

Appendix A. Supplemental movies

Supplemental movie 1 shows the failure of an agar gel prepared from a fresh agar sol ($\mathcal{T} \approx 1$ hour) together with the simultaneous evolution of the normal stress during a macro-indentation experiment. The corresponding data are pictured in Fig. 8 in the main text. **Supplemental movie 2** shows the result for a similar indentation experiment performed on a gel prepared from the same agar sol which has been submitted to $\mathcal{T} = 5$ days of incubation at $T = 80^\circ\text{C}$. The corresponding data are pictured in Fig. 10 in the main text.

Appendix B. Supplemental figures

Supplemental Fig. B.12 shows the viscosity of three solutions of different agar concentrations: $c = 0.5, 1$ and 2 mg/mL, determined after different incubation times \mathcal{T} ranging from a few hours to 5 days (colors from black to yellow). The three solutions are stored together in the same thermal chamber to ensure the same thermal history. The viscosity of samples drawn at regular time intervals are determined by steady shear experiments over the following range of shear rates $1 \leq \dot{\gamma} \leq 100 \text{ s}^{-1}$ (see subsection 2.2.1 in the main text for technical details).

Supplemental Fig. B.13 shows the diffraction spectra of hydrated gels prepared after different incubation

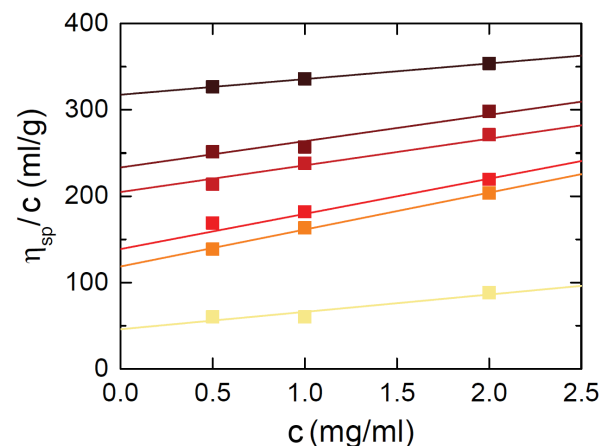


Figure B.12: (Color online) Reduced viscosity $(\eta - \eta_s)/\eta_s c$ vs. the polymer concentration c , where η_s denotes the viscosity of the solvent (water at $T = 50^\circ\text{C}$). Colors from black to yellow correspond to different incubation times of the solutions at $T = 80^\circ\text{C}$: $\mathcal{T} = 1$ hour, 1 day, 2 days, 3 days, 4 days and 5 days. Measurements are performed in a cone and plate geometry at $T = 50^\circ\text{C}$. Each point corresponds to an average over the following range of shear rate: $1 \leq \dot{\gamma} \leq 100 \text{ s}^{-1}$. Lines denote the best linear fit of the data and the intercept provides an estimate of the intrinsic viscosity $[\eta]$ of the solution as a function of the incubation time \mathcal{T} .

times \mathcal{T} of the same agar solution, for \mathcal{T} ranging from of a few hours to 5 days. Contrarily to the data reported in Fig. 5(d) in the main text of the manuscript which concern dried gels, the present experiments were conducted on fully hydrated gels enclosed in sealed glass capillaries. The diffraction spectra show mainly a single maximum at $q_3 = 19.3 \text{ nm}^{-1}$ also visible on dry gels, and whose amplitude decreases with increasing incubation times \mathcal{T} . The two other maxima visible on dry gels at $q_1 = 9.45 \text{ nm}^{-1}$ and $q_2 = 13.86 \text{ nm}^{-1}$ [see Fig. 5(d) in the main text] are barely visible here. Indeed water molecules in the gel, linked to the polymer network through hydrogen bonds are responsible for a modulation of the scattered peaks, thus degrading the angular spectrum resolution.

Supplemental Fig. B.14(a) shows the apparent elastic modulus E^* as determined by the slope of the stress-strain relation $\sigma(\epsilon)$ at strains lower than a few percents for various gel thicknesses H . The former physical quantity is measured by macro-indentation experiments similar to the one reported in Fig. 8 in the main text, and performed at constant indentation velocity using a flat-ended cylinder (see subsection 2.2.1 in the main text for technical details). To convert the apparent compression modulus E^* which increases with the gel thickness, into a true compression modulus E , we take into account the cylindrical shape of the indenter, the finite thickness H of the gel disk which is of comparable size to the indenter diameter $2r = 10 \text{ mm}$ and the stress singularity at the sharp edge of the indenter.

The true compression modulus reads as follows

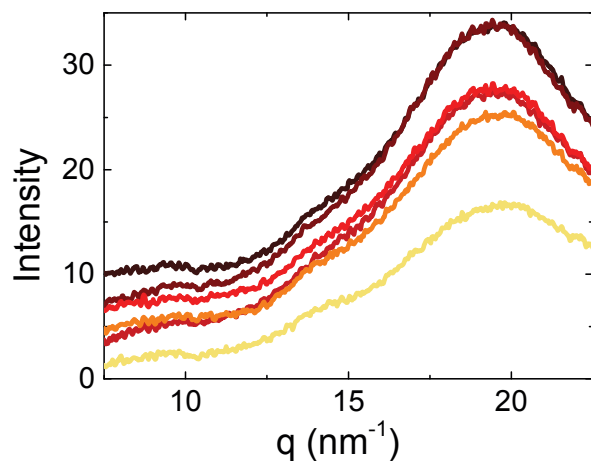


Figure B.13: (Color online) X-ray diffraction spectra $I(q)$, where q stands for the wavenumber. Colors from black to yellow correspond to gels prepared after different incubation times at $T = 80^\circ\text{C}$ of the same agar solution: $\mathcal{T} = 1$ hour, 1 day, 2 days, 3 days, 4 days and 5 days. Experiments are performed on the hydrated gels.

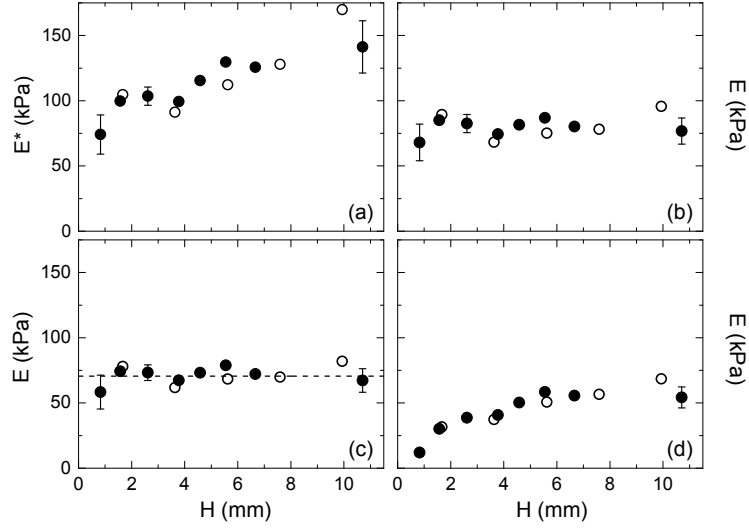


Figure B.14: (a) Evolution of the apparent compression modulus $E^* = \partial\sigma/\partial\epsilon$ as determined during indentation experiments vs the gel thickness H . The two types of symbols correspond to experiments performed at different indentation velocities: (\circ) $v = 50 \mu\text{m/s}$ and (\bullet) $v = 100 \mu\text{m/s}$. Each point corresponds to a gel prepared from a fresh agar sol, i.e. from an agar solution incubated at $T = 80^\circ\text{C}$ for less than a day. (b)–(d) Compression modulus E derived from E^* shown in (a) using the expression (B.1) with a Poisson coefficient $\nu = 0.0$ in (b), $\nu = 0.3$ in (c) and $\nu = 0.5$ in (d). The black horizontal dashed line in (c) corresponds to the best linear fit of the data, leading to $E = 70 \pm 7\text{kPa}$

(Hayes et al., 1972):

$$E = (1 - \nu^2) \frac{r}{H} \frac{\pi}{2\kappa} E^* \quad (\text{B.1})$$

where ν denotes the Poisson coefficient of the gel, and κ is a numerical correction related to the finite size of the sample which depends on r , H and ν . The Poisson coefficient ν is unknown and necessary to determine the value of κ . We report in Fig B.14(b)–(d) the compression modulus computed for three different values of ν , namely $\nu = 0.0, 0.3$ and 0.5 . In each case, the value of κ is determined using the integral expression proposed in ref. (Haider & Holmes, 1997) for $\nu = 0$, and in ref. (Hayes et al., 1972) for $\nu > 0$. Relying on the assumption that the true compression modulus E should neither depend on the gel thickness H , nor on the indentation speed, we can rule out the value $\nu = 0.5$ [Fig. B.14(d)]. Moreover the data obtained with $\nu = 0.0$ also exhibit a non-negligible dependence with H [Fig. B.14(b)]. Finally, the lowest dependence of E with the gel height is obtained with the following interval ν : $0.1 \leq \nu \leq 0.3$, as illustrated in Fig. B.14(c) for $\nu = 0.3$. The latter range of values is considered in the main part of the manuscript.

Supplemental Fig. B.15 shows gelation experiments of samples extracted from an agar sol after various incubation times, in a similar fashion to the data reported in Fig. 4 in the main text. Here the experiments are performed exceptionally with an agar powder provided by BioMérieux instead of Sigma-Aldrich. The former agar

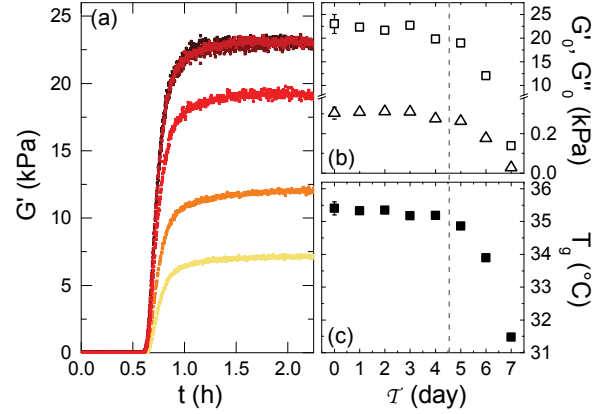


Figure B.15: (Color online) Gelation experiments performed on a 1.5% wt. agar sol, which agar is provided by BioMérieux instead of Sigma-Aldrich. (a) Elastic modulus G' vs time t during the cooling from $T = 70^\circ\text{C}$ down to 20°C , at $\dot{T} = 1^\circ\text{C}/\text{min}$ of various samples extracted from the same agar sol after various incubation times $\mathcal{T} = 1$ hour, 2 days, 4, 6 and 7 days coded in color from black to yellow. (b) Steady-state values of the elastic (G' , \square) and viscous (G'' , \triangle) moduli reached at the end of the gelation process vs \mathcal{T} . (c) Gelation temperature T_g defined as the crossing temperature of G' and G'' , vs the incubation time \mathcal{T} . Error bars in (b) and (c) are only indicated on the first point and were determined by repeating the experiment with three different agar solutions.

also consists of 70% of agarose and 30% of agarpectin, but comes from a different geographic origin than the one commercialized by Sigma-Aldrich and may contain

different ions, surfactants, etc., which allows us to test the robustness of our result. Here, an incubation period at $T = 80^{\circ}\text{C}$ larger than 5 days is necessary to form weaker gels that display a delayed gelation [Fig. B.15(b) and (c)]. Although the agar provided by BioMérieux is more resistant to extended heating durations than the agar from Sigma-Aldrich, the same phenomenology is observed which shows that the results reported in the main text are not specific to a certain brand of agar.