

NONMETALLIC SOLID FOAMS - A NON-EXHAUSTIVE OVERVIEW

Martin Meier

Foam Group, LAS, BTU Cottbus, Germany, meier@tu-cottbus.de

Abstract - Nonmetallic solid foams are cellular materials produced by different routes. A communality of all processing routes – also with metal foam production routes - is one step where the liquid phase is up-foamed by a blowing gas or by blowing in gas, followed by a *freezing* of the structure. The production routes for anorganic glass and ceramic foams, and the main plastic foams, like Polystyrene, Polyethylene and Polyurethane foams are described. Within the field of polymer foams, food technology, cosmetics, flotation, waste water management or oil recovery the chemistry of foam systems, which means mainly surface and colloid chemistry and reaction kinetics, is the more dominating research area in comparison with the physics of foams.

INTRODUCTION

Everybody is familiar with aqueous foams as beer foams, shaving foams or in a bubble bath and most of us are fascinated about the fragility and the moving colours on the bubbles surfaces looking like little rainbows. Foam produced at the sea-shore (see Fig. 1) is also well-known and can be found in poetries like the one below.

-----.....
*He took the anchor on his back
And leaped into the main;
Through **foam** and spray he clove his way,
And sunk and rose again!*

*Through **foam** and spray, a league away
The anchor stout he bore;
Till, safe at last, he made it fast
And warped the ship ashore!*
-----.....

[part of the ballad "A Sailor's Yarn" by James Jeffrey Roche (from Davy Jones' Yarns and Other Salted Songs, by Thomas R. Ybarra, Henry Holt and Company)]



Fig.1, Foam at the sea-shore

Another famous kind of foam is not salted but sugared - like whipped cream or “mousse au chocolat”. All these foams are not stable (obviously and thermodynamically) due to the flow of liquid in this disperse system. Freezing the liquid gives a solid foam (e.g. *ice cream*). Below there are some examples of foam-like structured or cellular solid materials. Cellular solid materials can be found everywhere in the nature, e.g. bone (see Fig. 2) or cork (Fig. 3). These natural materials have been used a long-time by mankind due to their lightweight or thermal isolating properties.

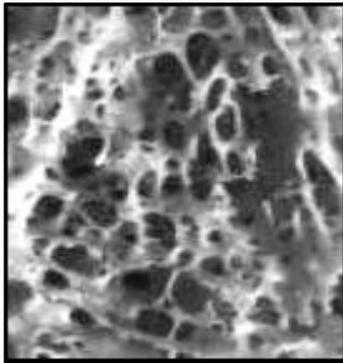


Fig. 2, Bone



Fig. 3, Cork

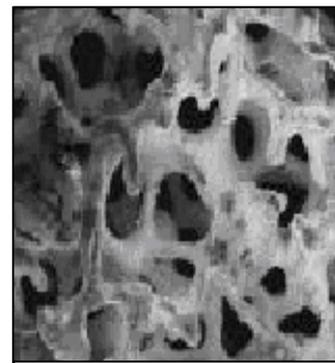


Fig. 4, Slag foam

The first artificially commercially produced solid foam material was glass foam, available since the 1930's, used today mainly for isolation purposes in house-buildings. The main advantage of rigid glass foam as part of the isolation of a building is the extreme long-life stability combined with an impermeability to water and gases. The predecessor of this material had been slag-foams (a really "frozen foam", see Fig. 4), a kind of waste-product during smelting. An important application for slag-foams and, later, glass foam was the use as material for buoys due to its high resistivity to seawater.

Solid foams can have excellent heat- and sound-insulation properties due to their high resistance against mass transport. Other foams have the ability to absorb a lot of energy, which makes them very useful in cushioning and packaging applications. Another advantage of foams is the low amount of mass needed to obtain the same volume as the unfoamed solid. This is due to the introduction of gases. A disadvantage is the relatively expensive production process and the fact that the knowledge about foams and foaming is mainly based on empirical observations.

GLASS FOAM

The basic principle of glass foam manufacture is to generate a gas in molten glass at a temperature between 700 and 900 °C. The gas expands and forms a structure of cells resulting in a porous body. The glass foam can be either made from a glass melt or by sintering glass particles. The latter process requires ground glass to be mixed with a foaming agent, while heating the foaming agent it releases a gas and expands the molten glass mass. There are numerous patents on glass foam production since the 30ties of the last century. The early products were blocks or preshaped articles, and used specially formulated glasses to form the glass foam such as alumino-borosilicate glass, either by a route from molten glass or mixing the glass components and a foaming agent, e.g. Carbon, then firing. The main glass foam producers in Europe and North America use a high percentage of waste glass in their products nowadays. Originally glass foam was manufactured from a specially formulated glass composition using virgin glass only. Currently, there are a number of glass foam production plants that are using up to 98% waste glass in their product.

Currently, there are three main product types of glass foam:

- Loose glass foam aggregate - continuous production of sheets of glass foam that are broken into glass foam aggregates and classified (Fig.5).
- Panels, Blocks and Tubes – generally continuous production of blocks and shapes in moulds that are then cut and shaped. Also manufactured by a batch process (Fig. 6).
- Pelletisation – continuous production of spherical pellets of glass foam that are used in the manufacture of lightweight blocks, panels and slabs.



Fig. 5, Loose glass foam



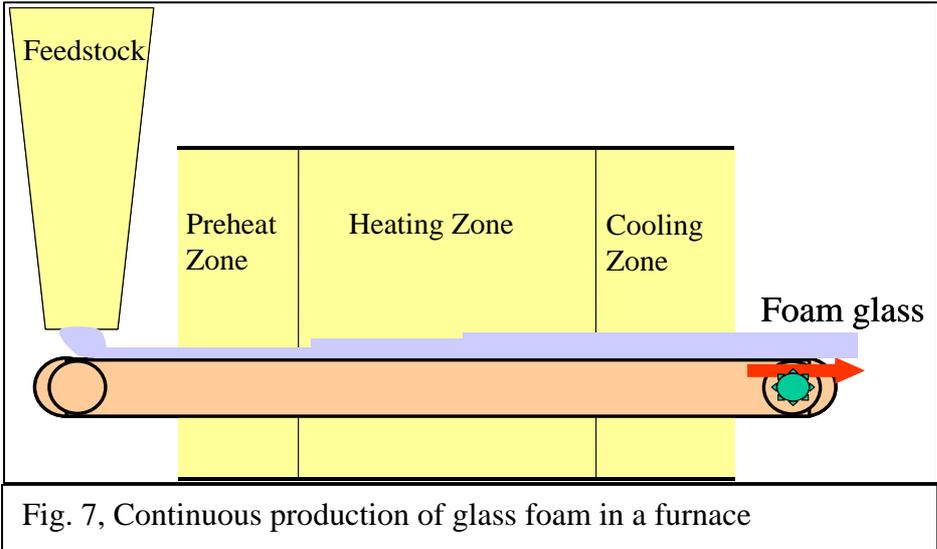
Fig. 6, Glass foam

The application of glass foam is mainly as a rigid insulation material. Due to its excellent long-life structural properties, it is suitable for use as insulation in roofs, walls and traffic areas.

The principle of the glass foam process is that between 700 and 900°C the glass powder becomes a viscous liquid and then the foaming agent decomposes into a gas that in turn forms bubbles. The glass needs to have sufficient viscosity to hinder the gas bubbles rising up so that they remain in position during the foaming heat cycle. If the temperature is too high the bubbles will rise and the body will collapse and not form a foam body. Therefore, the control of the heating rate is one of the most important factors in optimising the glass foam product. Rapid heating can cause the glass foam feedstock to crack, whilst slow heating will lead to early release of the gas from the foaming agent before the viscosity of the glass is low enough to allow the glass to expand. A further complication is that the glass foam feedstock is relatively insulating. Therefore, there is the potential to overheat the top surface in order to heat the bottom of the feedstock. This overheating can cause the top cells to collapse resulting in an inferior product.

The finely ground glass powder is mixed with the foaming agent which is the feedstock for the foaming furnace (Fig. 7). Suitable foaming agents can be calcium sulphate (CaSO_4) or calcium carbonate (CaCO_3). Gypsum is a readily available source of CaSO_4 and limestone is a readily available source of CaCO_3 . If the air in the furnace at the foaming zone is replaced with either SO_2 or CO_2 the thermal conductivity of the glass foam will be decreased. Fly ash which is a waste mainly from coal-fired power stations, has been used as a foaming agent. The main constituents of fly ash are SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and SO_3 . SO_3 is the active foaming agent evolving SO_2 at the blowing temperature. However, fly ashes are waste materials from incinerators and therefore can contain toxic compounds and heavy metals. Silicon carbide (SiC) is also a known and used foaming agent that gives controlled and precise cell sizes. The SiC reacts with the SO_3 within the glass structure to form CO_2 and S. The foaming agent particle size affects the cell size, which will influence the performance

and characteristics of the glass foam. Gypsum particle sizes between 110 and 160 microns (limestone: 105 and 155 microns) should be used to achieve a desired cell size. This in turn determines the density of the product. The lower the product density the lower the thermal conductivity (more thermally insulating). Slightly increased atmospheric pressure (1.1 bar) during firing is reported to give a better degree of control of the foam formation. The smaller the cell size the higher the compressive strength of the glass foam body is, as it is a function of the inverse square root of the cell size.



CERAMIC FOAM

Ceramic foam is made by making a slurry of finely ground ceramic particles (<10 microns), a foaming agent and a setting polymer. The slurry is whipped to entrap gas and is poured into a mould and the foam body sets at room temperature to form a solid body. It is then fired to sinter the ceramic particles together to form a strong porous ceramic body. Applications of open cell ceramic foams (reticulated foams) are in the areas of filtration (also for high-temperature filtration), catalysts and heat exchangers. Due to their high-temperature applications most of the ceramic foams are made of Silicon-compositions like SiC or Si₃N₄. A glassy carbon foam material is also supplied for special applications.

POLYMER FOAM

Similar to the metal foam routes described in another chapter, there are several processing techniques to produce plastic foams, either as open- or closed-cell foam.

A foam can be made from nearly every polymer. The polymer selection for foam applications mainly depends on the properties of the polymer, the foam production process and the economics of the process. Polyurethane (PUR), and to a lesser extent polystyrene (PS), and polyvinylchloride (PVC) foams, combine excellent physical and mechanical properties with relative easy and cheap production processes. Approximately 70 – 80% of all produced polymeric foams is based on PUR, PS, or PVC.

In the last few years the production of polyethylene foams is rapidly increasing. Their good mechanical properties and the low polyethylene price are responsible for this. The choice of the polymer determines whether the resulting foam will be rigid or flexible. In general, elastomers will result in flexible foams, whereas glassy polymers will produce rigid foams. An important property of all foams is their density. It is possible to distinguish three different classes of polymer foams, considering their density. High density foams have a density between 0,5 g/cm³ and 1 g/cm³. Main applications of high density foam are in coaxial cables, due to their relative low dielectric constant, in wood substitutes and in automotive applications. Medium density foams have a density between 0,1 g/cm³ and 0,5 g/cm³. These foams are mainly used in packaging applications and as insulation in buildings. Low density foams are foams with a density lower than 0,1 g/cm³. These foams have a ratio of the gas volume to polymer volume larger than 10. Due to their low heat- and sound conductivity these foams are mainly used in insulation applications.

The formation of polymeric foam takes place in the stages of mixing, nucleation, bubble growth formation of spherical and polyhedral foam and, in the end, in the curing stage. There are basically two processes that are used to mix the polyurethane raw materials. The low-pressure mixing method employs mechanical stirrers or stationary mixing elements. High-pressure mixing works according to the impingement injection principle or the parallel-stream injection principle where highly pressurized (>120 bar) reaction components are injected into a mixing chamber.

In order to make a polymeric foam, a vapour or gas (blowing agent) is applied, which expands within the polymer. In Fig. 8 the succeeding states during the development of a solid polymeric (here: polyurethane) foam are shown.

Within the following stage, very small, dispersed gas bubbles form the nuclei into which the developing or released gas propellant diffuses as the reaction proceeds. Distribution, number and size of the nuclei determine the resulting foam structure. The nucleation gas, usually air or nitrogen, is dissolved in the reaction components prior to processing. The total amount of gas dissolved in the components depends on the gas pressure load on the liquid, the exposure time and the diffusion surface of the liquid. The gas nuclei are released during the mixing stage.

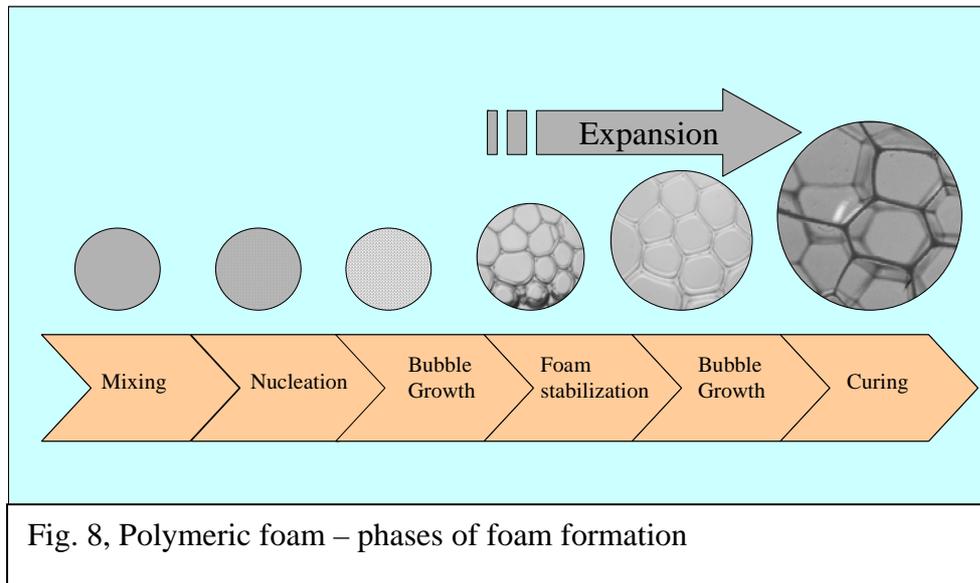


Fig. 8, Polymeric foam – phases of foam formation

The gas propellant is formed as the urethane reaction begins. This may be done by way of a chemical process, i.e. by a water–isocyanate reaction that runs parallel to the urethane reaction and produces gaseous CO_2 . The gas propellant can also be produced by evaporating added physical blowing agents. The exothermic reaction process causes a supersaturation of the solution consisting of gas propellant and reactive mixture. The gas is expelled from the solution and diffuses into the gas nuclei. The same process may also take place when lowering the mixture pressure under the equilibrium limit of the relevant solution. The so-called spherical foam develops towards the end of the bubble formation phase. It consists of small and larger-sized spherical bubbles that grow as the gas propellant diffuses in. Once the bubble growth has advanced to a point where the bubbles are located sufficiently close to each other, bubbles of different sizes coalesce. Owing to the higher internal pressure of the smaller bubble, the gas permeates from the small bubble into the large one. The internal bubble pressures are built up through the surface tension of the liquid and the relevant bubble radii.

The bubble growth proceeds until as much liquid has been used that the individual bubbles are separated by nothing but the cell membranes. As soon as this state has been reached, the bubbles change their shape from a spherical to a polyhedral form. During the entire period of bubble growth, the frothing process is influenced by stabilizers. During foam formation and the urethane reaction progress, temperature and viscosity of the mixture rise steadily until the foam has been cured. The coordination between reaction progress, bubble development and its stabilization largely decides the future cell structure of the foam, i.e. whether it will be an open-cell foam (flexible foams) or a closed-cell foam (insulation foams). Through the crystallization of the urethane hard segments, the bubbles of open-cell foams are weakened to an extent that the cell membranes rupture due to overstretching at the end of the rising

process. The latter needs to happen precisely at the time when the reaction has advanced to a degree that the remaining cell ridges are able to carry their own foam weight.

A mismatch between bubble growth, stabilization and reaction progress results in either the collapse of the rising foam mass due to a premature rupture of the cell membranes and the inability of the remaining cell ridges to carry the foam weight or in the foam remaining in a closed-cell state because the cell membranes have been overstabilized.



Fig. 9, Polyurethane foam with local foam collapse

For a mould-production of foams, further obstacles can be observed during the curing stage. The bubble growth is interrupted after the complete filling of a cavity when using the foam moulding method. However, the reaction has not yet been completed at that time. Hence, further heat is released, leading to a rising gas pressure in the cells. The cells cannot burst as they support each other and hold on to the mould walls. At this stage, it is of particular importance to prevent the young, low-viscosity foam mass from escaping from any part of the cavity by excessively large venting ports or the parting line of the moulding tool. If the foam escape cannot be avoided, the surrounding cells burst causing either a major or a minor collapse in those areas, which can be seen in Fig. 9.

Polyethylene foam

Basically there are two ways to introduce gases in polyethylene to produce a foam. Firstly, polyethylene foam can be produced using a chemical blowing agent. Chemical blowing agents are materials, with a relatively low decomposition temperature. Decomposition of these materials results in the release of a large amount of gas.

For example, Azodicarbanamide (ACA) will decompose at about 200 °C, and will release 200 and 300 cm³ gas per gram ACA, mainly nitrogen and carbon monoxide. In chemical foaming the chemical blowing agent will be mixed with polyethylene. Subsequent heating will have two effects, the decomposition of the chemical blowing agent and the melting of polyethylene. Combination of these two processes will result in bubble nucleation and the formation of a cellular structure. However due to the fact that the decomposition of chemical blowing agents is an endothermic process and the temperature will be increased, crosslinking of the polyethylene is necessary to provide mechanical stability of the resulting foam. This process is mainly applicable for high density foams. The use of a physical blowing agent e.g. in a two step extrusion process is the other important technique to produce polyethylene foams. In the first extruder the polymer is blended with other compounds, such as additives or other polymers, and mixed with the blowing agent under high temperature ($T > 100$ °C) and pressure (between 10 and 100 bar). This mixture is fed to a second extruder, which homogenises and cools this composition to the optimal foaming temperature. Extrusion into

ambient conditions results in the nucleation of bubbles due to expansion of the blowing agent. Subsequent cooling, also due to the expansion of the blowing agent, freezes in this structure and the foam is formed (see Fig. 10).

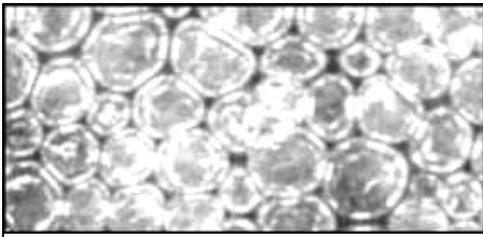


Fig. 10, Polyethylene Foam

“CFCs” (ChloroFluoro-Carbons) were used normally as physical blowing agent until 1990, mainly Dichlorotetrafluoroethane. It is known, that CFCs are largely responsible for the depletion of the ozone layer and contribute to the greenhouse effect. The Montreal protocol stated in 1987 that the use of CFCs would be prohibited after 1995. This led to the use of hydrocarbons, especially (iso-) butane and (iso-) pentane, as alternative blowing agent for polyethylene and, also polyurethane. However, these gases contribute to the greenhouse effect as well and, therefore, in the near future this will lead to the use of carbon dioxide as physical blowing agent for the production of low density, closed cell polyethylene foam. Compared to hydrocarbons, carbon dioxide has a low greenhouse potential, when using the same volume.

Polystyrene foam

Expandable polystyrene is the raw material or resin used for the molding of expanded polystyrene products. It is manufactured in the form of very small polystyrene beads with a weight-average molecular weight between 160,000 and 260,000 and contains 4 to 7% blowing agent, usually pentane or butane. The bead diameter can vary between 0.2 mm to 3.0 mm.

The first production methods developed involved a two step process. Polymerization of styrene monomer was followed by impregnation of the polymerized polystyrene bead with a blowing agent. Nowadays, almost all processes carry out polymerization and impregnation in a one-step process. The reactions occur in a single reactor designed to control the temperature and pressure of the reaction. Styrene monomer and water is charged to the reaction kettle equipped with an agitator. Various chemicals are added to effect suspension of the monomer in water and to control the polymerised bead growth, molecular weight and other parameters. The polymerization is an exothermal reaction and is controlled by reactor temperatures and pressures, as well as various catalysts. In the second phase of the process, the blowing agent is added under pressure and impregnates the soft polystyrene beads. The total batch cycle takes a little less than ten hours. When completed, the entire batch consisting of water and the impregnated polystyrene beads are dumped to de-watering systems. Following the de-watering process, the beads are transferred to dryers for drying. The conditions used to polymerize the beads play a controlling part in determining the exact shape and or skewness of the particle size distribution. The dried beads are then screened to provide the desired size cut. Various surface lube systems are added at this point to aid in screening and to eliminate potential lumping during pre-expansion. The resulting bead size(s) are defined as: Large "A", Medium "B", Small "C", Cup Grade "T", and various intermediate cuts may be made to meet specific processes and applications.

Expanded polystyrene is a closed-cell, lightweight, rigid plastic foam. It is manufactured either by extrusion or steam molding.

The extrusion process (XEPS) is currently used to produce rigid boards for building insulation, flotation, and Geofom applications or thin sheets of foam which are subsequently thermoformed into desired shapes such as meat trays or disposable food containers (density in the range of about $0,02 \text{ g/cm}^3$).

The steam molding process is referred to as EPS. EPS is primarily used for building insulation, Geofom, flotation, and for packaging of virtually anything requiring cushioning or insulation properties (density in the range of about $0,035 \text{ g/cm}^3$). An example can be seen in Fig. 11.



Fig. 11, EPS as packaging material

Molded expanded polystyrene (EPS) is manufactured by the expansion and subsequent steam molding of expandable polystyrene. There are two basic types of expandable polystyrene, regular and modified. The regular grades are designed primarily for packaging and related uses. Usually these grades comply with FDA requirements for use in direct food contact use. The modified grades contain a flame retardant to decrease the potential of fire spread from a small flame source.

The production of expandable polystyrene has three stages. In the first stage, the beads are fed to a vertical tank containing an agitator and a controlled steam input. This is referred to as pre-expansion. At this stage the final material density is determined. The expanded beads, whose volume can be up to 40 times the volume of the beads prior to expansion, are then stored for several hours in the open air; in this stage, the low pressure developed in the cell structure of the prepuff is equilibrated with the ambient atmosphere. After pressure stabilization, the prepuff is fed to a closed mold and again subjected to steam heat. The prepuff at this point has no room for further expansion and consequently fuses solid, producing a part defined by the mold. In order to mold the desired part at the required density, it is necessary to generate a prepuff particle with the size of the required density first. The pre-expansion of this raw material is carried out in vessels (pre-expanders) equipped with a controlled steam inlet, an air inlet, agitation and an automatic system for feeding the raw bead into the vessel. By controlling the bead feed rate, the steam and air flow, and the agitator rotation rate, the bead will soften at around $90 \text{ }^\circ\text{C}$, which is above the normal boiling temperature of the blowing agent, in this case pentane, at around $35 \text{ }^\circ\text{C}$. The internal vapor pressure will increase and these two simultaneous phenomena cause the bead to expand to the required density. This initial pre-expansion process can be carried out in either a continuous

or batch (discontinuous) operation. In the continuous pre-expander, expandable polystyrene beads are introduced continuously by an endless screw at the bottom of the pre-expander and the expanded beads (prepuff) come out the top (similar to a popcorn popper). In the batch process, the beads are loaded from the top and emptied after the operation at the bottom of the apparatus. Density adjustment of the product is carried out by controlling the period of time the beads remain in the expander and/or the pressure in the pre-expander. With batch pre-expanders, a very low density can be obtained as a result of being able to operate under pressure and higher temperatures. The prepuff exiting the pre-expander is usually fed to a fluid bed drier where it is gently dried.

CONCLUSION

Nonmetallic cellular materials belong to the most common used materials. Beside natural cellular materials artificial solid foams as glass, ceramic and plastic foams are produced and used in millions of tons per year mainly for building purposes and as packaging material.

The up-foaming procedure, done either by a blowing agent or a gas blown into the liquid is the most critical step of all processing routes. A sum of strongly time dependent parameters like the liquids viscosity, thermal conductivity, reaction kinetics or surface tension determine the coalescence, disproportion and buoyancy behaviour of the bubbles and the resulting foam structure and, hence, the main product properties, like the density, the pore size and the pore size distribution.

The usual industrial approach to optimise a product by small variations of a running process at the production line is sometimes not sufficient and not suitable when introducing new materials or new processes. Here, the first attempt are experiments with model fluids supplemented by computational simulations. The flow of liquid in wet foams is called *Drainage* and mainly caused by the gravity force. The effect of *Drainage* in a solid particle laden aqueous foam can be seen in Fig.12.

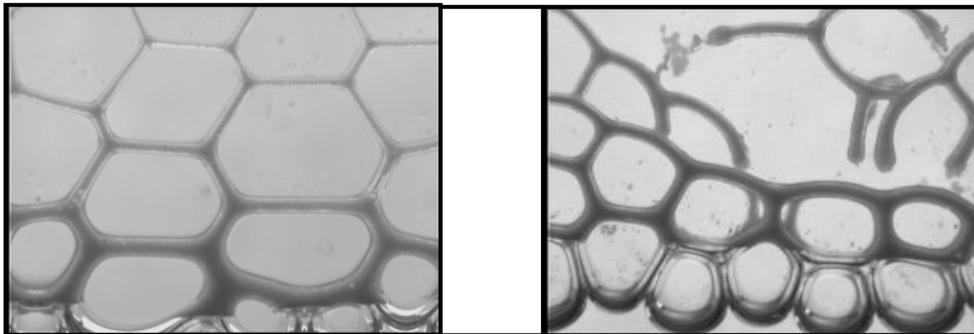


Fig. 12, Drainage of aqueous foam with solid particles. Left: 5 min after up-foaming; right: nearly collapsed foam structure 2 min later

Surface tension and capillary forces are the other main physical forces in a gas/liquid foam system. To distinguish between the gravity driven and boundary tension driven effects, experiments in an environment of simulated weightlessness (*microgravity experiments*) are suitable. Within the field of polymer foams, food technology, cosmetics, flotation, waste water management or oil recovery the chemistry of foam systems, which means mainly surface and colloid chemistry and reaction kinetics, becomes the dominating research area. Therefore, a huge amount of further *foam research* is necessary and has to be done in the field of the physics and the chemistry of foams.

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