Charge-driven interfacial gelation of cellulose nanofibrils across the water/oil interface

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OCNF coverage at W/O interface

Assuming a single oxidised cellulose nanofibril (OCNF) as a perfect cylinder, its volume (V_f) is

$$V_f = \pi\, r^2\, L = 616\, nm^3 = 6.16 \cdot 10^{-24}\, m^3$$

where r and L are respectively the radius (3.5 nm) and the length (160 nm) of OCNF. (DOI:10.1039/C8CP00355F)

The mass of a single OCNF (g_f) is

$$g_f = \rho \cdot V_f = 9.24\ \cdot 10^{-18}\, g$$

Where ρ is the OCNF density (*ca.* 1500 Kg/m^3).(10.1002/jps.20459)

Since the total mass of the fibrils (g_t) is known (for the case of interfacial shear rheology experiments 18.2 ml of 100 ppm OCNF were employed $g_t = 1.82 \cdot 10^{-3}$ g), it is possible to calculate the total number of fibrils (Nf) as:

$$N_f = \frac{g_t}{g_f} = 1.97\ \cdot 10^{14}$$

Assuming a perfect single layer 2D packing of OCNF at the W/O interface, it is possible to consider OCNF as a 2D object, hence, the surface area at W/O interface occupied by a single OCNF (Si_f) can be estimated as for a rectangular object.

$$Si_f = (2r) \cdot L = 1120\, nm^2 = 1.12\ \cdot 10^{-11}\, cm^2$$

and the total surface area occupied by N_f (*Si*) calculated as

$$Si = N_f \cdot\ Si_f = 2.21\ \cdot 10^3\, cm^2$$

For the case of interfacial shear rheology experiments, Si for the concentration of OCNF used was much greater than the W/O interface generated in the Couette cell geometry (18.81 cm^2).

Bulk contribution at the W/O interface

The bulk contribution to the surface stress needs to be estimated. The Boussinesq number, Bo, estimated using the following equation, allows decoupling of these two effects.[1,2]

$$Bo = \frac{|G_i^*|}{(\eta_1 + \eta_2)\omega r}$$

Where $|G_i^*|$ (Pa·m) is the interfacial complex modulus, defined as

$$|G_i^*| = |\sqrt{G_i'^2 + G_i''^2}|$$

(G_i' being the interfacial storage modulus and G_i'' the interfacial loss modulus), η_1 and η_2 are the viscosities of the bulk phases (Pa·s), ω is the angular frequency (rad·s^{-1}) and *r* is a characteristic distance of the flow geometry (7 ×10^{-4} m).[3] For Bo $\gg$ 1, the contribution of the bulk phase can be neglected, whilst for Bo ~ 1 the bulk contribution must be considered. For $|G_i^*|$ > 10^{-3} Pa·m, the low viscosity of the 100 ppm OCNF dispersion (similar to that of pure water) and the low value of ω employed in this study generated a value of Bo $\gg$ 1 (e.g., Bo > 1000 after 1000 s in TS1 measurements), ensuring a negligible bulk contribution. On these grounds, we assert that the rheological measurements performed at the W/O interface effectively capture interfacial phenomena only.

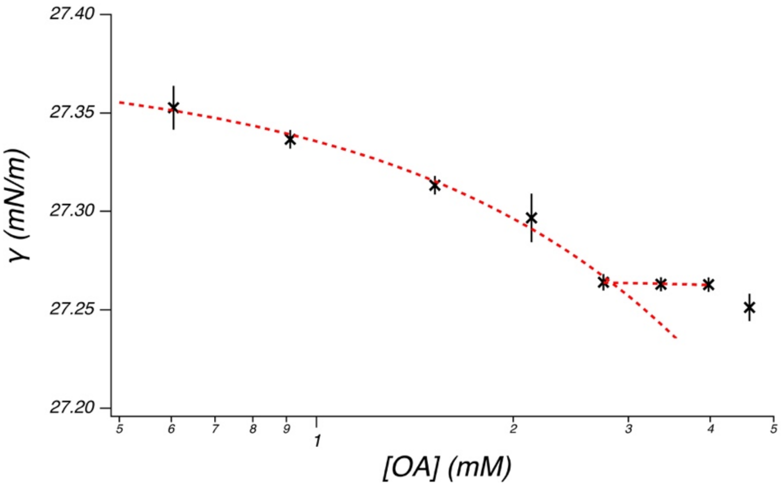

Fig. S1 Surface tension (γ) *vs* OA concentration (mM) measured at Oil-Air interface. The change in slope, considered as the CMC, was obtained by fitting the data to two linear equations.

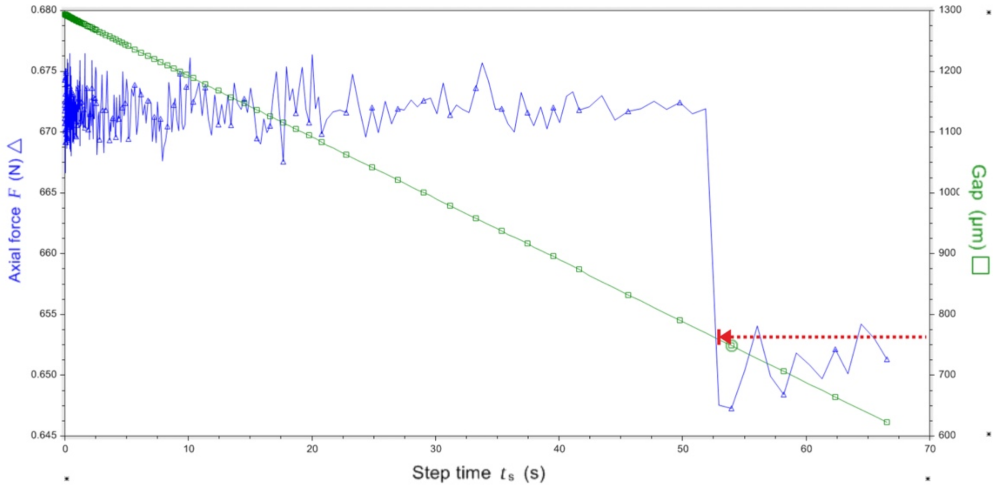

Fig. S2 Axial force (N) as a function of DWR Gap distance (µm). The distance corresponding to the water-DWR first contact is observed by the drop in axial force (arrow).

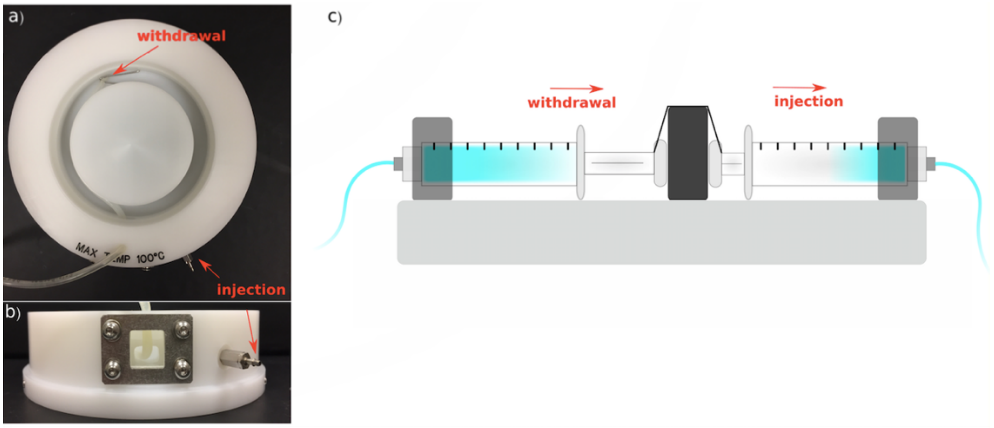

Fig. S3 Customised cuvette cell geometry displayed in (a) top view and (b) side view. Sketch of the customized syringe pump (KD Scientific®) displayed in (c).

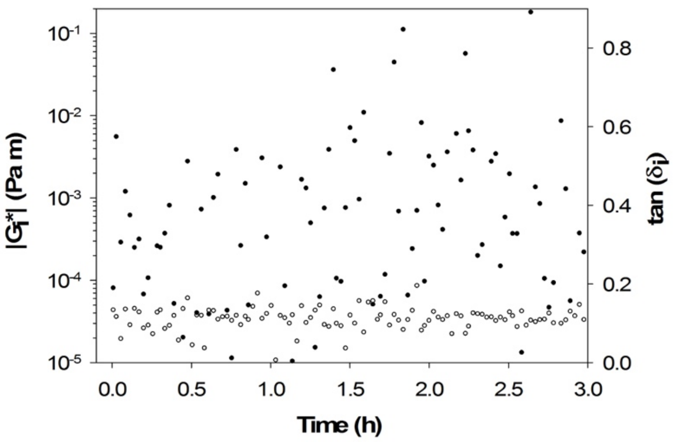

Fig. S4 Evolution of $|G_i{*}|$ (empty symbol) and *tan* (δ_i) (filled symbol) at the W/O interface composed by a water phase of 100 ppm OCNF and a pure oil phase (in the absence of OA in the oil phase).

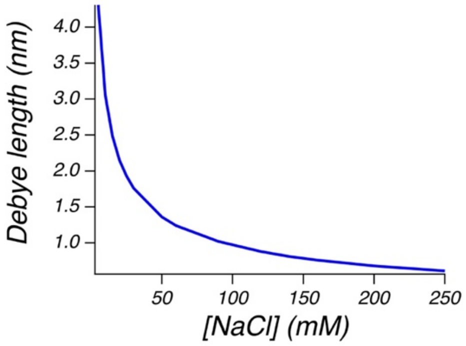

Fig. S5 Debye length (nm) as function of NaCl calculated as described by Fukuzumi et al.[4]

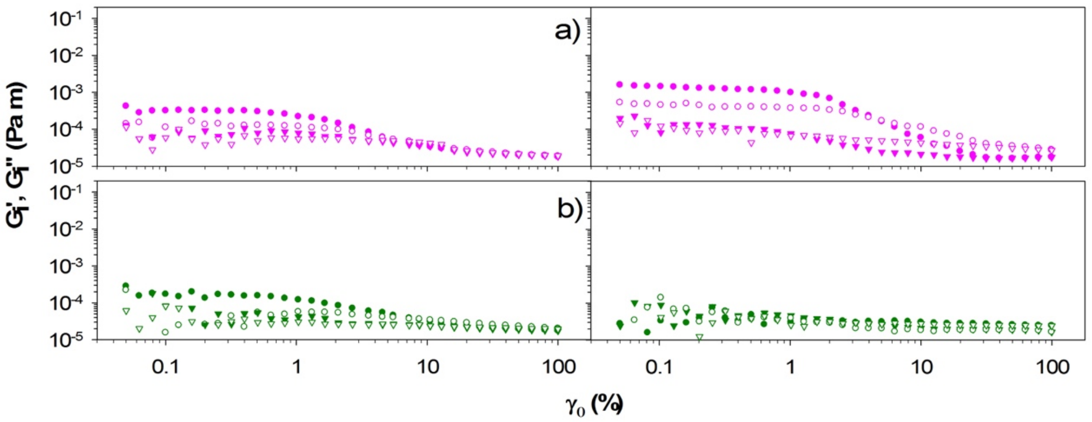

Fig. S6 Strain sweep cycle at the W/O interface composed by a water phase of 100 ppm OCNF with (a) 130 and (b) 250 mM NaCl and an OA-doped oil phase. SSC1 and SSC2 shown on the left and right, respectively.

Fig. S7 Images of 24 h aged water droplets containing 0, 55 and 250 mM NaCl, from left to right respectively, in OA-doped oil.

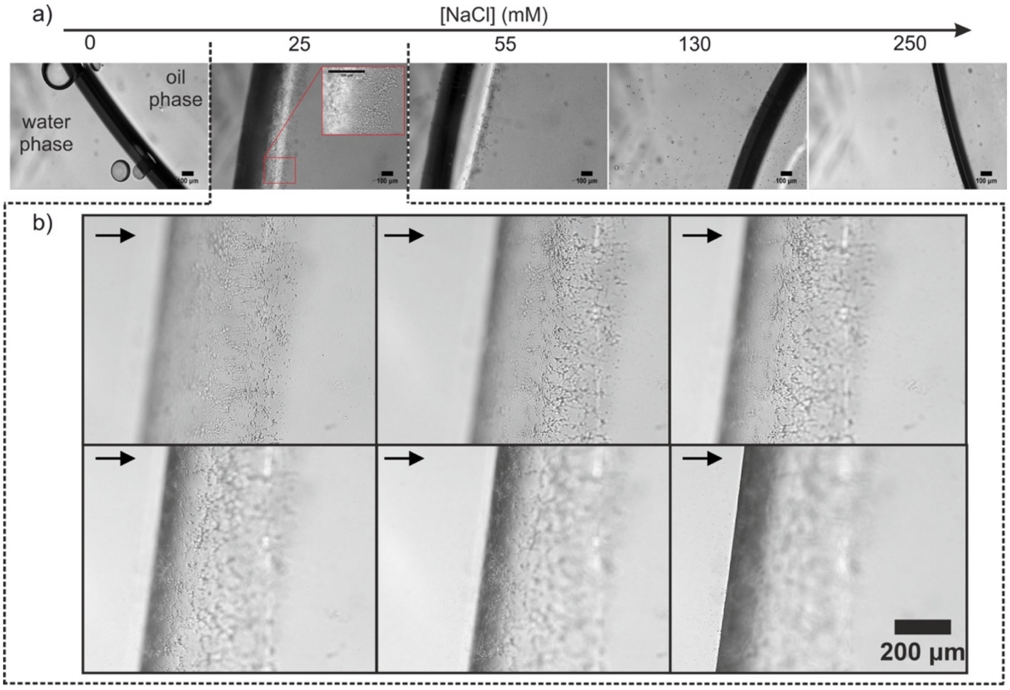

Fig. S8 (a) Optical micrographs of 24 h aged W/O interface assembled from 100 ppm OCNF suspensions at different NaCl concentrations and the OA-doped oil phase. The left-hand side of the meniscus shows the water phase. (b) Gradual change in focal plane, displayed by the direction of the arrow, for the sample containing 100 ppm OCNF with 25 mM NaCl as the water phase.

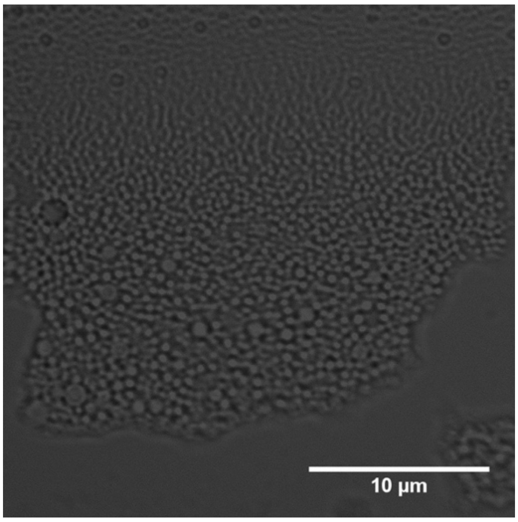

Fig. S9 Optical micrograph of the interfacial gel formed at the interface between 100 ppm OCNF in 55 mM aqueous NaCl and OA-doped oil.

References

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