Highly structured porous solids from liquid foam templates

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\textbf{Abstract}

We demonstrate the generation of highly structured porous solids from liquid foam templates, using ordered foam layers and threads made from hydrogels. For this purpose we separate sufficiently foam generation and solidification: well known and highly controllable liquid foam structures are created, which are thereafter ‘frozen’ in situ through polymerisation and cross-linking. Being extendible to a large range of materials and length scales, such an approach opens up a plethora of opportunities in material development.

\section{Introduction}

Composed of gas bubbles integrated in a continuous polymer phase, polymer foams display a vast range of complex properties (excellent thermal and acoustic insulation, mechanical damping, liquid absorption, light scattering, ...) making them extensively used materials in numerous applications. More recent developments see foams as increasingly fancy meta-materials: with large surface-to-volume ratios they make for ideal catalysts, nanofoams offer nearly perfect insulation, and foams containing carbon nanotubes provide conductivity and especially material strength within a single material [1].

The complex properties of foams are governed in particular by their structural parameters, such as the average size and size distribution of the bubbles and their spatial order. Relationships between these parameters and the overall foam properties are by now quite well understood. Still lacking, however, is the ability to control these parameters in solid polymer foams to a high degree of accuracy. This is due to the fact that in most standard large-scale production techniques (such as extrusion), foam generation and solidification are coupled in highly complex ways. An elegant solution to this problem consists of sufficiently separating both processes by using liquid foams (stabilised by surface active agents) as templates for polymerisation. As such one can exploit the vast expertise developed in the physics of liquid foams over the past few decades [2–4]. The feasibility of such an approach has already been successfully demonstrated for disordered TiO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5} foams and silica scaffolds within a movement towards an “integrative chemistry towards designing novel and multiscale architectures” (see [5] and references therein). It is also becoming common practice in the generation of metal foams [6]. A closely related subject is that of emulsion polymerisation, in which droplets or droplet shells of monomeric solutions are polymerised to obtain highly monodisperse particles of various geometries (7) and references therein).

We demonstrate here the feasibility of this approach for polymer foams by using the example of highly structured, monodisperse wet foams generated with a milli-fluidic flow-focusing technique [8–13], which is described in detail in Section 3. These foams consist of small bubbles (a few hundred micrometers in diameter) in which capillary forces outweigh gravitational drainage of liquid such that the bubbles remain spherical. This leads to spontaneous ordering of the bubbles into close-packed structures under the influence of gravity or confinement [14–17], which is further discussed in Section 4.
Our liquid foams are made from aqueous monomer (acrylamide) solutions, in which polymerisation/cross-linking starts during foam generation. Polymerisation times are chosen in such a way that the liquid foam has sufficient time to find its equilibrium structure before solidifying (Section 5). The two major stumbling blocks of foam polymerisation in past attempts [18,19] have been insufficient foam stability and phase separation, during which water and bubbles are expelled from the polymer network. We could solve both problems simultaneously by significantly accelerating the polymerisation (here less than 15 s).

2. Chemistry

The ingredients for the polymerisation reaction employed here are based on an old work-horse of hydrogel formation [20], in which acrylamide is polymerised and cross-linked in an aqueous solution, using sodium peroxodisulfate and N, N’-methylenebisacrylamide as initiator and cross-linker, respectively. We add TEMED (N, N’, N’-tetramethyl ethylene diamine) as an accelerator to ensure sufficiently rapid polymerisation (less than 15 s). Table 1 lists all the chemical ingredients used. The resulting material consists of a three-dimensional polymer network which can absorb many times its own weight of water in an entirely reversible manner. This absorption is sensitive to (and therefore controllable by) a variety of factors, such as solvent composition, ionic strength, pH value, and temperature. We add the non-ionic surfactant Lutensol® AT18 (fatty alcohol alkoxylate) for foam stabilisation.

We choose the chemical composition in such a way that polymerisation times are about 11 s. This is short enough to avoid phase separation and long enough to allow the formation of a structured liquid foam before significant solidification sets in at the final stage of polymerisation. In order to have sufficient control over the onset of polymerisation we prepare two separate solutions A and B, of which solution A contains the monomers, the cross-linker, the accelerator, surfactant and water, while solution B contains only the initiator, surfactant and water. Polymerisation only starts once both solutions are put together and is sufficiently slow at the beginning to allow foam structures to equilibrate. The detailed chemical composition of the solutions A and B are shown in Table 1. All chemicals were provided by BASF. We generally worked at room temperature. To extend polymerisation times, we sometimes cooled the solutions in an ice bath before injecting them into the device.

3. Foam generation

We generate highly monodisperse foams using a flow-focusing technique [8], in which air and liquid are simultaneously forced through a narrow capillary at constant flow rate (Fig. 1). Within the right parameter ranges (flow rates Q and capillary diameter $D_c$) [9–13], a thin gas thread is formed which breaks up to the liquid.

Table 1

<table>
<thead>
<tr>
<th>Solution</th>
<th>Component</th>
<th>Function</th>
<th>Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Acrylamide</td>
<td>Monomer</td>
<td>20 g</td>
</tr>
<tr>
<td>A</td>
<td>N, N’-Methylenebisacrylamide</td>
<td>Cross-linker</td>
<td>0.53 g</td>
</tr>
<tr>
<td>A</td>
<td>N, N’, N’-Tetramethyl ethylene diamine</td>
<td>Accelerator</td>
<td>1.57 g</td>
</tr>
<tr>
<td>A</td>
<td>Lutensol® AT18</td>
<td>Surfactant</td>
<td>0.18 g</td>
</tr>
<tr>
<td>A</td>
<td>Distilled water</td>
<td>Solvent</td>
<td>48 ml</td>
</tr>
<tr>
<td>B</td>
<td>Sodium peroxodisulfate</td>
<td>Initiator</td>
<td>4 g</td>
</tr>
<tr>
<td>B</td>
<td>Lutensol® AT18</td>
<td>Surfactant</td>
<td>0.18 g</td>
</tr>
<tr>
<td>B</td>
<td>Distilled water</td>
<td>Solvent</td>
<td>50 ml</td>
</tr>
</tbody>
</table>

The ingredients are separated into two solutions labeled A and B such that radical polymerisation starts once both solutions are put together. This is done in a volume ratio of 1:1.

![Figure 1. Foam generation: air and the two solutions A and B are simultaneously forced at constant flow rate $Q_l = 1$ ml/min through a thin capillary ($D_b = 500 \mu$m), in which the gas thread breaks up into highly monodisperse bubbles. Polymerisation starts during bubble formation, i.e. when the solutions A and B come into contact.](image)

form extremely monodisperse bubbles (polydispersity generally less than 2%) down to a few micrometres in size. Bubble diameters $D_b$ produced with such a device are of the order of the capillary diameter $D_c$, and can be tuned further by adjusting the ratio of the liquid flow rate $Q_l$ to the gas flow rate $Q_g$. We find for our device geometry:

$$D_b = (1.19 \pm 0.2)D_c \left[ \frac{Q_g}{Q_l} \right]^{0.33 \pm 0.06},$$

which is in line with previously reported results [10–13]. The devices were built by drilling millimetric holes into a small Plexiglas block into which the capillary was glued. The air and liquid flow rates where provided using syringe pumps at flow rates of the order of $Q_g \approx Q_l \approx 1$ ml/min. When working with flow rate controlled systems, neither the liquid viscosity, nor the orifice length play a role for the determination of the bubble size generated by the device. The bubble size is also independent of the surfactant used for foam stabilisation. Since the ratio $Q_g/Q_l$ also sets the gas fraction and the production rate, the properties of the final foam can be accurately controlled by adjusting the capillary size and the flow rates. We choose here to work with a capillary diameter of $D_c \approx 0.5$ mm and therefore obtain bubbles sizes between 0.2 and 1 mm. As indicated in Fig. 1, we inject the two solutions A and B (see Table 1) separately (but simultaneously) at equal flow rates into either side of the bubble generator. The solvent concentrations of the solutions were adapted to enable addition by equal volumes.

Due to the highly laminar flow on such small length scales, the two fluids do not mix. However, we find that in our case this does not pose a problem, as diffusion between the solutions seems sufficiently efficient.

4. Control over foam structures

In liquid foams in equilibrium, capillary forces counteract gravitational drainage of liquid [3]. For small bubble sizes, capillary forces are sufficiently strong to maintain a region of height $H$ (Fig. 2) in which the bubbles remain spherical (liquid fraction of 26%) and self-organise into hexagonally close-packed structures if all bubbles have the same diameter $D_b$ [14–16,21]. Unlike solid colloidal systems, bubble “colloids” do not require an additional energy input.
to encourage ordering, which is likely to be due to the lack of solid friction between its constituents. The approximate height of this wet foam region can be obtained by equilibrating capillary and hydrostatic forces, which gives [15]

$$H \approx \frac{l_c^2}{D_B},$$

where $l_c = \sqrt{\gamma/(\rho g)}$ is the capillary length, $\gamma$ the surface tension, $\rho$ and $g$ the liquid density and the gravitational acceleration, respectively. This means that $N$, the number of layers of bubbles which remain spherical, is given by

$$N \approx \left( \frac{l_c}{D_B} \right)^2.$$ (3)

We typically work with bubble sizes of the order of 0.5 mm, which provides us with of the order of 10 layers of spherical bubbles. For larger, dry bubbles (> 1 mm diameter) and hard-sphere colloids it is known that the presence of boundaries and confinement induce order [22–24]. In particular, bubbles confined in tubes of diameters of a few bubble diameters very easily form cylindrically close-packed structures with hexagonal (phyllotactic) surface patterning which are determined by the ratio of the bubble diameter to the tube diameter [3,25].

For equal-volume, spherical bubbles deposited between narrowly spaced glass plates we find a behaviour very similar to that of hard-sphere colloids: the structures are always hexagonally close-packed but assume different orientations which minimise the packing density for a given plate spacing. We demonstrate this in Fig. 3, where a monodisperse foam is confined between two glass plates which make an angle of 1.1°. The observed structures alternate between regions of the (1 0 0) direction of the fcc (face-centered-cubic, Fig. 4 a) packing (symbol □), which has a square arrangement of bubbles at the surface, and the (1 1 1) direction of the fcc packing (symbol △), which has the classical hexagonal bubble arrangement at the surface. In the latter case, the hexagonal layers are sometimes packed in an ABAB (hcp structure)… or random close-packed fashion (e.g. ABACB…), but the fcc structure, which corresponds to an ABCABC… packing is certainly dominant—as observed in other experiments [15,16].

The alternation between the two structures fcc(1 0 0) and fcc(1 1 1) is due to the difference in the height $H_L$ of the bubble layers parallel to the confining plate. For fcc(1 0 0), $H_L = \sqrt{2R}$ (Fig. 4b), while for fcc(1 1 1) $H_L = \sqrt{8/3R}$ (Fig. 4b). In a wedge, this leads to a transition sequence of 1△ → 2□ → 2△ → 3□ → 3△ → 4□ → 4△, etc., as shown in Fig. 3.

![Fig. 2. Ordered liquid foam: a monodisperse foam (400 µm bubble diameter) resting on a liquid pool under the influence of gravity. If the bubbles are small, capillary forces are sufficiently strong to maintain a large region $H$ just above the liquid pool, where bubbles remain spherical and self-order into hexagonally closed-packed structures.](image1)

![Fig. 3. Forced order under confinement: bubbles (400 µm in diameter) under confinement in a wedge with an angle of 1.1° starting with no spacing at the left side. From left to right the following transitions take place: 1△ → 2□ → 2△ → 3□ → 3△ → 4□ → 4△.](image2)

![Fig. 4. Layer thickness of different fcc structures: the unit cell of the fcc structure (a) and a sketch of the determined layer thickness, $H_L$, dependent on the bubble radius $R$, which is $\sqrt{2R}$ for layers stacked in the fcc(1 0 0) orientation (b) and $\sqrt{8/3R}$ for layers stacked in the fcc(1 1 1) orientation (c).](image3)
An illustrative example of the ability to force a specific bubble structure is shown in Fig. 5, where the spacing between parallel plates is chosen such that three bubble layers are forced to form large arrays of the fcc(1 0 0) structure. Without confinement, such extended fcc(1 0 0) arrangements do not occur. This image also illustrates a problem which any application of self-organised bubble crystals faces: the presence of grain boundaries. However, their number can be reduced by adapting the way the foam is deposited.

When working with low-viscosity fluids, as is the case here, the formation of the bubble structures occurs instantly after deposition and is not hindered by a short polymerisation time. In general we find that order can be forced up to 6 bubble layers.

With this knowledge on how to control liquid foam structures we deposit the foams immediately after their generation between narrowly spaced glass plates or in narrow silicone tubes. Less dense ordered structures containing polyhedral, instead of spherical, bubbles, can be generated by applying pressure gradients to the bubble structure, as demonstrated by Hoehler et al. [16].

5. Polymerisation

The foam structures polymerise without changing their bubble structure if polymerisation times are kept sufficiently short, which is 15 s for our recipe and in our conditions. Otherwise a phase separation occurs, which appears to push the bubbles out of the polymer matrix, such that one obtains a solid polymer block separated from a highly stable aqueous foam which remains unpolymerised. The general mechanism of such phase separation is well known for hydrogels [26], but the precise implication in the presence of a foam is not yet clear to us. Figs. 6 and 7 show examples of ordered polymerised foam structures once they have been removed from the confining glass plates and silicone tubes, respectively.

We generally obtain open-cell foams, in which the thin films separating bubbles break during polymerisation. This may be due to the sensitivity of thin film polymerisation to the presence of oxygen radicals in the air or the solution. We succeeded in generating more closed-cell foams when using nitrogen instead of air, after degassing of the solutions and by using an even more rapid polymerisation.

Since the created foams are made from hydrogels, they can be dried and re-swollen repeatedly after polymerisation. We find that this can be done entirely reversibly, i.e. without destruction of the foam structure. In the case of open-cell foams, this greatly accelerates the adsorption of water in a sponge-like fashion: due to the small bubble sizes, capillary forces drive the water rapidly into the interconnected bubble network from where it can slowly penetrate the hydrogel.
6. Conclusions and outlook

The presented research demonstrates that by matching appropriately the time scales of the equilibration of the foam structure, of the polymerisation, foam destabilisation and phase separation, one obtains a system that allows straightforward polymerisation of highly controllable aqueous foam structures without loss of the bubble order. We would like to emphasise that the foams are sufficiently stable with a standard technical grade surfactant (here Lutensol® AT18) and that no particular working conditions are required to generate highly structured porous polymeric solids. To optimise such procedures, for instance by prolonging the onset of polymerisation or, ideally, by entirely separating foam generation and polymerisation, different polymerisation routes need to be explored and, in particular, the mechanisms driving the phase separation in the presence of bubbles needs to be understood (and hence controlled), as well as thin film polymerisation. This will be particularly important for the polymerisation of polyhedral, i.e. dry, foam structures.

We believe that with the in situ polymerisation of liquid foams a new cornerstone may be laid for the production of porous polymer materials with highly controlled, self-organised pore structures. Being extendible to a large range of materials and length scales, such an approach opens up a range of opportunities in the development of materials, which could eventually be doped with agents (carbon nanotubes, nano-particles, etc.) that respond to external stimuli, such as electric, magnetic or electro-magnetic fields [27].

On the more fundamental side, the controlled solidification of well characterised foam structures may allow us to better understand how the physical properties of the same foam structure change with the solidification of the liquid network in an attempt to link our understanding of the properties of liquid and solid foams. Furthermore, the availability of highly structured solid foams will provide means to test quantitatively a range of analytical and computational predictions made for the properties of ordered foam structures [28,29], which up to now could not be verified experimentally due to the lack of the availability of perfectly ordered foam structures.

Unfortunately, a limiting factor for material development is given by the fact that the crystalline bubble order is of finite extent, i.e. the production of large-scale, three-dimensional ordered materials is probably not feasible. We would like to emphasise, however, that the realm of materials with at least one limited dimension is vast, containing geometries such as structured foam sheets (membranes, filters, container walls, etc., as in Fig. 6) or foam threads (as shown in Fig. 7). The latter, for example, can be woven, knitted or knotted with ease to be transformed into different kinds of products (Fig. 8).

Last but not least, the separation of liquid foam generation and foam solidification may also be applied for the generation of monodisperse, disordered polymer foams. Despite lack of bubble order, such an approach promises a not yet available control of the final material properties, such as bubble size and relative density. In this case, material dimensions are unlimited, but foam production needs to be upscaled significantly, for example, by parallelising the mini-fluidic bubble generation technique.

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References