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Electronic Supplementary Information: Nonlinear elasticity and transition to macroscopic irreversibility in composite hydrogels

Ippolyti Dellatolas,^{*a} Thibaut Divoux,^{b,c} Emanuela Del Gado,^d and Irmgard Bischofberger^{*a}

Microscopic evidence of local hydrogel densification around nanofillers

To characterize the microstructure of the filler-hydrogel composites, we perform small-angle X-ray scattering experiments at the Brookhaven National Laboratory (NSLS-II, CMS11) on nanofiller suspensions and filler-hydrogel composites at $T \approx 25$ C. Figure S1A shows the scattering intensities for a suspension of nanofillers ($r_f = 100$ nm, $\phi_f = 0.04$) and for a filler-gelatin composite with gelatin concentration $c_{\text{gel}} = 10$ wt% containing nanofillers of the same radius and volume fraction as the suspension. In both cases, the scattering intensities exhibit well-defined peaks, consistent with the form factor of spherical nanoparticles, confirming that the nanofillers are well dispersed in the hydrogel. For the suspension, the peaks are consistent with nanofillers of average radius $r_f \approx 100$ nm. In contrast, the composite exhibits peaks shifted to lower wave vector q , indicating a larger effective particle size. This shift provides direct evidence of local hydrogel densification around the nanofillers, giving rise to "effective fillers" composed of nanofillers and their surrounding densified hydrogel layer.

Local densification is further confirmed by atomic force microscopy (AFM) nanoindentation experiments (Nanowizard 4, JPK) in which we quantify the spatial variation of the gel elastic modulus E as a function of the radial distance ΔR from the nanofiller surface. We report the elastic modulus normalized by that of the pure gelatin far from any filler, E/E_0 , as a function of the normalized distance, $\Delta R/r_f$. The local elastic modulus decays exponentially with distance to filler surface, as shown in Fig. S1B. Fitting this decay yields a characteristic length scale comparable to that of the nanofiller radius r_f , indicating that the mechanically stiffened region extends roughly one particle radius into the surrounding polymer matrix. Close to the nanofiller, the gel is significantly stiffer, and the modulus relaxes monotonically to that of the pure gel at larger distances. This spatial profile is consistent with the presence of a locally densified hydrogel shell surrounding each nanofiller.

^a Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139. E-mail: ippolyti@mit.edu, irmgard@mit.edu

^b ENSL, CNRS, Laboratoire de Physique, F-69342 Lyon, France.

^c International Research Laboratory, French American Center for Theoretical Science, CNRS, KITP, Santa Barbara.

^d Department of Physics and Institute for Soft Matter Synthesis and Metrology, Georgetown University, Washington, DC 20057.

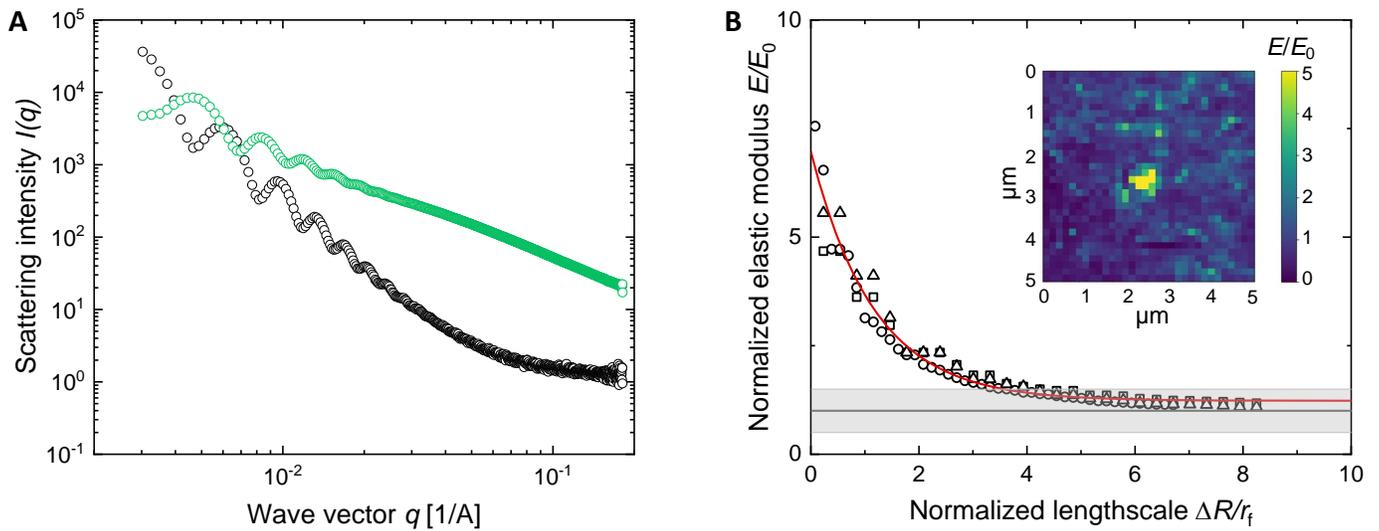


Fig. S1 Local hydrogel densification around the nanofillers. (A) Small angle X-ray scattering (SAXS) intensities $I(q)$ of a suspension of nanofillers of radius $r_f = 100$ nm and volume fraction $\phi_f = 0.04$ (black symbols) and of a nanofiller-gelatin hydrogel composite with gelatin concentration $c_{\text{gel}} = 10$ wt% containing nanofillers of radius $r_f = 100$ nm at a volume fraction of $\phi_f = 0.04$ (green symbols). The shift of the peaks in scattering intensity to lower values of the wave vector q is consistent with a denser layer of hydrogel around the nanofillers in the composite and provides evidence of local hydrogel densification. (B) Elastic modulus of the composites E normalized by the elastic modulus of the pure gel E_0 as a function of normalized distance to the nanofiller surface $\Delta R/r_f$. Different symbols denote different samples. The solid red line corresponds to an exponential fit. The fit identifies a characteristic length scale corresponding to a densification layer thickness of the order of the nanofiller radius. The solid gray line corresponds to a value of 1. Inset: Color map of the normalized elastic modulus in an area $5 \mu\text{m} \times 5 \mu\text{m}$ centered around a nanofiller.

Characteristic strains in composite systems

We consider the following characteristic strains in the viscoelastic response of the composite hydrogels: (i) the strain γ_{nl} characterizing the onset of nonlinearity defined as the strain at which G' and G'' are no longer within 5% of the linear value, (ii) the strain γ'_{max} at which G' reaches its maximum, (iii) the strain γ''_{max} at which G'' reaches its maximum, and (iv) the strain γ_c corresponding to the crossover of G' and G'' . We identify these characteristic strains in the pure hydrogel ($c_{gel} = 10$ wt%, $\phi_f = 0$) and in composites containing nanofillers at volume fractions $\phi_f = 0.0005 - 0.09$. All characteristic strains decrease with increasing nanofiller volume fraction, indicating that smaller deformations are sufficient to induce nonlinearity, including the overshoot of G' associated with strain stiffening, and the overshoot of G'' , as shown in Fig. S2. This trend is consistent with the fact that the nanofillers induce global stiffening of the composite hydrogel by suppressing fluctuations of gel strands.¹

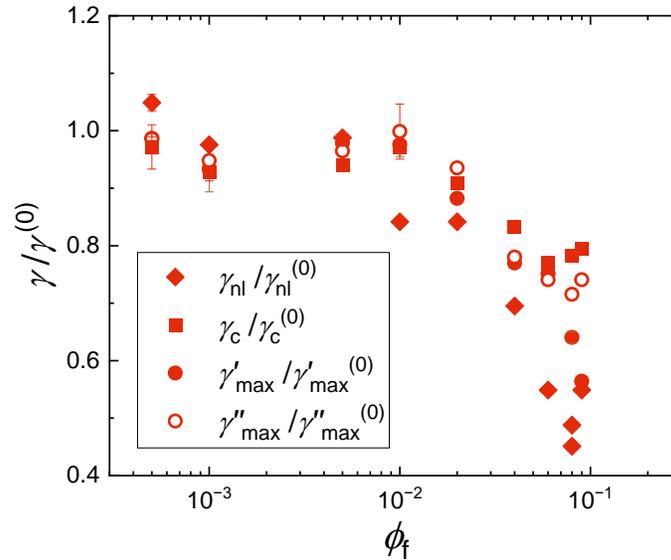


Fig. S2 Characteristic strains in hydrogel composites. Strain γ_{nl} characterizing the onset of nonlinearity, strain γ'_{max} at which G' reaches its maximum, strain γ''_{max} at which G'' reaches its maximum, and strain γ_c at which G' and G'' cross over, normalized by the corresponding strains in the pure gelatin hydrogel ($\gamma^{(0)}$), as a function of filler volume fraction ϕ_f . All characteristic strains decrease in a similar way with ϕ_f .

Extent of strain stiffening

To compare the extent of strain stiffening in pure and composite hydrogels, we report the normalized difference between the maximum of the elastic modulus and the modulus at the onset of nonlinearity, $\Delta G'/G'_{nl} = (G'_{max} - G'_{nl})/G'_{nl}$. This measure is reported for pure hydrogels with concentrations $c_{gel} = 10 \text{ wt\%} - 18 \text{ wt\%}$ and for composites with gelatin concentration $c_{gel} = 10\%$ and nanofiller volume fractions $\phi_f = 0.0005 - 0.09$. The extent of strain stiffening is reported as a function of the gel plateau modulus G'_p , which varies with both gelatin concentration and filler content. We find that the strain stiffening depends only on the hydrogel modulus and decreases similarly for pure gels and composites, as shown in Fig. S3.

This behavior contrasts with that observed in filled rubbers, where the addition of nanofillers typically leads to strain softening, where the elastic modulus G' decreases with applied strain^{2,3}, attributed to the breakup of the network of nanofillers under large deformations. In our case, nanofillers do not form a network in direct contact, but are instead surrounded by a densified layer of hydrogel matrix. These structures act as "effective fillers" composed of the nanofillers and their surrounding matrix shell. Any breakup of an effective filler network would therefore require bond breakage within the hydrogel network itself, rather than mere disruption of filler–filler contacts.

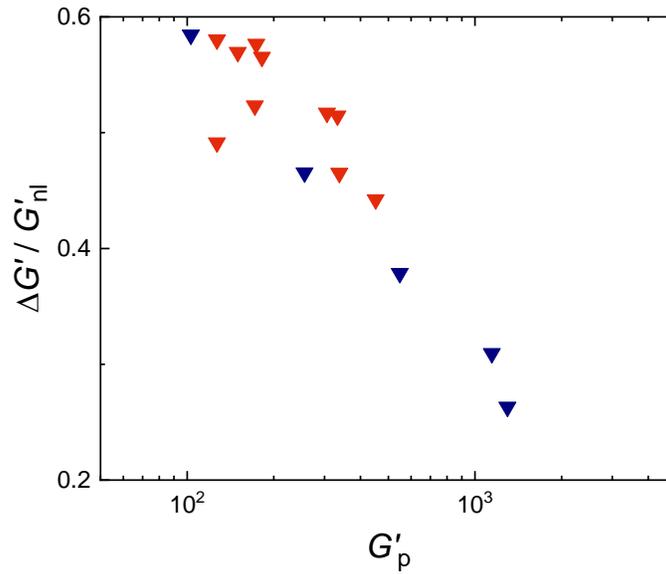


Fig. S3 Extent of strain stiffening in pure hydrogels and composites. Extent of strain stiffening defined as the difference between the maximum elastic modulus G'_{max} and the elastic modulus at the onset of nonlinearity G'_{nl} , normalized by G'_{nl} , $\Delta G'/G'_{nl} = (G'_{max} - G'_{nl})/G'_{nl}$, as a function of the modulus of the gel in the linear regime, *i.e.*, the plateau modulus G'_p , for pure hydrogels (blue symbols) and for composites with filler volume fractions $\phi_f = 0.0005 - 0.09$ (red symbols). The extent of strain stiffening decreases similarly in the pure hydrogels and in the composites, and only depends on the hydrogel modulus.

Recovery of the linear viscoelasticity in strain sweep series

When the gel is subject to a series of strain amplitude sweeps, it can recover its linear viscoelasticity even when the final strain amplitude γ_f in the strain amplitude sweeps is deep within the macroscopically irreversible regime. The moduli G' and G'' recover their plateau values after a certain delay time t_{rec} corresponding to a transient regime, as shown in Fig. S4A. This delay time increases with the final value of the strain in the strain amplitude sweep: The further the gel has been brought into the macroscopically irreversible regime, the longer it takes for it to recover its linear viscoelasticity, as reported in Fig. S4B.

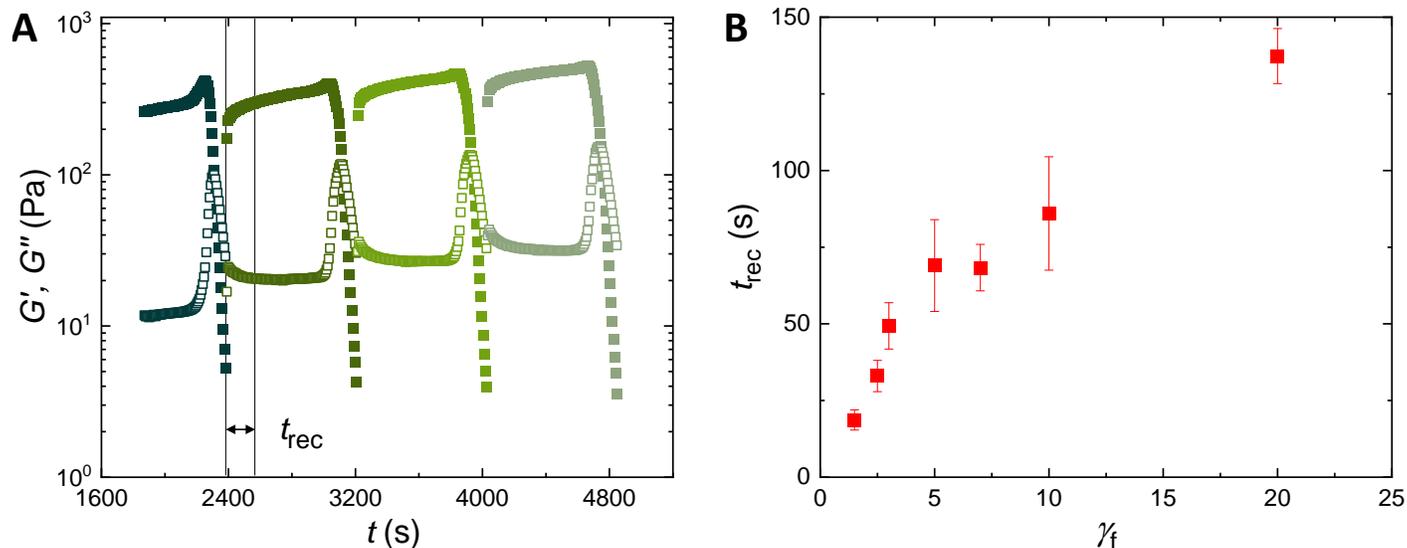


Fig. S4 Time to recover linear viscoelasticity in strain sweep series. (A) Elastic G' and viscous G'' moduli during a series of strain amplitude sweeps of maximum final strain amplitude $\gamma_f = 20$ for a composite hydrogel containing a filler volume fraction $\phi_f = 0.08$. The elastic and viscous moduli in the linear regime are recovered after a time t_{rec} . (B) The time to recover the linear viscoelasticity t_{rec} increases with the maximum final strain amplitude of the strain amplitude sweeps, indicating that the gel undergoes more extensive rearrangements when it is brought further into the macroscopically irreversible regime.

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