion” coefficient D_{app} is given by:

$$D_{\text{app}} = \frac{EK_s}{\eta} = \frac{Er_{\text{pore}}^2}{8\eta} \quad (\text{S15})$$

It should be stressed that even though the mathematical form of eq. S13 corresponds to the general form of diffusion equations for heat and molecules by thermal agitation, the water flow in the hydrogels is not technically a diffusive process, but rather bulk laminar flow in the small pores.

Fitting of experimental data

Given that the pore pressure P and the excess pore water volume are proportional, the local pressure will also follow the linear mathematics for a diffusing substance or heat, and the stress relaxation process in our disk-shaped samples can be described by adopting the solution for heat diffusion, with an originally homogeneous temperature, from a circular region bounded by a different temperature. The solution to this problem is known⁴, and by integration over the disk, we can write for the temporal evolution of the force $F(t)$ measured during the stress relaxation experiment :

$$F(t) = F_{\text{relaxed}} + 4(F_0 - F_{\text{relaxed}}) \sum_{n=1}^{+\infty} \frac{\exp\left(-j_{0,n}^2 \frac{t}{\tau}\right)}{j_{0,n}^2} \quad (\text{S16})$$

where F_{relaxed} is the force remaining after complete stress relaxation, F_0 the initial force, and $j_{0,n}$ is the n -th zero of the Bessel function of the first kind J_0 , while τ is the stress relaxation time we desire to obtain. Eq. S16 essentially describes an exponential decay of the stress, with only minor corrections namely at small times t , arising from the terms with $n > 1$. The relaxation time constant τ is linked to the physical radius the disk R_{sample} , as well as the underlying apparent diffusion coefficient⁴:

$$\tau = \frac{R_{\text{sample}}^2}{D_{\text{app}}} \quad (\text{S17})$$

such that we finally obtain for the pore radius:

$$r_{\text{pore}} = R_{\text{sample}} \sqrt{\frac{8\eta}{E\tau}} \quad (\text{S18})$$

which is given in the main text as eq. 13.

Bibliography

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4. E. W. Carslaw and J. C. Jaeger, *Proc. London Math Soc.*, 1940, **46**, 361-388.