Foamability and stability of foams obtained with silica/PEI gels

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HighlightsPEI/silica mixtures, which are yield stress fluids, can be used to produce highly stable foams.

There is an optimum silica concentration for which we obtain the highest foamability and the highest foam stability.

Graphical abstract
The amount of air incorporated during foaming decreases with particle concentration

The drainage rate decreases with the particle concentration

<InlineImage1>
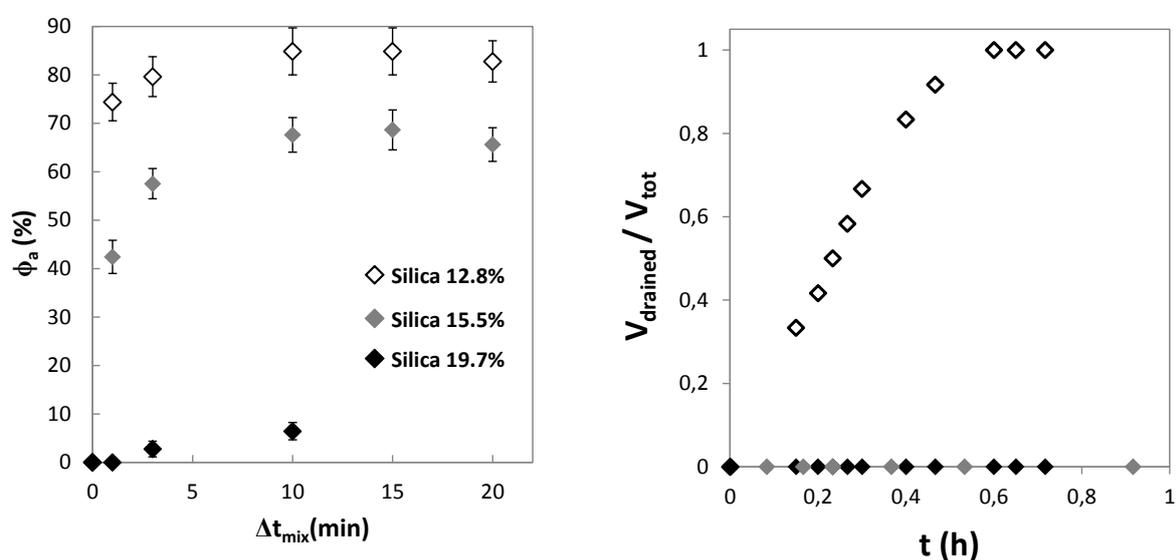
Abstract

In this article we examine the foamability and foam stability of a series of PEI/silica gel suspensions

with varying particle concentrations in the presence of a neutral surfactant, $C_{12}E_{23}$. These suspensions,

which were recently developed for 3D printing applications, exhibit a finite yield stress whose value can be tuned by varying the particle concentration and the pH. Our study aims at evaluating whether this system is suitable to produce stable foams that could be further be used as precursors for the 3D printing of porous materials and to evaluate the relation between the yield stress and the foam stability against drainage and ripening. At pH7 where all the suspensions are in the fluid state, the maximum air fraction reaches 80% however the foams are very unstable to drainage. At pH 10.5, the suspensions are in the gel state due to Van der Waals driven aggregation of the particles. In the gel state, the obtained maximum air fraction decreases with the suspension concentration, from $\phi_{air} = 80\%$ for the 12.8 wt % suspension to $\phi_{air} = 65\%$ for the 15.5 wt % suspension. The most concentrated suspension, i.e 19.7 wt % could not be foamed. At pH 10.5, the yield stress of the 12.8 wt % suspension is 10 Pa, which enables to overcome the buoyancy acting on the particles and therefore arrest drainage. However the yield stress is too low to overcome the Laplace pressure in the bubbles, therefore Ostwald ripening is observed. The 15.5 wt % suspension exhibits a yield stress of 200 Pa, which is high enough to arrest drainage. Ostwald ripening occurs at early times and is arrested when the bubble radius reaches 400 μm as the yield stress equals the Laplace pressure.

The results obtained in this study show that there is an optimal silica concentration which combines good foamability and large stability to drainage and Ostwald ripening. These materials are promising for the development of 3D printable foams even though the size of the bubbles will limit the spatial resolution of the printing to a few millimeters.

1. Introduction

Aqueous foams are composed of air bubbles dispersed in an aqueous phase. While the foaming process and stability of aqueous foams in which the continuous phase is newtonian have been extensively studied[1,2], the case of foams in which the continuous phase is a complex fluid has attracted less attention. Nevertheless, dispersing bubbles in complex fluids such as colloidal suspensions or polymer systems has numerous applications. For example, in the field of building materials, incorporating air into cement[3]

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or plaster pastes enables the production of insulating and low density materials. Aeration of food products,[4] which may enhance shelf life and create new textures, also requires to foam complex fluids. Recent studies have focused on foams made with complex fluids such as concentrated emulsions[5,6], polymer gels[7–10] or particle suspensions such as clays[11–14], granular suspensions[15,16], surfactant/particle suspensions[12,13,17–22]. When particles or particle aggregates are large enough, they accumulate in the Plateau borders of the foams and help slowing down the drainage of the foams[15,16,23]. When the particle suspensions exhibit a finite yield stress, this may lead to a complete arrest of the drainage flow[17,24,25]. Lesov *et al*. showed that their CAPB/silica system builds up a percolated network over time and that foam drainage is arrested when the yield stress of the network overcomes the hydrostatic pressure[17]. The same authors found that the Ostwald ripening can also be arrested, provided the yield stress is higher than the capillary pressure of the bubbles. Kloek *et al.* found numerically that ripening may be arrested for sufficiently high bulk elastic moduli of the continuous phase[4].

Yield stress fluids exhibit an elastic response below a critical yield stress σ_0 and flow above σ_0. Among a large number of applications, yield stress fluids are promising systems for the development of new types of matrices that can be processed in 3D printing. Indeed 3D printing applications requires fluids that flow through a needle under a given stress and keep their shape at rest once deposited on a surface. In principle the same type of properties is required for producing stable foams. Indeed the foamability is enhanced as the viscosity decreases[17] while a large elastic modulus as well as a yield stress enable arresting drainage and coarsening[4,17].

In this article, we examine the foamability and foam stability of yield stress fluids obtained from suspensions containing PEI, Poly(ethylenimine), silica particles and a non ionic surfactant, $C_{12}E_{23}$. PEI/silica suspensions were recently developed for 3D printing applications[26]. It was shown that at pH7, the PEI chains contain protonated amine groups which are positively charged. The positively charged PEI chains adsorb on the negatively charged silica particles through strong electrostatic interactions. The resulting PEI/silica particles are positively charged and the corresponding suspensions exhibit a low shear modulus. As the pH is raised, the number of protonated groups on the PEI chains decreases and the neutralized PEI chains collapse on the silica particles and PEI/silica particles aggregate through Van

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der Waals forces. The corresponding mixtures exhibit high elastic moduli and yield stresses ranging from 10 to 10^5 Pa depending on the particle concentration. In the present article, we study foams containing PEI/silica mixtures and $C_{12}E_{23}$. We study the foaming behavior of these mixtures as well as the stability of the obtained foams.

The two goals of our study are i) to evaluate whether this system is suitable to produce stable foams that could be further used as precursors for the 3D printing of porous materials. In this article we focus on the foamability and stability of the aqueous precursor foams. We focus on the influence of the particle concentration, which controls the yield stress and elastic modulus of the suspensions. ii) to evaluate the relation between the yield stress and the foam stability against drainage and ripening and compare it to previously published results.

We find that the maximum air fraction in the foams decreases with the particle concentration. However the stability of the foams increases with the yield stress of the suspensions. When the yield stress exceeds 10 Pa, the drainage is completely arrested. We find that the Ostwald ripening cannot be arrested at early times as the capillary pressure in the bubbles exceeds the value of the yield stress. However at longer times, as the size of the bubbles increases, the capillary pressure decreases and eventually becomes equal to the yield stress. As a consequence, the size of the bubbles reaches a plateau around 400 µm. Our results show that there exists an optimum particle concentration which enables optimizing the amount of foam produced and its stability and that PEI/silica suspensions can be used as precursors for the production of porous materials.

2. Materials and methods

2.1. Materials

The PEI M_W=2000 g/mol was purchased from Sigma-Aldrich. The silica particles (Tixosil 365) were purchased from Solvay, the size of the particles ranges between 3.5 and 4 µm and their specific area is 0.6 mg/m^2. To produce these foams we used a neutral surfactant, Brij L-23, $C_{12}E_{23}$, or Polyoxyethylene-(23)-lauryl ether, purchased from Aldrich.

2.2. TOC measurements

TOC, Total Organic Content, measurements (Shimadzu-VCSH) enable the amount of carbon in the solutions to be obtained, from which we can deduce the concentration of the free polymer in the solutions hence the amount of adsorbed molecules on the particles. We prepare PEI/silica mixtures containing 400 mg/L of silica particles and a PEI concentration ranging from 0 to 400 mg/L. The pH is adjusted to 7 or 10 using a 1M NaOH solution. The solutions are then sonicated for 5 minutes and then left to equilibrate for 24 hours under magnetic stirring. 2 mL of these particle–PEI mixtures were ultracentrifuged at 11 000 rpm for 24 hours (Beckman Coulter OptimaMAX Ultracentrifuge). The amount of Non Purgeable Organic Carbon (NPOC, given in mg L^{-1}) in the supernatant is measured by using the instrument. It is then converted into the molar concentration of the free PEI which was originally present in the supernatant referring to a calibration curve. The surface coverage of the particle by the polymer, Γ, is calculated from the following equation

$$\Gamma = \frac{C_{pei0} - C_{peiTOC}}{C_{silica}S_{silica}}$$

where C_{pei0} is the initial PEI concentration in the suspension, C_{peiTOC} is the concentration of free PEI in the supernatant measured by the TOC experiment C_{silica} is the silica concentration and S_{silica} is the specific area of the silica particles. We note that the TOC measurements are performed for PEI/Silica suspensions without $C_{12}E_{23}$.

2.3. Zeta potential measurements

The zeta potential of the particles was calculated from the electrophoretic mobilities measured by using a Malvern Zetasizer Nano Series ZS90 instrument, using the Smoluchowski equation[27]. The samples used for this measurement were 250-fold diluted in Milli-Q water to reach a particle concentration of 0.01 wt% and avoid multiple scattering of light. At least 3 measurements were performed for each sample.

2.4. Rheological measurements

Rheological measurements were performed using an ARG2 rheometer from TA instruments equipped with a rough plane with 0.5 mm deep and 1 mm wide stripes to avoid slippage.

2.5. Preparation of the gels and foams

The gels were prepared at pH7 where the suspensions are in a fluid state and stirred for 24 hours. Then the pH is raised to 10.5 to reach the gel state and the neutral Brij surfactant is added to obtain the suspension to be foamed. We found using TOC measurements that the $C_{12}E_{23}$ adsorbs on the silica particles (see SI) therefore in the following the $C_{12}E_{23}$ concentration is fixed at equal to 3.3 g/L to have a large excess of surfactant in excess in the suspension. As explained in the following the ratio of PEI to silica concentrations is fixed equal to 0.75.

We produce foams with the silica/PEI gels using a planetary mixer (Kenwood Chef Premier KMC 560, 1000 W) using an amount of initial liquid of 200 mL and at a velocity of 165 rpm. The variation of the air fraction of the foams with the mixing time is obtained by weighing known volumes of foamed suspensions.

To study the foam stability, the foams are poured into large glass syringes (25 mm diameter) covered with a cap to prevent evaporation. The volume of drained liquid is measured as a function of time by measuring the height of drained liquid using a camera. The size of the bubbles at the syringe walls is measured using a camera. We note that the size of wall bubbles may be larger than inside the foam, by a factor $\Pi^{1/2}$.

3. Results

Characterization of the PEI/silica gels

We use TOC and zeta potential measurements to characterize the adsorption of PEI on the silica particles. Figure 1 shows that for a suspension containing 400 mg/L of silica particles, the surface coverage of PEI on the particles increases to 0.6 mg/m^2 and then reaches a plateau above 200 mg/L of PEI. The measured surface coverage is similar at pH 7 and pH 10 and does not depend on the salt concentration. The zeta potential, ξ, of the silica particles alone is negative at pH7 and it becomes positive above 3 mg/L of PEI as the positively charged PEI adsorbs on the particles. The zeta potential reaches a plateau above 20 mg/L of PEI. In the following we choose to work with a PEI/silica ratio of 0.75 corresponding to the plateau in surface excess, Γ, and zeta potential, ξ. For this PEI/silica ratio, the PEI coated silica particles become neutral at pH=10.5 as the number of protonated groups on the PEI

molecules decreases. At this pH, in the absence of electrostatic repulsions, the PEI-coated particles strongly aggregate because of Van der Waals forces. We note that the point of zero charge is slightly different from what is reported in Ref 26, which is probably due to the fact that the silica we use is purchased from a different supplier.

Consequently at pH=10.5, the suspension turns into a strong gel, as shown in Figure 2, which presents G' and G'' as a function of the stress amplitude. The yield stress is the critical stress above which G' drops and the deformation steeply increases[28]. The elastic modulus and the yield stress of the gel depend on the particle concentration. The elastic modulus ranges between 20 Pa and 10^5 Pa as the silica concentration is raised from 12.8 wt % to 19.7 wt %. The yield stress increases from 10 Pa to 2000 Pa when the silica concentration is increased from 12.8 wt % to 19.7 wt %. We checked that the $C_{12}E_{23}$ does not have any influence on the rheological results.

Foaming of the PEI/silica gels

We produce foams with the silica/PEI gels using a kitchen mixer and we measure ϕ_{air}, the volume air fraction of the foams as a function of time. For the lowest silica concentration, 12,8wt %, ϕ_{air} rises to 80% in a few minutes and then reaches a plateau. For 15,5wt % silica, ϕ_{air} reaches a maximum of 65% and then decreases with time. The 19.7wt % silica suspension could not be foamed therefore ϕ_{air} remains below 8%. Therefore our results show that increasing the particle concentration leads to lower ϕ_{air}. Similarly Lesov et al.[17] found that increasing the particle concentration leads to less air entrapment in silica/surfactant mixtures. Indeed, they showed that increasing the particle concentration leads to an increase of the viscosity, which prevents air entrapment.

In an attempt to increase ϕ_{air}, we performed two step foaming experiments, similarly to the method we used for another gel system[8]. We first foam the PEI/silica suspension (containing the surfactant) at pH7 corresponding to the fluid state. Secondly the NaOH is added to the foam, which is continuously sheared in the mixer, to rise the pH up to 10.5 to reach the gel state. As shown in Figure 4, as the liquid suspension at pH7 is foamed, ϕ_{air} quickly rises to 80% for the 15.5 wt % silica suspension, which is higher than what is measured when the 15.5 wt % suspension is directly foamed in the gel state at pH10.5. However

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as NaOH is added, ϕ_{air} rapidly drops to 60% and remains constant afterwards. Therefore the gelation of the suspension does not enable to increase the air fraction in the foam and that in both processes the foams reach the same stationary state

3.1. Stability of the PEI/silica foams

After 25 minutes of foaming, 150 mL of foam were transferred into a glass syringe covered with a cap to record the stability of the foam to drainage and Oswald ripening. We find that the foam prepared with a 15.5 wt % suspension at pH7 is highly unstable and destabilizes in about an hour. After 30 minutes the size of the bubbles has increased from 0.1 to 2 mm and the total volume drains in about an hour.

The foams made with 12.8 and 15.5 wt % of silica particles and PEI at pH10.5 are much more stable to drainage and ripening. We do not detect any drained liquid for 1 hour. The size of the bubbles increases from 200 μm to 2 mm for the 12.8 wt % silica suspension over an hour. For the 15.5 wt % suspension the size of the bubbles increases from 200 μm to 400 μm and then reaches a plateau after one hour.

For the 12.8 wt % suspension at pH10.5, the yield stress is $\sigma_0 = 10$ Pa. As shown by Lesov *et al.* and previously by Chaplain *et al.*,[29] when the yield stress σ_0 is higher than the buoyancy pressure ΔP_{buoy}, then the drainage flow is suppressed. This statement enables to define a critical yield stress which writes $\sigma_{0c} \sim \Delta P_{buoy} \sim \Delta\rho g R$, where $\Delta\rho$ is the mass density difference between bubbles and the surrounding suspension, g is gravity acceleration and R is the bubble radius. Taking R=125 μm we find σ_{0c}=1,3 Pa, which is below the yield stress of the 12.8 wt % suspension. Therefore the yield stress of the 12.8 wt % PEI/silica suspension is sufficiently high to prevent the drainage flow in agreement with our observations. However the foam bubbles ripen over time. According to Lesov et al.[17], to arrest bubble Ostwald ripening, the yield stress has to overcome the difference in capillary pressure of the bubbles, which writes $\sigma_{0c} \sim \Delta P_{cap} \sim 2\gamma/R$, where γ is the surface tension and R is the radius of the bubbles. At early times, R is of the order of 125 μm and $\gamma = 40$ mN/m therefore $\Delta P_{cap} \sim 640$ Pa, which is much higher than the yield stress of the 12.8 wt % suspension. Hence the yield stress is not sufficiently high to arrest Ostwald ripening. However in the case of the 15.5 wt % suspension, we find that the radius of the bubbles increases at early times and then it reaches a plateau of 400 μm after an hour. Indeed the yield

stress is $\sigma_0 = 200$ Pa, which is higher than ΔP_{buoy} but lower than ΔP_{cap} at early times. As time goes on, as the size of the bubbles increases, ΔP_{cap} decreases. When R reaches R = $2\gamma/\sigma_0 \sim 400$ µm, the Ostwald ripening is theoretically arrested consistently with our measurements. We note that our results are not consistent with Kloek et al. numerical simulations, which predict that when the bulk shear elastic modulus of the aqueous phase is above 10^4 Pa the Oswald ripening is completely arrested[4]. In our case, Oswald ripening is observed at early times for the 15.5 wt % suspension although the value of its shear elastic modulus is 10^4 Pa. In their simulations, Kloek *et al*. consider one single spherical bubble while in our case our bubbles are not spherical and surrounded by other bubbles.

<InlineImage6>
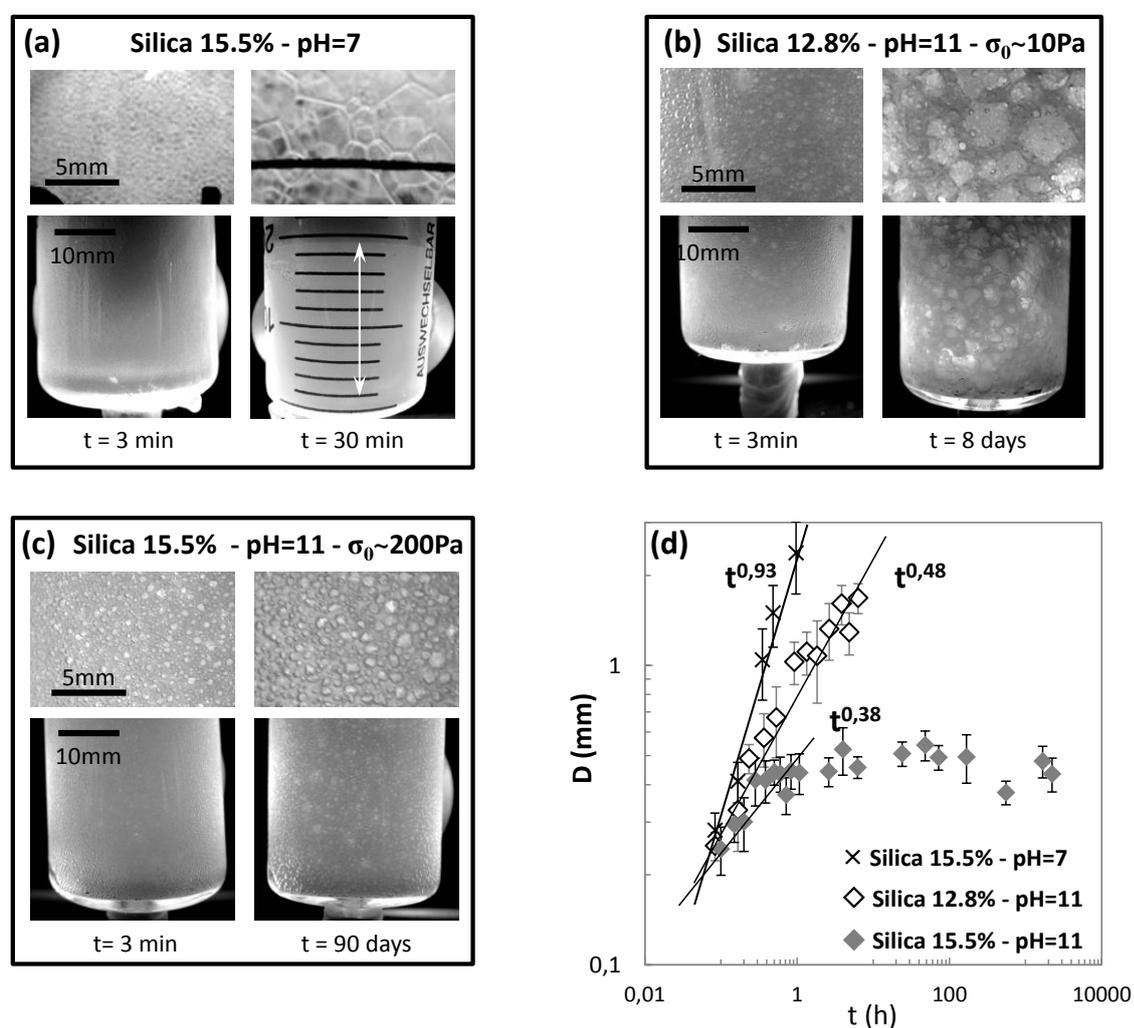
Figure 6. Photographic image of the foams obtained with a) the PEI/silica suspension with 15.5 wt % silica at pH7, b) the PEI/silica suspension with 12.8 wt % silica at pH10.5, c) the PEI/silica

suspension with 15.5 wt % silica at pH10.5. d) mean diameter of the bubbles (measured at the syringe wall) as a function of time for the same suspensions as in a), b), c) $C_{12}E_{23}$ concentration 1.65 g/L

Conclusion

In this article we examined the foamability and foam stability of a series of PEI/silica gel suspensions with varying particle concentrations. These suspensions exhibit a finite yield stress whose value can be tuned by varying the particle concentration and the pH when all the suspensions are in the fluid state – at pH7 – the air fraction is relatively high (80% for the 15,5 wt % suspension) however the foams are very unstable to drainage, when the suspensions are in the gel state – at pH10.5 –, the obtained air fraction decreases for increasing suspension concentration, from $\phi_{air} = 80\%$ for the 12.8 wt % suspension to $\phi_{air} = 8\%$ for the 19.7 wt % suspension. The most concentrated suspension, i.e 19.7 wt % could not be foamed. In the gel phase – at pH10.5 – depending on the yield stress, the drainage and Oswlad ripening may be hindered. For a yield stress of about 10 Pa – at 12.8wt% suspension – the buoyancy force is overcome and drainage is arrested. However it is too low to prevent Ostwald ripening. But a yield stress of 200 Pa, is high enough to arrest drainage. At short times, Ostwald ripening is observed. At longer times as the size of the bubbles increases, the capillary pressure decreases and becomes lower than the yield stress. As a consequence the Ostwald ripening is arrested when the bubble radius reaches 400 µm for a yield stress of 200 Pa.

The results obtained in this study show that there is an optimal silica concentration which combines good foamability and large stability to drainage and Ostwald ripening. Moreover the yield stress appears to be a way to control the bubble radius. Moreover these PEI/silica suspensions are promising systems for the development of 3D printable porous materials even though the size of the bubbles, of the order of 400 µm, limits the spatial resolution that can be reached when printing the foamed gels. Finally the results obtained in this study confirm previously obtained results which show that drainage and coarsening can be arrested for sufficiently high yield stress.

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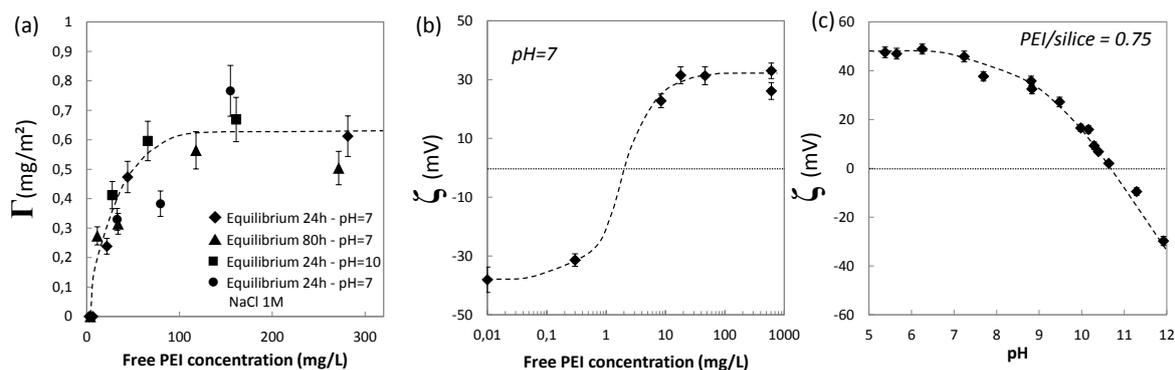
Figure 1. a) Surface coverage of PEI on the silica particles as a function of the free PEI concentration for suspensions without $C_{12}E_{23}$b) zeta potential of the silica particles as a function of the free PEI concentration at pH7 for 400mg/L of silica particles, C) zeta potential as a function of pH for PEI/silica ratio of 0.75, ie silica concentration 400 mg/L and PEI concentration of 300 mg/L. Dashed lines are guides for the eye to see the trends.

<InlineImage3>
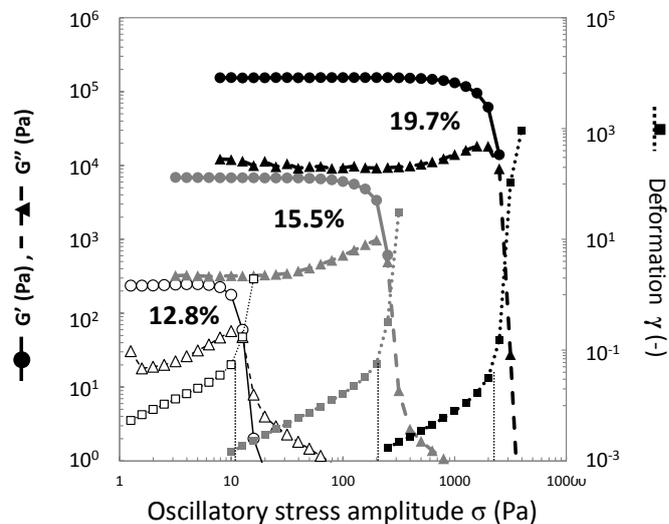
Figure 2. Storage modulus, G', loss modulus, G'' and deformation amplitude as a function of oscillatory shear amplitude, for PEI/Silica suspensions at pH 10.5, with various Silica concentration, keeping a PEI/silica ratio of 0.75. Vertical lines stand for the yield stress, determined as the stress for which G' collapses and the slope of the deformation/stress curve changes, according to Reference 28.
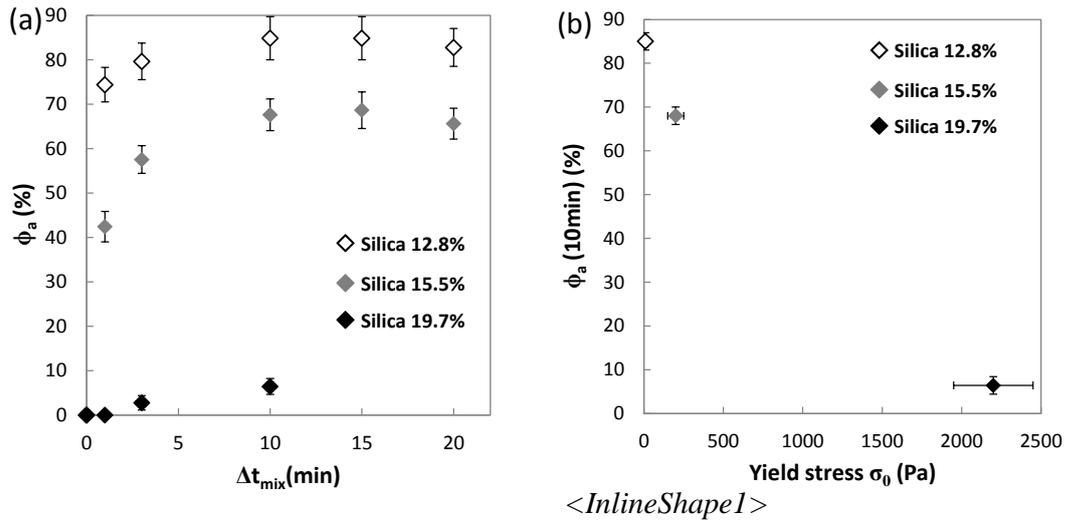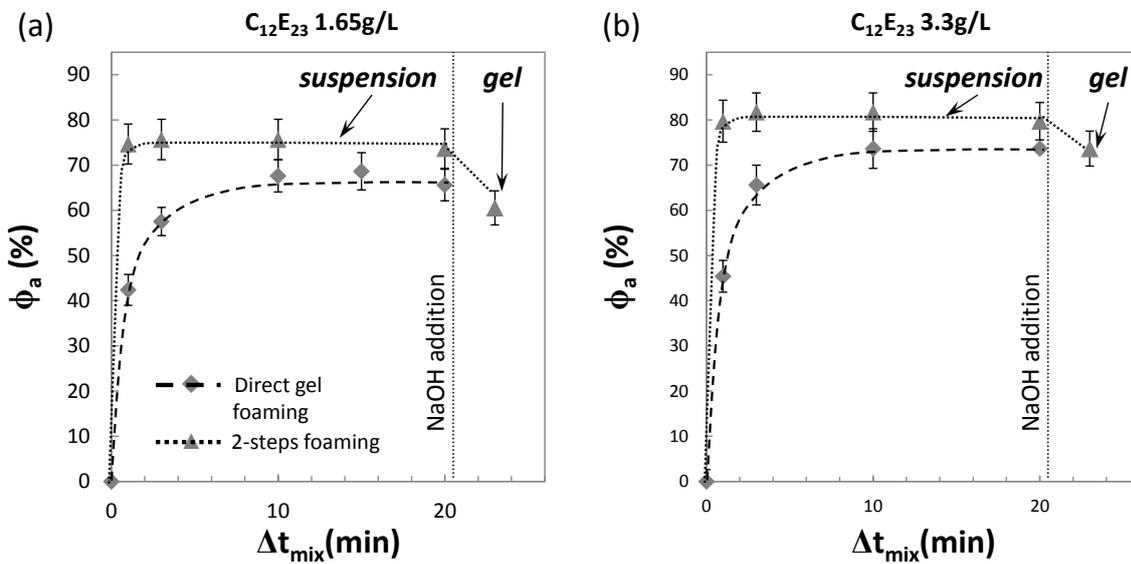
Figure 3. (a) Air fraction incorporated into the foams as a function of the shearing time for three particle concentrations, 12.8wt %, 15.5 wt %and 19.7wt %. The $C_{12}E_{23}$ concentration is 1.65 g/L. and pH=10.5 (b) Value of the air fraction after 10 minutes mixing as a function of the silica content

<InlineImage4>

Figure 4. Air fraction as a function of time during the two-step foaming process for PEI/silica suspension containing 15.5 wt % silica, 11.6 wt % PEI and 1.65 g/L of $C_{12}E_{23}$ in a), and 3.3 g/L of $C_{12}E_{23}$ in b. In a) and b), the suspension is foamed at pH7 as the suspension is fluid and then the NaOH is added to obtain a strong gel. The foaming of the suspension in the fluid state is higher

than when the suspension is foamed at pH10.5 directly, however as NaOH is added, the air volume fraction decreases from 75% to 60% in a), and from 80% to 70% in b).
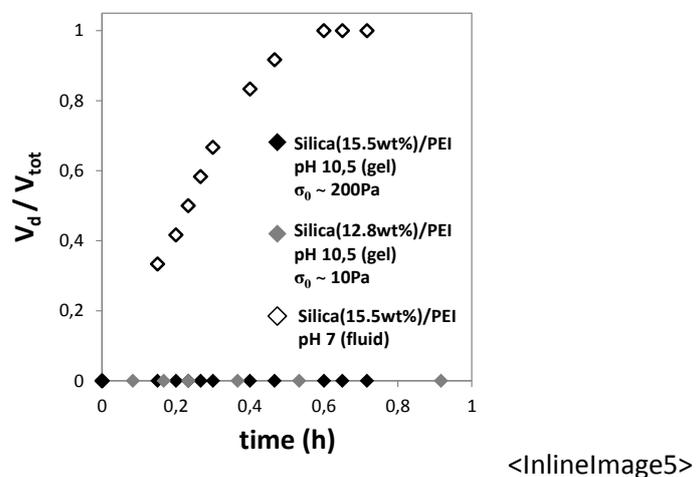

<InlineImage5>

Figure 5. Drainage flow of the PEI/silica foams with varying silica concentrations. V_d/V_{tot} as a function of time. V_d is the volume of drained liquid and V_{tot} is the total volume of drained liquid. $C_{12}E_{23}$ concentration is 1.65 g/L