

Supplementary information

Time scales for drainage and imbibition in gellified foams. Application to decontamination processes

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SI 1- Viscoelastic properties of PVA/Borax mixtures

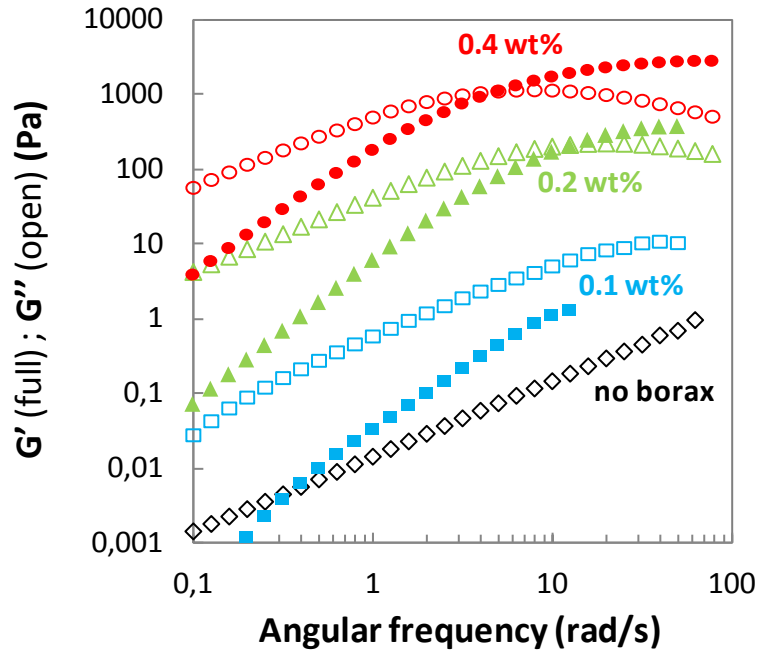


Figure S1 - Elastic (G') and loss (G'') moduli of PVA-Borax mixtures with PVA (Mowiol 8-88) 5wt%, and various borax concentrations. Due to the transient nature of the PVA/Borax complexes, the PVA/Borax network behaves as a viscous liquid below a characteristic angular frequency $\omega_0 \sim 10$ rad/s and elastically above ω_0 . The zero shear viscosity (slope of $G''(\omega \rightarrow 0)$) and elastic modulus at large frequencies are controlled by the borax concentration.

Borax (wt%)	Bulk viscosity $\eta(\gamma \rightarrow 0)$ (Pa.s)
0	0.01
0,1	0.05
0,2	25
0,4	500

Figure S2 - Zero shear viscosity of PVA/Borax mixtures just after preparation as a function of Borax concentration (for 5%wt in PVA Mowiol 8-88)

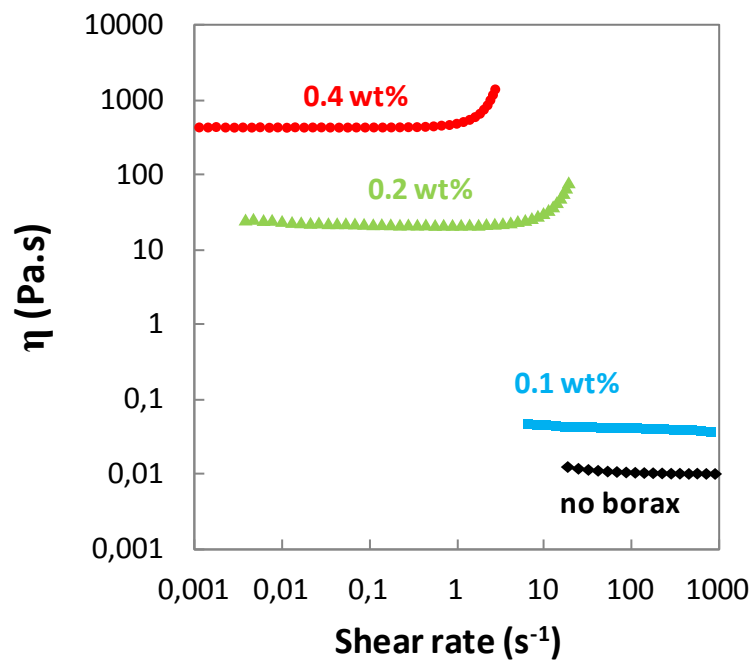


Figure S3. Flow curves of PVA/Borax mixtures just after preparation at various Borax concentrations (for 5%wt in PVA Mowiol 8-88)

For shear rates between 0.001 s^{-1} and 10 s^{-1} the viscosity is constant. The solutions become shear-thickening for larger shear rates.

SI2- Theoretical background on drainage

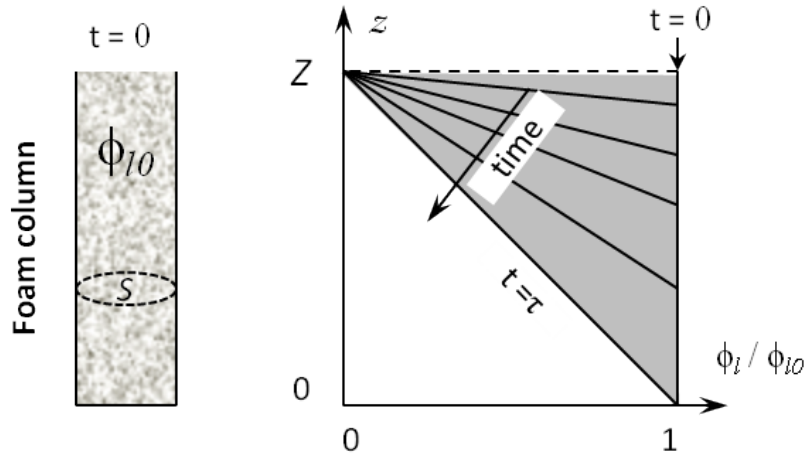


Figure S2. Left, foam column of initial liquid fraction ϕ_{l0} and section S and height Z . Right, schematic diagram of the evolution of the normalized liquid fraction profile, $\phi_l(z)/\phi_{l0}$ as a function of height, z , in the sample and time, t , according to reference^[1]

Let us consider a foam sample of uniform liquid fraction $\phi_l(t=0) = \phi_{l0}$, in a column of height Z and section S , left to drain freely under gravity. Darcy's law establishes that the front of the draining liquid moves at a velocity u_f (capillary forces are neglected) given by:

$$u_f = \frac{k(\phi_l)}{\eta} \rho_l g \quad \text{S1}$$

where η is the viscosity of the aqueous phase, ρ_l its density, and $k(\phi_l)$ is the foam permeability.

The expression for the permeability, $k(\phi_l)$, depends on the boundary conditions for the flow at the air-water interface, which is set by the ratio of the surface and bulk viscosities, the Boussinesq number Bo , which writes

$$Bo = \eta_s / \eta r \quad \text{S2}$$

with η_s the surface viscosity of the surfactant layer adsorbed at the air-water interface, η the bulk viscosity, and r the width of the foam channels.

For $Bo \gg 1$, interfaces behave as ‘rigid’ layers. The viscous dissipation mainly occurs inside the channels, and the drainage flow can be described by the *channel dominated regime*. According to this regime, the permeability scales as

$$k(\phi_l) = K_c(Bo)L^2\phi_l \quad \text{S3}$$

With

$$K_c(Bo) = K_{c0} \times \beta \quad \text{S4}$$

The dimensionless coefficient β , defined by Leonard and Lemlich^[2] and Desai and Kumar^[3], represents the flow acceleration due to the finiteness of the surface viscosity, and writes:

$$\beta(Bo) \approx 1 + 4.38 \times Bo^{-1} + 1.84 \times Bo^{-4/3} - 3.996 \times Bo^{-5/4} \quad \text{S5}$$

For strictly immobile interfaces, $Bo \rightarrow \infty$, $\beta \rightarrow 1$, and $K_c(Bo) = K_{c0} \approx 6.32 \times 10^{-3}$

At a given time t , considering the slice of foam at the very bottom of the column which keeps a liquid fraction ϕ_{l0} , the volume drained out of the foam writes

$$V_d(t) = \int_0^t \phi_{l0} S u_f dt \quad \text{S6}$$

At given time t , the drained volume V_d drained out of the foam is also given by

$$V_d(t) = \phi_{l0} S \int_0^z \left(1 - \frac{\phi_l(t)}{\phi_{l0}} \right) dz \quad \text{S7}$$

Numerical simulations have shown^[1] that in the channel dominated regime, the liquid fraction variation varies linearly with z from the top of the column – where $\phi_l \rightarrow 0$ –, to the front – where $\phi_l \rightarrow \phi_{l0}$. In that case, the half drainage time, τ , defined as the time at which the

liquid front reaches the bottom of the column is also the time for which half of the liquid has drained,

$$V_d(\tau) = \frac{\phi_{l0}SZ}{2} = \frac{V_{tot}}{2} \quad \text{S8}$$

Combining Equation S1, S3, S6 and S8 we obtain

$$\int_0^\tau \frac{K_c L(t)^2 \phi_{l0}}{\eta(t)} dt = \frac{Z}{2\rho_l g} \quad \text{S9}$$

In the case of a foam with constant bubble size L and constant fluid viscosity η , we simply have :

$$\tau = \frac{Z \eta}{2\rho_l g K_c (Bo) L^2 \phi_{l0}} \quad \text{S10}$$

The Plateau border length L can be estimated by $L \approx 0.36D$, where D is the bubble diameter.

- [1] I. Cantat, *Foams: Structure and Dynamics*, Oxford University Press, Oxford ; New York, NY, United States of America, **2013**.
- [2] R. A. Leonard, R. Lemlich, *AIChE J.* **1965**, *11*, 18.
- [3] D. Desai, R. Kumar, *Chem. Eng. Sci.* **1982**, *37*, 1361.

SI3-Viscosity measurements of the PVA Borax mixtures over time

Viscosity at zero shear rate was measured for PVA/borax mixtures of the same composition that in the reported foams. One should notice that viscosity in such mixtures decreases slowly but significantly with time (Figure S3). Maerker and Sinton reported such viscosity drop (reference [27] in the text) and related it to the decrease of pH due to the slow saponification of acetate moieties in partially hydrolyzed PVA, favored by the basic nature of Borax. The decrease of pH results in a decrease of the Borax concentration hence a decrease of the cross-linking density and viscosity. We tried to use fully hydrolyzed PVA to prevent the viscosity variation, but this polymer showed lower foamability, was more difficult to solubilize and can show recrystallization behaviors with long ageing. Viscosity drop has been taken into account in the drainage experiments and models.

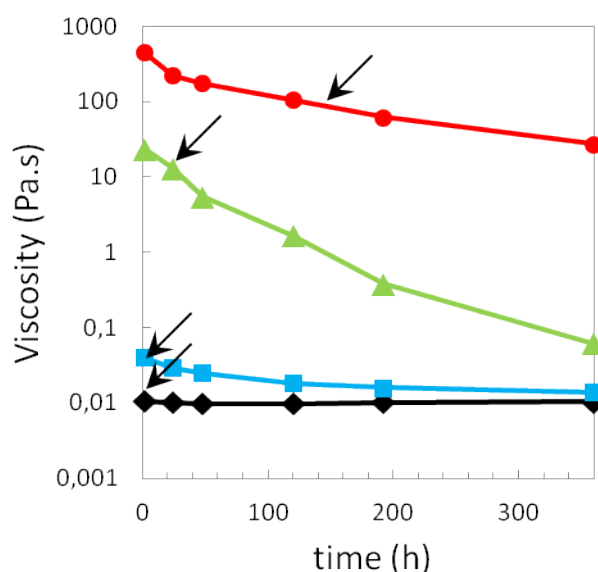


Figure S4. Viscosity as a function of time for PVA solutions (Mowiol 8-88, 5%wt) with borax 0wt% (◆), 0.1% (■), 0.2% (◀) and 0.4% (●). Arrows indicate the half-drainage time τ in the corresponding foams.

SI4-Surface viscosity measurements of PVA solutions using a double-wall ring apparatus described in reference [28].

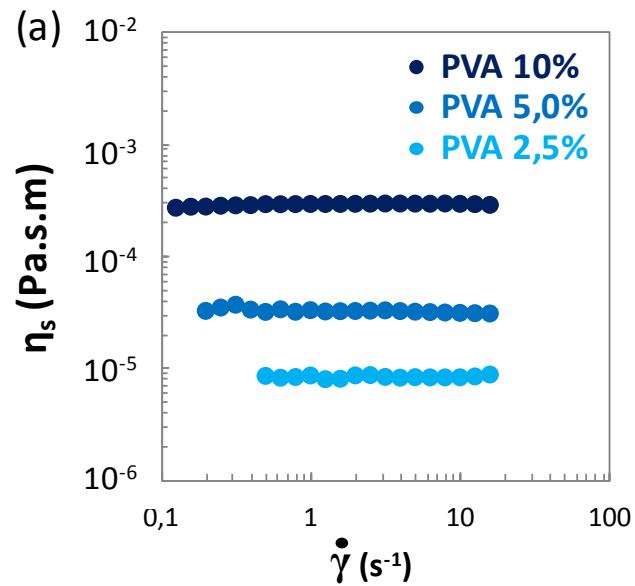


Figure S5. Surface shear viscosity as a function of surface shear rate for PVA (Mowiol 8-88) solutions with concentration varying from 2.5 to 10%. The values obtained here are in excellent agreement with the values obtained from the fit of the half-drainage times to the channel dominated regime model.