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Foaming transient polymer hydrogels

Rémi Deleurence[a,b], Tamar Saison[c], François Lequeux[a,b] and Cécile Monteux[a,b,d*]

a Laboratoire Sciences et Ingénierie de la Matière Molle, CNRS, ESPCI Paris, PSL Research University, 10 rue Vauquelin, Paris, France
b Laboratoire Sciences et Ingénierie de la Matière Molle, Université Pierre et Marie Curie, Sorbonne-Universités, 10 rue Vauquelin, France
c Saint-Gobain Recherche, 39 Quai Lucien Lefranc, 93300 Aubervilliers, France
d Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Hokkaido 060-0808, Japan

remi.deleurence@saint-gobain.com

tamar.saison@saint-gobain.com

francois.lequeux@espci.fr

cecile.monteux@espci.fr

Abstract

Foams made with polymer hydrogels can be used in a variety of applications, such as scaffolds for biomedical applications or decontamination processes. However from a practical point of view it is difficult to introduce bubbles into viscous or viscoelastic fluids and to produce large volumes of hydrogel foams. In the present article we investigate the foaming process of PVA/Borax transient hydrogels, where PVA chains reversibly bind to Borax molecules. In a previous article we showed that foams obtained with PVA/Borax mixtures are highly stable due to both high interfacial and bulk viscosities and can be used to quickly absorb liquids, which makes them suitable for detergency or decontamination processes. To produce these foams we use a two-step foaming process which consists in first shearing a PVA solution to obtain a PVA foam and, second adding Borax to the PVA foam under continuous shearing. The obtained PVA/Borax foams are stable for weeks. In this study, we observe a shear-induced collapse of the foams for formulations containing a low Borax/PVA ratio while they remain stable under shear for high PVA/Borax ratios. Using scaling

arguments we find that the shear induced collapse of the foams and bubbles is obtained below a critical ratio, N_E/N_B = 15, of the number of entanglements per chain, N_E, and number of Borax per chain, N_B. Rheology measurements show that the samples present a shear thickening behavior which increases with the Borax concentration. We suggest that during the foaming process when the shearing rate is of the order of 100 s^{-1}, the viscosity of these samples diverges leading to a viscous to fragile transition. To mimic the fast stretching of the PVA/Borax thin films during the foaming process we study the stretching of individual PVA/Borax catenoid-shaped thin films at high stretching rates. We observe that the films containing low PVA/Borax ratios do not minimize their surface area unlike what is theoretically expected for standard surfactant films. Moreover the films tend to be unstable and fracture because the PVA/Borax network does not have time to rearrange and relax stresses for high stretching rates.

Introduction

Foams, which are composed of air bubbles in a continuous matrix, are commonly used in multiple applications such as cosmetics, detergency and also as precursors for the production of lightweight materials. However, foams made with standard surfactants have a limited life time because of three destabilization mechanisms, ie the gravity-induced drainage flow of the continuous phase, Oswald ripening and bubble coalescence. Complex fluids such as polymer or peptide hydrogels[1–8] or colloidal suspensions[9–14] can be used to produce highly stable foams as their high viscosity enables to slow down the drainage flow. Hydrogel foams were recently used for biological applications such as wound healing, tissue culture[5,6]. In a recent article, we showed that foams made of PVA-Borax physical hydrogels can be used to quickly absorb liquids, which makes them good candidates for a wide range of detergency applications, including decontamination during the dismantling of nuclear facilities. In the

latter application, the high viscosity of the PVA/Borax mixtures enables to obtain foams that can remain highly stable during long decontamination processes. However foams made with hydrogels are delicate to produce and to handle. Indeed their high viscosity and elasticity prevents the incorporation of air bubbles during the foaming process. Moreover the handling and processing of foams made with covalent hydrogels is delicate because hydrogels are fragile and tend to fracture very easily.

The most current knowledge on foaming science is for Newtonian fluids[15] and there is very little knowledge concerning foams made with complex fluids although it would help producing new types of aerated materials with controlled structure. During the mechanical foaming of standard surfactant solutions, the foam volume and air fraction are controlled by the amount of air which is trapped into the fluid while the bubble size distribution is controlled by the balance between bubble break up and bubble coalescence which occurs as the bubbles and the fluid are sheared. The deformation and break up of a single bubble in a shear flow is controlled by the capillary number, Ca, which is a balance of capillary and viscous forces acting on the bubble. Grace[16] showed that the break-up of a single bubble in a Newtonian fluid in a shear flow occurs above a critical capillary number, Ca_c, which value depends on the viscosity of the bulk phase. However it was recently shown that in foams, ie concentrated assemblies of bubbles, bubble breakup occurs for much lower capillary numbers[17]. It is likely that the thin films between the bubbles play a role in this behaviour[15]. Indeed in a sheared foam, the thin liquid films between the bubbles are strongly deformed and topological rearrangements of bubbles occur[18,19] which lead to bubble coalescence in the case of very thin films[20,21].

In this article, we study the foaming of transient polymer networks made with Polyvinyl alcohol/Borax mixtures as well as the stability of the obtained foams under shear. PVA/Borax mixtures are non-Newtonian shear thickening fluids, whose viscosity increases with the shear

rate and whose rheological properties can be tuned with the PVA/Borax composition. We showed in a recent article that PVA/Borax transient networks can be used to produce foams with a ultra-slow rate of drainage due to high bulk and interfacial viscosities[1]. To produce these foams we used a two-step foaming process, where a PVA solution is first foamed and then a Borax solution is added to the PVA foam under shear to obtain the PVA/Borax foams. In the present article we show that the PVA/Borax foams with a low PVA/Borax ratios become highly unstable and collapse while they are sheared. Using scaling arguments we find that the shear induced collapse of the foams and bubbles is obtained below a critical ratio, $N_E/N_B = 15$, of the number of entanglements per chain, $N_{E,}$ and number of Borax per chain, $N_{B,}$. Rheology measurements show that below this critical N_E/N_B ratio, the viscosity of the samples diverges. We suggest that the shear induced collapse of the foams is due to the fact that the PVA/Borax solutions are shear thickening and the thin films undergo a viscous to fragile transition break as they are stretched during the foaming process leading to a coalescence of the bubbles. A series of catenoid-shaped thin film stretching experiments show that the thin films break as they are stretched at high velocity below a critical PVA/Borax ratio, which is much higher than the critical ratio for foam collapse.

Materials and methods

Sodium tetraborate decahydrate $Na_2B_4O_7.10H_2O$, or Borax is purchased from Aldrich and used without further purification. In water, it dissociates into Na^+ and $B(OH)4^-$. PVA of various molar mass and degree of hydrolysis were purchased from either Sigma-Aldrich or Polyscience. The entanglement concentration C* was obtained using rheology measurements as explained below. The PVA solutions with concentrations ranging from 2.5 to 15wt% are heated to 85°C under vigorous stirring during 3 hours to reach total polymer dissolution, and then cooled to room temperature before use. For all PVA/Borax mixtures, Borax solutions are

added to a tenfold greater volume of PVA solution, so that final Borax concentrations are approximately ranging from 0.1 to 0.5wt%.

Product Name		**Degree of Hydrolysis (mol%)**	**MW (Molar mas) (±500g/mol)**	**PDI (polydispersity index)**	**C* (g/L)**
Mowiol® 4-88	Sigma-Aldrich	88	28000	1,38	40
Mowiol® 8-88	Sigma-Aldrich	88	51000	1,76	25
Mowiol® 10-98	Sigma-Aldrich	98	53000	1,52	25
PVA PS-6000	Polyscience	80	21000	1,4	45
PVA PS-25000	Polyscience	88	38500	1,4	30

Table 1. PVA molecules used

Foam preparation

200g of PVA, poly(vinyl alcohol) solution is placed into the bowl of a kitchen mixer (Kenwood® KWY90) and sheared (**Figure 1a**) at a maximal speed (100 s^{-1}) during 3 minutes. PVA, which is a surface active polymer – surface tension around 45 mN/m – is indeed a very good foaming agent and we obtain 3 to 4 L of low density fine foam (bubble size 400 µm, volume fraction of air from 93 to 95%). After the PVA foam is obtained, an appropriate volume of borax solution at a concentration 10 times the final one is added to the PVA foam under continuous mixing for time varying between 10 and 180 seconds. To ensure good homogeneity of the PVA/Borax gel, we add rhodamine to the Borax solution and find that 10 seconds is enough to homogenize the foam. The air fraction is measured by measuring the weight of a given volume of foam.

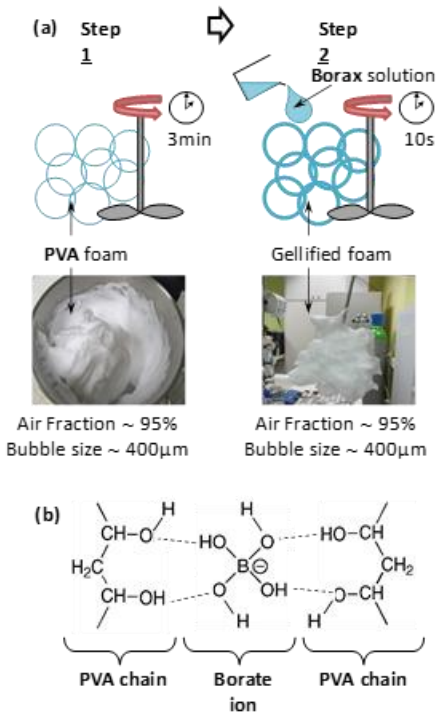


Figure 1. a) 2-step foaming process: a PVA solution is foamed using a mixer and Borax is then added to the foam b) Borate anion can form a complex with two PVA chains and create a transient cross-link. During the foaming process the shear rate is of the order of 100 s^{-1}. This Reproduced from Deleurence et al., [1] with the permission of the Royal Society of Chemistry.

Measurement of flow curves and storage and loss modulii

Rheological measurements of PVA/Borax solutions are carried out with a AR-G2 Rheometer (TA Instruments) using a cone-plate geometry (cone angle 2°, diameter 40mm, truncation 52µm). All measurements are made at 25°C, and with a solvent trap to avoid evaporation. The value of C*, the entanglement concentration, was obtained by measuring the steady shear viscosity as a function of the bulk concentration. The change of exponent of the viscosity variation with respect to concentration indicates C*. The PVA/Borax gel are prepared by mixing PVA and Borax and gently stirring the sample.

Catenoid stretching experiment

To mimic the stretching of foam bubbles during the foaming process where the foams are sheared, we performed an experiment where a catenoid shaped thin film is stretched. In this set up (Figure 2), two rings made of stainless steel (internal diameter, 2R = 15 mm, thickness 5 mm) are dipped into the PVA solution and some of the solution is collected between the two rings. The rings are then withdrawn from the solution and pulled apart by 1 cm to form a catenoid thin film. The PVA amount is measured by weighing the rings after dipping them in the PVA solution. The Borax is then added dropwise onto the film (homogeneity of the film is checked by adding a dye, rhodamine, to the Borax solution). Then the catenoid is stretched by letting the bottom ring fall. The resulting stretching velocity increases to approximately 450 mm/s corresponding to a stretching rate of the order of 40 s^{-1}. Using a high speed camera we then extract the neck radius, a and h the distance between the rings.

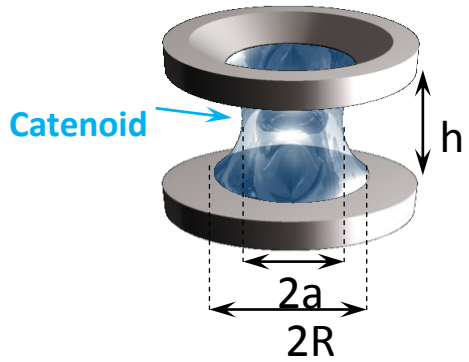


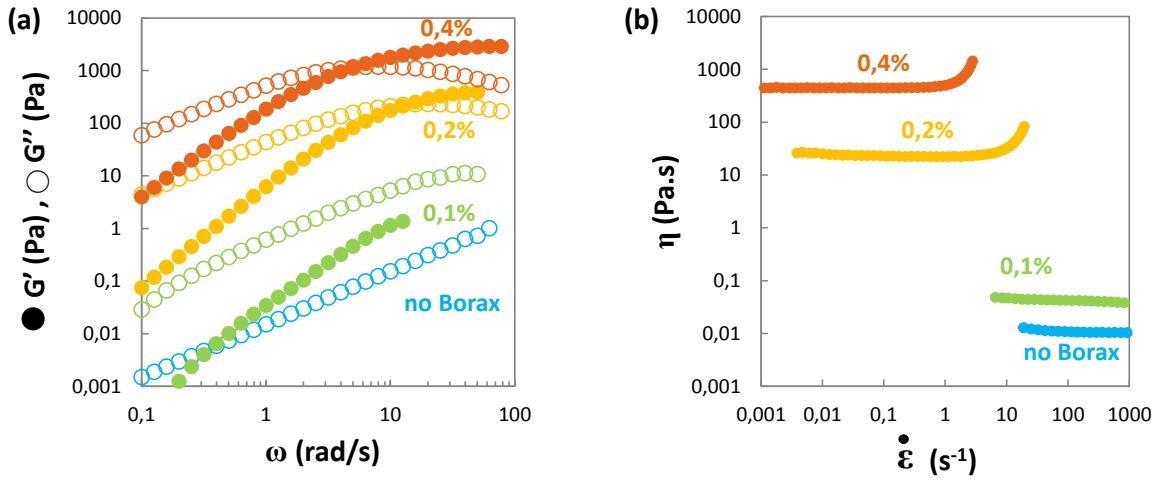
Figure 2. Experimental set up used to stretch catenoid thin films containing PVA/Borax mixtures.

Results and discussion

1. **Rheological properties of the PVA/Borax samples**

In Figure 3a and 3b we present the rheological measurements obtained for solutions of PVA 5% with increasing Borax concentrations. The PVA 5% solution with no Borax, behaves like a purely Newtonian viscous fluid. The solution which contains 0.1% Borax, has a weak shear elastic modulus but its flow curve shows a constant viscosity with the shear rate. For 0.2% and 0.4% Borax the samples are viscoelastic, with G' and G'' crossing at a frequency ω_c of the order of 5 to 10 rad.s^{-1}. The corresponding samples present a sharp increase of the viscosity at high shear rate. The shear thickening behavior appears at a strain rate of about ω_c evidencing that if the system does not have the time to relax its links it undergoes a strong shear thickening. The shear thickening behavior of PVA/Borax solutions was reported previously[22]. Above 20 s^{-1}, it becomes impossible to measure the viscosity as the samples get ejected from the rheometer gap.

In Figure 3c we present flow curves obtained for two PVA concentrations, 5% and 10%, and two Borax concentration of 0.2 and 0.4%. For a given Borax concentration the shear thickening is less pronounced for the highest PVA concentration. Similarly to us, Liu et al.[23] observed that the shear thickening behaviour of another type of polymer transient networks can be reduced by increasing the polymer concentration with a fixed cross linker concentration.



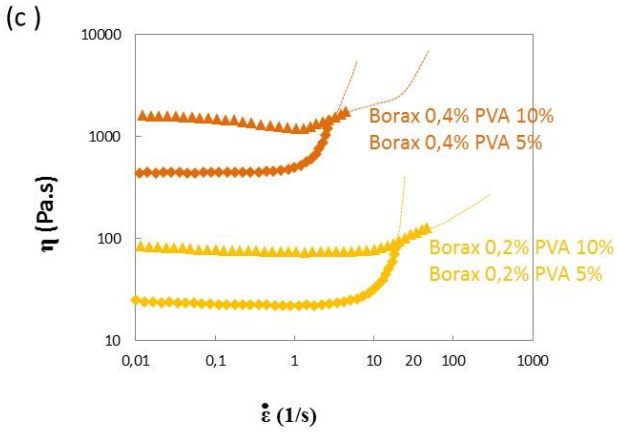


Figure 3. Rheological properties of PVA/Borax mixtures obtained for PVA 8-88.

a. Linear rheology of PVA 5% with increasing Borax concentration;
b. Flow curves of PVA 5% with increasing Borax concentrations.
c. Flow curves of PVA 5 and 10% with 0,2 and 0,4% Borax. At high shear rates, the samples get sometimes ejected from the rheometer, preventing any measurement. The dotted lines represent the evolution of the viscosity that we expect with respect to the collapse of the foams.

2. Shear instability of PVA/Borax foams

The PVA/Borax foams are produced in a two-step process consisting in shearing a PVA solution using a kitchen mixer and then adding the Borax under continuous shearing. For a given range of PVA/Borax compositions, the sheared PVA/Borax foams become highly unstable during the shearing process. Figure 4 provides an example of such a shear-induced collapse of the foams. For a foam containing 7.5% wt PVA (Mowiol 8-88) and 0.4% of Borax, the air fraction drops from 92% to 25% after 60 seconds of shear and the foam volume falls quickly. However for a foam containing the same PVA concentration with only 0,1% wt of Borax, the air fraction and foam volume remains stable while the foam is sheared over 3 minutes.

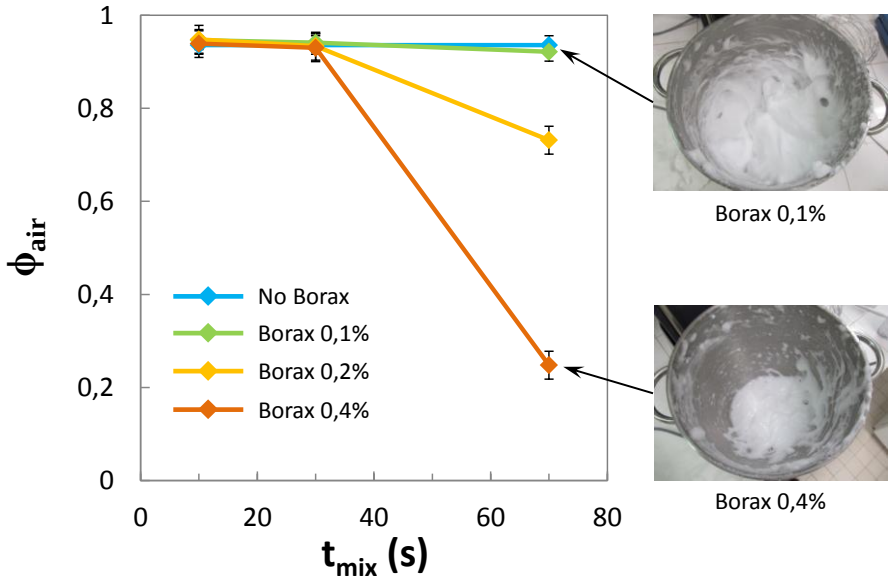
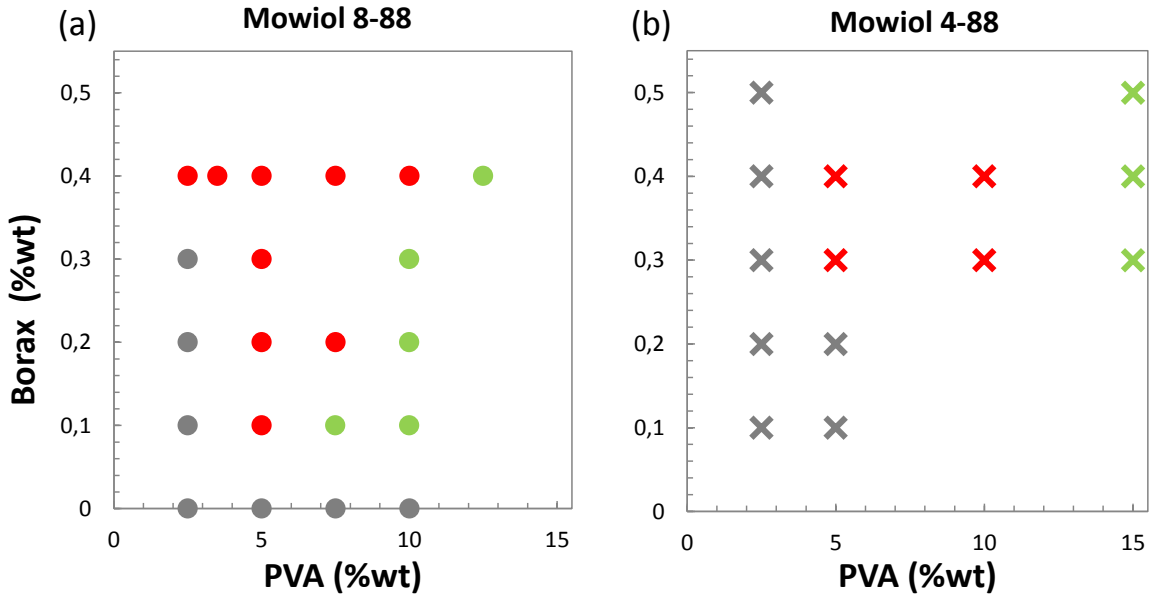


*Figure 4 Evolution of the air fraction of the PVA/*Borax *foams as a function of the mixing time for a shear rate of 100 s^{-1}. The two photos show the quantity of foam obtained in the mixing bowl in the case of two mixtures containing 0,1 and 0,4 % wt* Borax. *For 0.4%* Borax *the volume of foam collapses after 3 minutes of shear. These results are obtained for Mowiol 8-88 at 7,5% wt.*



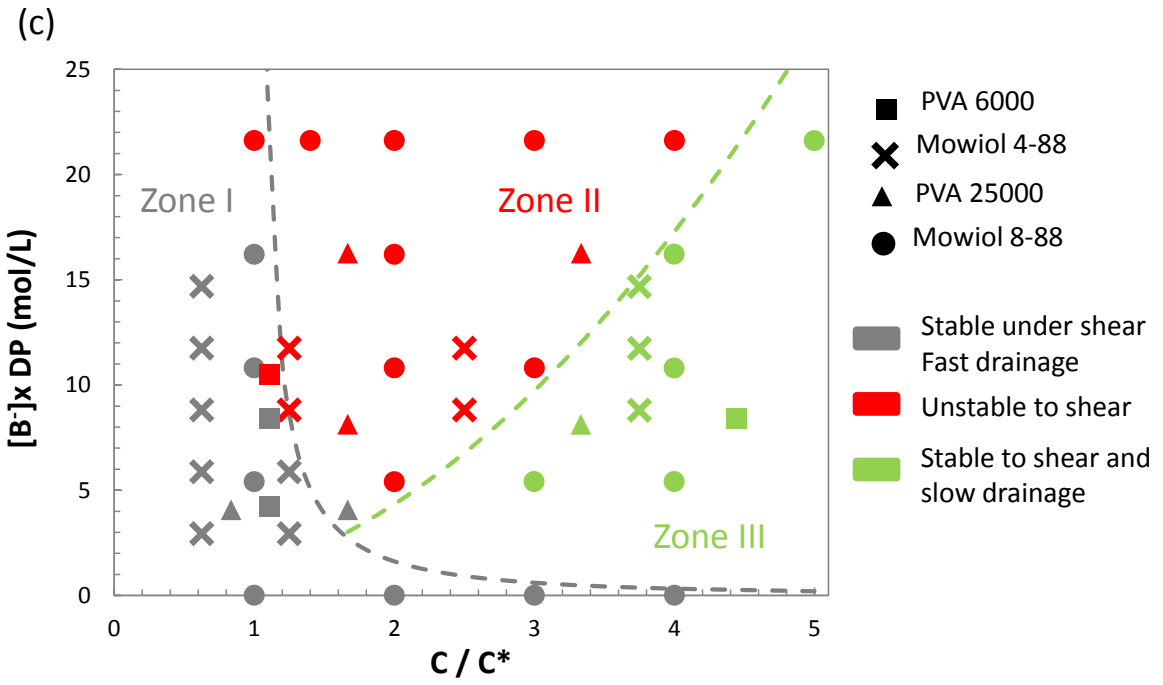


Figure 5a, b, c. Phase diagrams summarizing the stability of the PVA/Borax foams at rest and under shear. Figures a and b are obtained for Mowiol 8-88 and 4-88 respectively. Figure 5c is obtained PVA of various degrees of hydrolysis and molar mass. [B-] is the Borax concentration, DP is the degree of polymerization, C the PVA concentration, C the entanglement concentration. The axis have been renormalized following references [25-28] to account for variations of the molar mass and C* among the samples.*

Figures 5a, b and c show a phase diagram of the stability of these PVA/Borax foams -under shear and at rest- as a function of the borax concentration obtained for different PVA molar masses and degrees of hydrolysis. Three types of behaviors are observed on the phase diagram. At low PVA and Borax concentrations (zone I), the PVA/Borax foams are stable under shear however the obtained foams have a limited stability in time, below one day. In zone II, the PVA/Borax foams are highly unstable and collapse when they are sheared as illustrated in Figure 4. In zone III, corresponding to the highest PVA concentrations, the foams remain stable when they are sheared and the corresponding foams are stable, up to 4

weeks for the highest PVA/Borax concentrations in zone III, as reported in our previous article[1].

We note that when the mixer speed is reduced to its minimum, corresponding to a shear rate of approximately $20s^{-1}$, the frontier moves toward higher Borax concentrations. These results show that the collapse of the foams during mixing depends on the composition and on the mixing velocity.

Combining the rheology measurements and the foam collapse observations we suggest that the foam collapse during the mixing process is caused by a strong increase of the viscosity during the mixing which leads to a ductile to fragile transition, similarly to what was observed in other polymer transient networks[24]. Below we discuss in more details the influence of the composition on the shear thickening behavior and foam collapse.

Frontiers between zones I, II, III

The gelation of PVA/Borax mixtures was studied in References[25–28]. Keita and Ricard[28] investigated experimentally and theoretically the sol/gel transition of PVA/Borax mixtures. Above the gel point, the PVA chains form a percolated network. Their experimental gel point curve, which represents the critical Borax concentration for gelation as a function of C/C*, is very close to the frontier that we measure between zone I and zones II/III in Figure 5c, suggesting that in zone I the PVA/Borax mixtures are below the percolation point.

Keita and Ricard predicted the shape of the gel point curve is obtained as follows : the gel point is reached if all PVA chains contain at least one cross-link, either a PVA/Borax/PVA dicomplex or an entanglement between two PVA chains. The latter condition writes theoretically

$[B^-]DP \sim (C/C^*)^{-2}$ Equation 1

with [B^-] the concentration in Borate anions, DP the degree of polymerization of the PVA chains, C the PVA concentration and C* the overlap concentration above which PVA chains start overlapping. In our case, we find the frontier of zone I is well described by the following equation

$$[B^-]DP = \frac{A}{\left(\frac{C}{C^*}\right)^2 - 1}$$ Equation 2

with A=5. Equation 2 enables us to obtain a divergence of the Borax needed to obtain gelation for C=C*, a condition which is observed experimentally both in our case and in Keita's case.

For PVA and Borax concentrations above the gel point such that $[B^-]DP > \frac{5}{\left(\frac{C}{C^*}\right)^2 - 1}$, the foams are either stable (zone III) or unstable (zone II) during the mixing process depending on the PVA/Borax composition.

Interestingly the frontier between zones II and III corresponds to a critical ratio of the number of entanglements and Borax links per chain. The number of Borax per polymer chain, N_B, and number of entanglements, N_E, per polymer chains write respectively[25–27]

$$N_B \approx \frac{[B^-]}{C}$$ Equation 3

and

$$N_E \approx \frac{C}{C^*} DP^{1/2}$$ Equation 4

The dashed frontier between zones II and III shown in Figure 5c is obtained using a critical ratio N_E/N_B = 15. Hence the shear induced coalescence of the foams is obtained when $N_E/N_B<15$.

We note that when the mixer speed is reduced to its minimum, corresponding to a shear rate of approximately $20s^{-1}$, the critical ratio decreases down to $N_E/N_B=7$. This means that when the mixing velocity is lower, the frontier moves toward higher Borax concentrations.

In Table 2, we indicate the foam collapse observations made for two mixing velocities equal to 20 and 100 s^{-1} for the four PVA/Borax solutions which flow curves are given in Figure 3c, PVA 5 and 10% with Borax 0,2 or 0,4%. The solutions containing 5% of PVA with 0,2 or 0,4% Borax collapse at mixing velocities of both 20 and 100 s^{-1}, which can be correlated to the strong increase of the viscosity starting before 20 s^{-1}. The ejection of the sample at high shear rate makes the viscosity measurement impossible but the dotted lines in Figure 3c are a suggestion for the viscosity evolution that we expect for these two samples at high shear rate. The foam containing PVA 10% and Borax 0,2% is stable at 20 and 100 s^{-1}, which can be attributed to the slow increase of the viscosity with the shear rate. Finally, the foam containing 10% of PVA and 0,4% of Borax is stable for a mixing velocity of $20s^{-1}$ but collapses if the mixing velocity is increased to 100 s^{-1}. As suggested by the dotted line in Figure 3c, a weak increase of the viscosity up to $20s^{-1}$ followed by a sharp increase of the viscosity above 20 s^{-1} could explain such behavior.

We note that the foams containing 5% PVA and 0,1% Borax which are not shear thickening (Figure 3b) are noted as unstable in Figure 5c. In fact, the foam observations were not reproducible for this specific sample, which lies close to the frontiers between zones I, II and III, where the homogeneization of the samples is probably critical.

		20 s^{-1}	100 s^{-1}
Borax 0,4%	PVA 10%	Stable	Collapse
	PVA 5%	Collapse	Collapse
Borax 0,2%	PVA 10%	Stable	Stable
	PVA 5%	Collapse	Collapse

Table 2. Foam collapse observations for the same concentrations as in Figure 3c.

3. **Stretching catenoids of PVA/Borax mixtures**

When a foam is sheared, the thin liquid films between the bubbles are either stretched or compressed. To mimic the stretching of thin liquid films inside the foams during the shearing process we performed a series of experiments which consist in a fast stretching of catenoid-shaped films made with PVA/Borax mixtures.

In Figure 6 we present the shape variation of catenoids made from PVA 8-88 10% with Borax concentrations between 0 and 0,4%. Along with images of the catenoids, we present the variation of a/R as a function of h/R, where is a the neck radius, R the radius of the catenoid at the rings and h the height of the catenoid. The dashed line corresponds to the theoretical shape of surfactant catenoid in quasi static conditions, which corresponds to a minimal surface area[29]. Theoretically, a surfactant catenoid becomes unstable for h/R above 1,33. The behavior of the catenoids containing only PVA is very close to the theoretical dashed line for h/R up to 1,3. However we note that the rupture of the catenoids is delayed and occurs for h/R = 1,8 probably because of the fast stretching rate and to the relatively high viscosity of the PVA solution in comparison to standard surfactant films. The destabilization of the films is delayed. For increasing Borax concentrations, to 0,4%, the shape of the catenoids deviates from the theoretical prediction more and more significantly. Indeed a/R is higher than expected for a given h/R meaning that the surface area is not minimal. Moreover the catenoids break for lower values of h/R as the Borax concentration is increased. These simple experiments shows that the thin liquid films containing PVA/Borax mixtures undergo a viscous to brittle transition as the Borax concentration increases.

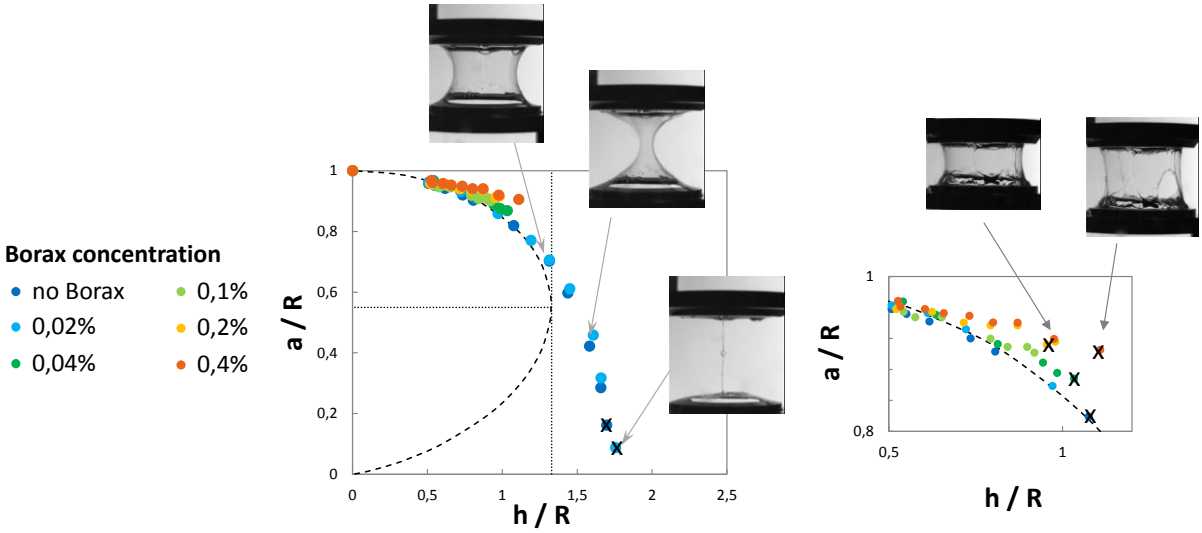


Figure 6. Stretching of the catenoids and values of a/R as a function of h/R for catenoid films containing 10% of PVA 8-88 solutions and increasing amounts of Borax, from 0% to 0,4%. . The crosses represent the deformation at which the films break

The deviation from minimal surface conditions and fragility of the thin films upon stretching is related to the ability of the PVA/Borax transient network to rearrange in the catenoid films. We suggest that for PVA/Borax mixtures for which the viscosity diverges strongly at high deformation rates, the PVA/Borax network cannot flow to minimize their surface energy and become brittle. We therefore suggest that the shear induced collapse of the foams that we observe during the foaming process is due to the rupture of thin liquid films as they are strongly stretched. We note that the critical Borax concentration for which the fracture of the catenoids occurs for a critical ratio N_E/N_B = 150, well above the ratio of 15 or 7 found in the shearing foam experiments for 100 or 20 s^{-1} showing that the thin films undergo a viscous to fragile transition for much lower Borax concentrations than in the foams. Moreover, for 0,1% Borax, the catenoid films undergo a fragile break up although the foams are stable during the mixing process and the solutions do not present any shear thickening behavior (see

Supporting Information S1). The catenoid experiment is a purely extensional flow, in contrary to the shear rheology experiments and the elongational viscosity of these PVA/Borax systems may be much larger than their shear viscosity.

Conclusion

In this article, we investigate the foaming process of foams made with PVA/Borax transient networks. To produce these foams we used a two-step foaming process, where a PVA solution is first foamed and then a Borax solution is added to the PVA foam under shear to obtain the PVA/Borax foams. For formulations with a low PVA/Borax ratio, we observe a shear-induced collapse of the foams. For high PVA/Borax ratios, the foams remain stable under shear (mixing velocity of 100 s^{-1}) and the produced foams are subsequently highly stable at rest. Using scaling arguments we find that the shear induced collapse of the foams is obtained below a critical ratio $N_E/N_B<15$ of the number of entanglements per chain, N_E and number of Borax per chain, N_B. For a mixing velocity of $20s^{-1}$, the critical ratio falls down to 7. Rheological measurements of the PVA/Borax solutions show that the solutions are shear thickening. The rate at which the viscosity diverges with the shear rate increases when the PVA/Borax ratio decreases.

Combining the foam observations and the rheological measurements, we suggest that the foam collapse is due to the strong increase of the viscosity during the mixing process, which induces a viscous to fragile transition of the samples. Experiments consisting in a fast stretching of PVA/Borax catenoids show that the thin films undergo a viscous to brittle transition below a critical PVA/Borax ratio : the films do not minimize their surface energy and become brittle upon stretching. However we note that the critical ratio for film fracture is much higher than the one measured for the foam collapse, of the order of 150 : the thin films break at very low Borax concentrations. We suggest that this discrepancy between films and foams measurements is due to the fact that in the film experiment the thin film is larger than

the ones is the foams increasing the probability of rupture. Moreover in the thin film stretching experiment the flow is purely elongational, possibly leading to higher viscosities than in a shear experiment. To summarize we suggest that the shear induced collapse of the PVA/Borax foams observed during the foaming process is due to the rupture of the thin liquid films and subsequent coalescence of the bubbles and is related to a transition from a viscous to a fragile behavior, which depends on the PVA/Borax ratio and shear rate.

Supporting information. S1. Shear rheology measurements of a PVA10% Borax 0.1% solution

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Bibliography

1. Deleurence, R., Saison, T., Lequeux, F. & Monteux, C. Time scales for drainage and imbibition in gellified foams: application to decontamination processes. *Soft Matter* **2015,** *11***,** 7032–7037.
2. Testouri, A., Honorez, C., Barillec, A., Langevin, D. & Drenckhan, W. Highly Structured Foams from Chitosan Gels. *Macromolecules* **2010,** *43***,** 6166–6173.
3. Andersen, T., Melvik, J. E., Gåserød, O., Alsberg, E. & Christensen, B. E. Ionically Gelled Alginate Foams: Physical Properties Controlled by Operational and Macromolecular Parameters. *Biomacromolecules* **2012,** *13***,** 3703–3710.
4. Andersen, T., Melvik, J. E., Gåserød, O., Alsberg, E. & Christensen, B. E. Ionically gelled alginate foams: Physical properties controlled by type, amount and source of gelling ions. *Carbohydr. Polym.* **2014,** *99***,** 249–256.

5. Barbetta, A., Rizzitelli, G., Bedini, R., Pecci, R. & Dentini, M. Porous gelatin hydrogels by gas-in-liquid foam templating. *Soft Matter* **2010,** *6***,** 1785.
6. Colosi, C. Costantini, M.; Barbetta, A.; Pecci, R.; Bedini, R.; Dentini, M. Morphological Comparison of PVA Scaffolds Obtained by Gas Foaming and Microfluidic Foaming Techniques. *Langmuir* **2013,** *29***,** 82–91 .
7. Li, T., Nudelman, F., Tavacoli, J., Vass, H., Adams, D.,Lips, A., Clegg, P.. Long-Lived Foams Stabilized by a Hydrophobic Dipeptide Hydrogel. *Adv. Mater. Interfaces **2016,** 3***,** 1500601.
8. Malcolm, A. S., Dexter, A. F. & Middelberg, A. P. J. Foaming properties of a peptide designed to form stimuli-responsive interfacial films. *Soft Matter* **2006,** *2***,** 1057.
9. Guillermic, R. M., Salonen, A., Emile, J. & Saint-Jalmes, A. Surfactant foams doped with laponite: unusual behaviors induced by aging and confinement. *Soft Matter* **2009,** *5***,** 4975.
10. Liu, Q., Zhang, S., Sun, D. & Xu, J. Aqueous foams stabilized by hexylamine-modified Laponite particles. *Colloids Surf. Physicochem. Eng. Asp.* **2009,** *338***,** 40–46.
11. Liu, Q., Zhang, S., Sun, D. & Xu, J. Foams stabilized by Laponite nanoparticles and alkylammonium bromides with different alkyl chain lengths. *Colloids Surf. Physicochem. Eng. Asp.* **2010,** *355*, 151–157.
12. Lesov, I., Tcholakova, S. & Denkov, N. Factors controlling the formation and stability of foams used as precursors of porous materials. *J. Colloid Interface Sci.* **2014**, *426***,** 9–21.
13. Lesov, I., Tcholakova, S. & Denkov, N. Drying of particle-loaded foams for production of porous materials: mechanism and theoretical modeling. *RSC Adv* **2014,** *4***,** 811–823.
14. Deleurence, R., Parneix, C. & Monteux, C. Mixtures of latex particles and the surfactant of opposite charge used as interface stabilizers – influence of particle contact angle, zeta potential, flocculation and shear energy. *Soft Matter* **2014,** *10***,** 7088–7095.
15. Drenckhan, W. & Saint-Jalmes, A. The science of foaming. *Adv. Colloid Interface Sci.* **2015,** *222***,** 228–259.

16. Grace†, H. P. DISPERSION PHENOMENA IN HIGH VISCOSITY IMMISCIBLE FLUID SYSTEMS AND APPLICATION OF STATIC MIXERS AS DISPERSION DEVICES IN SUCH SYSTEMS. *Chem. Eng. Commun.* **1982,** *14***,** 225–277.
17. Golemanov, K., Tcholakova, S., Denkov, N., Ananthapadmanabhan, K. & Lips, A. Breakup of bubbles and drops in steadily sheared foams and concentrated emulsions. *Phys. Rev. E* **2008,** *78*.
18. Dollet, B. & Raufaste, C. Rheology of aqueous foams. *Comptes Rendus Phys.* **2014,** *15***,** 731–747.
19. Jiang, Y., Swart, P., Saxena, A., Asipauskas, M. & Glazier, J. Hysteresis and avalanches in two-dimensional foam rheology simulations. *Phys. Rev. E* **1999,** *59*, 5819–5832.
20. Biance, A.-L., Delbos, A. & Pitois, O. How Topological Rearrangements and Liquid Fraction Control Liquid Foam Stability. *Phys. Rev. Lett.* ***2011,*** *106*.
21. Carrier, V. & Colin, A. Coalescence in Draining Foams. *Langmuir* **2003,** *19***,** 4535–4538.
22. Inoue, T. & Osaki, K. Rheological properties of poly(vinyl alcohol)/sodium borate aqueous solutions. *Rheol. Acta* **1993,** *32***,** 550–555.
23. Xu, D., Liu, C.-Y. & Craig, S. L. Divergent Shear Thinning and Shear Thickening Behavior of Supramolecular Polymer Networks in Semidilute Entangled Polymer Solutions. *Macromolecules* **2011,** *44***,** 2343–2353.
24. Ligoure, C. & Mora, S. Fractures in complex fluids: the case of transient networks. *Rheol. Acta* **2013,** *52*, 91–114.
25. Kurokawa, H., Shibayama, M., Ishimaru, T., Nomura, S. & Wu, W. Phase behaviour and sol-gel transition of poly(vinyl alcohol)-borate complex in aqueous solution. *Polymer* **1992,** *33***,** 2182–2188.
26. Pezron, E., Leibler, L., Ricard, A. & Audebert, R. Reversible gel formation induced by ion complexation. 2. Phase diagrams. *Macromolecules,* **1988,** *21,* 1126–1131.
27. Leibler, L., Pezron, E. & Pincus, P. Viscosity behaviour of polymer solutions in the presence of complexing ions. *Polymer,* **1988,** *29***,** 1105–1109.

28. Keita, G. & Ricard, A. Phase diagram of borate-PVA system: Sol-gel transition and demixtion. *Polym. Bull.* **1990,** *24***,** 633–640.

29. Salkin, L., Schmit, A., Panizza, P. & Courbin, L. Influence of boundary conditions on the existence and stability of minimal surfaces of revolution made of soap films. *Am. J. Phys.* **2014**, *82***,** 839–847.

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