Cellulose nanofibril gels with shear-controlled fibril orientation

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Supplementary information:
Theoretical prediction of diffusion-controlled gelation.

When salt or acid is injected into a semi-dilute dispersion of cellulose nanofibrils, a gel forms at the point of the injection and spreads as the ions diffuse through the system. This is measured indirectly by considering the development of the stiffness of the gelling system over time.

1 Plate–plate rheology

We consider the thin, cylindrical domain between the parallel plates of a rheometer. The gap size is denoted by h and the radius of the domain is R_0.

1.1 Diffusion

It is ssumed that Einstein diffusion governs the development of the ion concentration c between the plates. Because $h \ll R_0$, we may consider two-dimensional diffusion on a circular domain with radius R_0. Using polar coordinates (r, ϕ), the concentration $c(r, \phi, t)$ is described by

$$\frac{\delta c}{\delta t} = D\Delta c, \qquad \left.\frac{\delta c}{\delta t}\right|_{r=R_0} = 0, \quad (1)$$

with D the diffusivity and Δ the Laplace operator. If acid is injected at a distance a from the origin at time $t = 0$, the initial concentration can be approximated by

$$c(r, \phi, t) = \bar{c}\delta(r\cos\phi - a, r\sin\phi), \quad (2)$$

where $\bar{c}$ is the average concentration of ions in the entire domain and $\delta(x, y)$ is the Dirac delta function in two dimensions.

The gel region includes the points (r, ϕ) such that $c > c_{gel}$, where $c_{gel} = 0.1$ mM (pH 4) for protons. Hence, the shear modulus of at any point is

$$G(r,\phi,t) = G_{gel}\Theta\big[c(r,\phi,t) - c_{gel}\big].$$

Here, G_{gel} is the shear modulus of the gel and Θ is Heaviside's function. The development of the gel, and thus the local shear modulus, is obtained numerically.

1.2 Apparent shear modulus

In a plate–plate geometry, the shear strain increases linearly with the radius: $\gamma = r\Delta\phi/h$, where $\Delta\phi$ is the rotation applied by the rheometer. The polar traction acting on the rheometer plate is thus

$$\tau(r,\phi,t) = G(r,\phi,t)\gamma = \frac{r\Delta\phi}{h}\,G(r,\phi,t). \qquad (3)$$

We find the torque T by integrating τ across the plate:

$$T(\Delta\phi,t) = \int_{r=0}^{R_0}\int_{\phi=0}^{2\pi} r^2\,\tau(r,\phi,t)\,d\phi dr = \int_{r=0}^{R_0}\int_{\phi=0}^{2\pi} r^3\ \Theta\big[c(r,\phi,t) - c_{gel}\big]\,d\phi dr. \qquad (4)$$

Understanding that the rheometer reports an apparent storage modulus $G' = \alpha T/\Delta\phi$ in the zero frequency limit, where α is a constant such that $G' = G'_{gel}$ when the gel fills the domain, we obtain

$$\frac{G'(t)}{G'_{gel}} = \frac{2}{\pi R_0^4}\int_{r=0}^{R_0}\int_{\phi=0}^{2\pi} r^3\ \Theta\big[c(r,\phi,t) - c_{gel}\big]\,d\phi dr. \qquad (5)$$

Now, combining the numerical solution for the development of the ion concentration c with Eq. (5) gives the time development of the apparent storage modulus at low frequencies.