PARTICLE-STABILIZED FOAMS

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# Table of Contents

## Summary .................................................................................................................. 1

## Zusammenfassung ..................................................................................................... 3

### 1 Introduction: Processing Routes to Macroporous Ceramics – A Review ........ 5  
1.1 Introduction........................................................................................................... 6  
1.2 Replica technique ............................................................................................... 9  
1.3 Sacrificial template method ............................................................................. 18  
1.4 Direct foaming methods ................................................................................... 23  
1.5 Summary............................................................................................................ 41  
1.6 References ....................................................................................................... 43

### 2 Ultrastable Particle-Stabilized Foams ............................................................. 49  
2.1 Introduction........................................................................................................... 50  
2.2 Experimental ..................................................................................................... 52  
2.3 Results and discussion ..................................................................................... 53  
2.4 Conclusions....................................................................................................... 61  
2.5 References ....................................................................................................... 61

### 3 Macroporous Ceramics from Particle-Stabilized Foams ............................. 63  
3.1 Introduction........................................................................................................... 64  
3.2 Materials and methods .................................................................................... 66  
3.3 Results and discussion ..................................................................................... 72  
3.4 Conclusions....................................................................................................... 86  
3.5 Acknowledgment .............................................................................................. 87  
3.6 References ....................................................................................................... 87
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Tailoring the Microstructure of Particle-Stabilized Wet Foams</td>
<td>4-89</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>4-90</td>
</tr>
<tr>
<td>4.2</td>
<td>Materials and methods</td>
<td>4-92</td>
</tr>
<tr>
<td>4.3</td>
<td>Results and discussion</td>
<td>4-95</td>
</tr>
<tr>
<td>4.4</td>
<td>Conclusions</td>
<td>4-116</td>
</tr>
<tr>
<td>4.5</td>
<td>Acknowledgment</td>
<td>4-116</td>
</tr>
<tr>
<td>4.6</td>
<td>References</td>
<td>4-117</td>
</tr>
<tr>
<td>5</td>
<td>Stabilization of Foams with Inorganic Colloidal Particles</td>
<td>5-119</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>5-120</td>
</tr>
<tr>
<td>5.2</td>
<td>Surface chemistry and modification of oxide particles in water</td>
<td>5-121</td>
</tr>
<tr>
<td>5.3</td>
<td>Materials and methods</td>
<td>5-124</td>
</tr>
<tr>
<td>5.4</td>
<td>Results and discussion</td>
<td>5-128</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusions</td>
<td>5-140</td>
</tr>
<tr>
<td>5.6</td>
<td>Acknowledgment</td>
<td>5-141</td>
</tr>
<tr>
<td>5.7</td>
<td>References</td>
<td>5-141</td>
</tr>
<tr>
<td>6</td>
<td>Processing of Particle-Stabilized Wet Foams to Porous Ceramics</td>
<td>6-143</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>6-144</td>
</tr>
<tr>
<td>6.2</td>
<td>Materials and methods</td>
<td>6-148</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and discussion</td>
<td>6-156</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusions</td>
<td>6-168</td>
</tr>
<tr>
<td>6.5</td>
<td>Acknowledgment</td>
<td>6-169</td>
</tr>
<tr>
<td>6.6</td>
<td>References</td>
<td>6-169</td>
</tr>
<tr>
<td>7</td>
<td>General Conclusions</td>
<td>7-171</td>
</tr>
<tr>
<td>8</td>
<td>Outlook</td>
<td>8-175</td>
</tr>
<tr>
<td>8.1</td>
<td>Porous scaffolds for hard tissue repair</td>
<td>8-175</td>
</tr>
<tr>
<td>8.2</td>
<td>Hollow particle-stabilized capsules</td>
<td>8-176</td>
</tr>
</tbody>
</table>
8.3 Particle-stabilized polymeric foams ................................. 178
8.4 Particle-stabilized metallic foams ........................................ 179

9 APPENDIX .................................................................................. 181

9.1 Additional tables ................................................................... 182
9.2 Taylor's model .................................................................... 186
9.3 References ........................................................................... 188

CURRICULUM VITAE.................................................................. 195


**Summary**

Foams are of great interest in food technology, cosmetics, biomedical applications and material manufacturing as well as in mining and oil refinery. This thesis aims at the development of a new versatile direct foaming method based on the idea of Pickering's emulsion. This novel method should enable the preparation of high-volume wet foams that show neither bubble coarsening nor drainage over long times. Therefore, particles are used as foam stabilizers. In order to partially hydrophobize them, their surfaces are modified by adsorbing amphiphilic organic molecules. These molecules were chosen as such that they adsorb with their polar head group on the particle surface and change the wetting behavior by leaving their hydrophobic tail in contact with the aqueous solution. The particles need to be sufficiently hydrophobic in order to adsorb to the air-water interface. On the other hand, strong particle agglomeration in the suspension needs to be avoided. Compared to surfactants, particles adsorb irreversibly at the air-water interface, resulting in enhanced resistance against bubble coarsening due to disproportionation, drainage and coalescence.

After reviewing the methods preparing porous ceramics, the new method is described in detail. It is based on the in-situ hydrophobization of initially hydrophilic colloidal particles using short-chain amphiphilic molecules as surface modifiers. The usage of short-chain amphiphiles allows for the surface modification of high concentrations of particles in suspension. These partially hydrophobized particles then adsorb to the air-water interface during the process of mechanical frothing of the suspension. A model is presented explaining the stabilization mechanism of the wet foams based on the example of alpha alumina particles. Furthermore, it is described in detail how the wet foam microstructure can be tailored and how the method is
extended to other particles with various surface chemistries. Last but not least, the processing of the wet foams which includes drying and sintering is developed and the properties of the obtained macroporous ceramics are evaluated and compared to those of porous ceramics prepared by other routes.

The key findings of this thesis are:

Preparation protocols for a new direct foaming method have been developed using particles as foam stabilizers based on Pickering's observations on emulsions. This method results in high-volume foams which are stable against bubble growth and drainage over days. The method is very robust and environmentally friendly.

Parameters were established for tailoring the microstructure of the wet particle-stabilized foams in a wide range by adjusting the particle hydrophobicity, the interparticle interactions as well as the particle concentration and size.

The versatility of this method is shown by processing particles with various surface chemistries ranging from positively charged alumina to negatively charged silica. The method was further extended to polymeric and metallic particles as well as to non-polar liquids.

Methods were developed for drying the wet foams in air to obtain crack-free porous solids after sintering with either closed or interconnected pores ranging from 10 to 300 μm and porosities of up to 95%. These porous materials show very high mechanical strength of up to 16.3 MPa in compression at 88.7% porosity.
ZUSAMMENFASSUNG


Die Hauptergebnisse dieser Arbeit sind:

Protokolle für eine neue Schäumungsmethode wurden entwickelt, die auf der Verwendung von Partikeln als Schaumstabilisatoren beruht. Diese Methode resultiert in hochvolumigen Schäumen, die stabil sind gegenüber Blasenwachstum und Dränage.


Trocknungsmethoden wurden entwickelt, die zu rissfreien porösen Keramiken führen. Diese Materialien besitzen Porositäten von bis zu 95 % mit geschlossenen oder offenen Poren, welche in der Grösse von 10 bis 300 μm variieren können. Die Materialien zeigen sehr hohe mechanische Festigkeiten von bis zu 16.3 MPa im Kompressionsversuch bei einer Porosität von 88.7%.
INTRODUCTION: PROCESSING ROUTES TO MACROPOROUS CERAMICS — A REVIEW


Abstract

Macroporous ceramics with pore sizes from 400 nm to 4 mm and porosity within the range 20 – 97 % have been produced for a number of well-established and emerging applications, such as molten metal filtration, catalysis, refractory insulation and hot gas filtration. These applications take advantage of the unique properties achieved through the incorporation of macropores into solid ceramics. In this article, we review the main processing routes that can be used for the fabrication of macroporous ceramics with tailored microstructure and chemical composition. Emphasis is given to versatile and simple approaches which allow one to control the microstructural features that ultimately determine the properties of the macroporous material. Replica, sacrificial template and direct foaming techniques are described and compared in terms of microstructures and mechanical properties that can be achieved.
1.1 Introduction

Materials containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Therefore, porous materials find nowadays many applications as end products and in several technological processes. Macroporous materials are used in various forms and compositions in every-day life, including for instance polymeric foams for packaging, aluminum light-weight structures in buildings and airplanes, as well as porous ceramics for water purification.

Contrary to metallic and polymeric porous structures, pores have been traditionally avoided in ceramic components due to their inherently brittle nature. However, an increasing number of applications that require porous ceramics have appeared in the last decades, especially for environments where high temperatures, extensive wear and corrosive media are involved. Such applications include for example the filtration of molten metals, high-temperature thermal insulation, support for catalytic reactions, filtration of particulates from diesel engine exhaust gases and filtration of hot corrosive gases in various industrial processes. The advantages of using porous ceramics in these applications are usually the high melting point, tailored electronic properties, high corrosion and wear resistance in combination with the features gained by the replacement of solid material by voids in the component. Such features include low thermal mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength and low dielectric constant.

These properties can be tailored for each specific application by controlling the composition and microstructure of the porous ceramic. Changes in open and closed porosity, pore size distribution and pore morphology can have a major effect on a
material's properties. All of these microstructural features are in turn highly influenced by the processing route used for the production of the porous material.

The most straightforward processing route for the preparation of porous ceramics is the partial sintering of initially porous powder compacts or the sintering of powder mixtures which undergo solid state reactions that lead to pore formation. This method often results in a relatively low porosity (< 60 vol%), with pores homogeneously distributed within the microstructure.

In addition to such a straightforward approach, many novel methods for the preparation of porous ceramics with controlled microstructure have been developed in response to the increasing number of new potential applications for cellular ceramics. Versatile techniques that allow one to deliberately tune the porosity, pore morphology and size distribution, and that can additionally be applied to ceramic materials of many different chemical compositions are especially demanded. Novel applications where specific chemical compositions and tailored microstructures are required include electrodes and supports for batteries and solid oxide fuel cells, scaffolds for bone replacement and tissue engineering, heating elements, chemical sensors, solar radiation conversion, among others.

The main processing methods used for the preparation of cellular ceramics such as foams, honeycomb structures and interconnected rods, fibers and hollow spheres were recently reviewed by Colombo. The fabrication and use of cellular ceramics in a vast number of different fields has also been described in a recent book edited by Scheffler and Colombo. While this valuable literature contains extensive information on the production and applications of cellular ceramics, the processing-microstructure-property relations for each of the main processing routes has not been fully explored. A
thorough understanding of these relations would greatly aid the selection of processing techniques that can provide the final microstructure and properties required for each specific application.

The aim of this article is to compare some of the processing routes currently available for the preparation of macroporous ceramics (i.e. pore size > 50 μm), with particular emphasis on the processing-microstructure-property relations inherent to each process. We also present a simple and versatile processing method recently developed by the authors which has not been included in previous reviews.

Due to the large number of articles in the field, we focus mainly on macroporous ceramics that exhibit total porosity higher than 50 vol%. We adopt here the nomenclature recommended by the IUPAC, according to which macroporous materials are those exhibiting pore width (d) larger than 50 μm. Recent articles on the processing of micro- (d < 2 μm) and mesoporous (2 μm < d < 50 μm) ceramic materials using a number of sol-gel, templating and other chemistry routes can be found in the literature. For reasons given above, honeycomb structures, interconnected rods, fibers, hollow spheres and porous materials prepared by solid freeform fabrication techniques have not been included in this article. However, references and are suggested for those interested in these important cellular structures. It is also worth noting that even though we gathered many examples to illustrate some of the processing routes developed so far, a number of other approaches can be found in the recent literature using similar concepts to those outlined here.

The processing routes described in this article have been classified into replica, sacrificial template and direct foaming methods, as schematically illustrated in Figure 1.1. The processing features of each of these methods are thoroughly discussed and
compared with regards to the versatility and ease of fabrication, as well as their influence on the microstructure and mechanical strength of the final macroporous ceramics. Finally, we summarize the main characteristics of the processing routes described and provide directions for future advances on this field.

![Scheme of possible processing routes used for the production of macroporous ceramics.](image)

**Figure 1.1**: Scheme of possible processing routes used for the production of macroporous ceramics.

### 1.2 Replica technique

The replica method is based on the impregnation of a cellular structure with a ceramic suspension or precursor solution in order to produce a macroporous ceramic exhibiting the same morphology as the original porous material (Figure 1.1(a)). Many synthetic and natural cellular structures can be used as templates to fabricate...
macroporous ceramics through the replica technique. Here, we focus mainly on those processes that allow for the fabrication of bulk ceramic structures, while references are given for the recent studies describing the preparation of ceramic macroporous films and particles.

1.2.1 Synthetic templates

The replica technique is in fact considered as the first method deliberately used for the production of macroporous ceramics. The original invention dates back to the early 1960s, when Schwartzwalder16 started using polymeric sponges as templates to prepare ceramic cellular structures of various pore sizes, porosities and chemical compositions. Since then the sponge replica technique has become the most popular method to produce macroporous ceramics and is today extensively used in industry to prepare ceramic filters for molten metal filtration3 and other applications. This success is primarily attributed to the simplicity and flexibility of the method.

In the polymer replica approach, a highly porous polymeric sponge (typically polyurethane) is initially soaked into a ceramic suspension until the internal pores are filled in with ceramic material. The impregnated sponge is then passed through rollers to remove the excess suspension and enable the formation of a thin ceramic coating over the struts of the original cellular structure. At this stage, the slurry has to be sufficiently fluid to be partially removed under the shearing conditions applied by the rollers, but the remaining ceramic wet coating should be viscous enough to avoid dripping. Therefore, ceramic suspensions exhibiting shear thinning behavior are needed to efficiently coat the polymeric template. Suspensions exhibiting a viscosity decrease from $10 - 30 \text{ Pa s}$ at a shear rate of $5 \text{ s}^{-1}$ down to $1 - 6 \text{ Pa s}$ at a shear rate of
100 s' have been shown to be suitable for this process17-19. This shear-thinning behavior is achieved using thixotropic and thickening additives such as clays, colloidal silica, carboxymethyl cellulose and polyethylene oxide in combination with conventional dispersants19,21.

The ceramic-coated polymeric template is subsequently dried and pyrolysed through careful heating between 300 °C – 800 °C20. Heating rates usually lower than 1 °C/min are required in this step to allow for the gradual decomposition and diffusion of the polymeric material, avoiding the build-up of pressure within the coated struts19. Binders and plasticizers are added to the initial suspension in order to provide ceramic coatings sufficiently strong to prevent cracking the struts during pyrolysis. Typical binders used are colloidal aluminum orthophosphate, potassium and sodium silicates, magnesium orthoborate, hydratable alumina, colloidal silica, polyvinyl butyral with polyethylene glycol as plasticizer, and polymerizable monomers19,21,24. After removal of the polymeric template, the ceramic coating is finally densified by sintering in an appropriate atmosphere at temperatures ranging from 1100 to 1700 °C depending on the material.

Macroporous ceramics of many different chemical compositions have been prepared using the sponge replica technique, as illustrated in Table 9.1. Descriptions of several other possible chemical compositions can be found in the extensive patent literature gathered by Saggio-Woyansky et al.20 The great flexibility of the method is partly due to the fact that it is applicable to any ceramic material that can be appropriately dispersed into a suspension. Various SiC-based porous ceramics have also been recently produced by replacing the ceramic suspension with preceramic polymers25-28 (Table 9.1). Alternatively, Sherman et al29 developed a similar process to the
original replica method, where the polymeric sponge is first converted into a vitreous carbon skeleton and is subsequently infiltrated with reactive gaseous species to form macroporous ceramics of many different carbides, oxides, borides, nitrides and silicides (Table 9.1).

Porous ceramics obtained with the sponge replica method can reach total open porosity levels within the range 40 – 95 % and are characterized by a reticulated structure of highly interconnected pores with sizes between 200 μm and 3 mm, as outlined in Figure 1.2 and Figure 1.4(a). The high pore interconnectivity enhances the permeability of fluids and gases through the porous structure28, making these reticulated materials very suitable for high through-put filtration.

Figure 1.2: Typical porosity and average pore size achieved via the replica, sacrificial templating and direct foaming processing routes.
Figure 1.3: Relative compressive strength as a function of the relative density of macroporous ceramics produced via replica, sacrificial template and direct foaming methods. The relative strength was calculated from the ratio between the compressive strength of the porous structure ($\sigma_p$) and the bending strength of its dense counterpart ($\sigma_d$). The data were obtained from porous ceramics of different chemical compositions, assuming a bending strength of 400, 450, 450, 400, 110 and 320 MPa for the alumina $^9$, silicon carbide $^5$, silicon oxycarbide $^5$, titania $^{12}$, hydroxyapatite $^{13}$ and mullite $^{35}$ dense materials, respectively. The y-scales on the right hand side indicate the corresponding absolute compressive strength for alumina, silicon carbide/oxycarbide and hydroxyapatite porous structures. The labels $a$ and $t$ indicate the strength data measured axially and tangentially, respectively, to the aligned pores of wood-derived structures. The relative strength theoretically expected for open- and close-cell porous ceramics according to the model from Gibson and Ashby $^6$ are indicated by the dashed lines.
The cell size of replica-derived porous ceramics is however limited to approximately 200 μm (Figure 1.2), due to the difficulty with impregnating polymeric sponges with excessively narrow cells. Predominantly open porous structures are produced with this method, since the original cellular sponge has to be accessible for the impregnation of the ceramic suspension or precursor. However, the ratio of open to closed pores in the final ceramic foam may be adjusted to a certain extent by controlling the suspension viscosity and shear thinning behavior.

A disadvantage of the sponge replica technique is the fact that the struts of the reticulated structure are often cracked during pyrolysis of the polymeric template (Figure 1.4(b)), markedly degrading the final mechanical strength of the porous ceramic. Figure 1.3 shows that the strut flaws reduce the compressive strength of replica-derived porous ceramics to levels usually lower than the strength theoretically predicted for open cell structures. Many attempts have been made to avoid this shortcoming by, for instance, improving the wetting of the suspension on the sponge with the help of additives, performing a second impregnation step to fill the cracks in the ceramic struts, and introducing fibers or reactive compounds to enhance the material's integrity. In contrast to ceramic suspension-derived reticulated structures, cellular materials obtained from preceramic polymers have crack-free struts due most likely to the improved wetting on the sponge and the partial melting of the cross-linked polymer during pyrolysis.
Figure 1.4: Microstructures of macroporous ceramics produced via the replica technique. (a) Alumina-based open-cell structure obtained using polyurethane sponge templates, (b) detail of a strut of a cellular ceramic produced from polymeric sponges, illustrating the typical flaws formed upon pyrolysis of the organic template, (c) transversal view of a highly-oriented SiC porous ceramic obtained after infiltration of a wood template with Si gas (the longitudinal view is shown in the inset), (d) macroporous hydroxyapatite obtained from a coral structure.

1.2.2 Natural templates

In addition to synthetic polymer foams, other cellular structures have been used as templates for the fabrication of macroporous ceramics through the replica approach, as outlined in Table 9.1. Cellular structures available in nature are particularly interesting as natural replica templates, due mainly to their special pore morphology and intricate microstructures, which might be difficult to produce artificially.
Corals have long been applied as a natural template for the preparation of macroporous ceramic materials, particularly for the production of scaffolds for tissue engineering and bone replacement\textsuperscript{44, 45}. In the 1970s, White \textit{et al.}\textsuperscript{45} employed a lost-wax method named "replamineform" to replicate the structure of corals and other marine invertebrate skeletons. In this technique, the coral is first impregnated with wax under vacuum to obtain a negative form of the cellular structure. After hardening the wax, the calcium carbonate of the coralline skeleton is leached out using a strong acidic solution. The macroporous ceramic is obtained by impregnating the negative wax model with a ceramic suspension and subsequently removing the organic material by pyrolysis. This approach has been successfully used to produce macroporous PZT ceramics with tailored piezoelectric properties\textsuperscript{46, 47}. The cellular structure of corals has also been directly converted into macroporous hydroxyapatite scaffolds by submitting the marine skeleton to hydrothermal treatments at high temperatures and pressures\textsuperscript{44} (Figure 1.4(d)). This treatment is performed in a phosphate solution, so that the carbonate ions from the aragonite material (CaCO\textsubscript{3}) originally present in the coral are partially or totally replaced by phosphate ions to form hydroxyapatite\textsuperscript{44, 45}. Sol-gel chemistry has also been lately used to prepare macroporous hydroxyapatite scaffolds with improved mechanical properties from coral templates\textsuperscript{41}.

Following the same biomimetic approach used in the "replamineform" technique, many investigators have studied the transformation of wood cellular structures into macroporous ceramics (Figure 1.4(c)). The presence of oriented vessels in the structure of wood enables the preparation of macroporous ceramics with highly anisotropic aligned pores which cannot be achieved with the other replica techniques\textsuperscript{49}. 
The most common approach is to first prepare a carbon cellular preform by heat treating the wood structure under inert atmosphere at temperatures within 600-1800 °C. The carbon preform is subsequently infiltrated with gases or liquids at high temperatures to obtain the macroporous ceramic. Alternatively, the carbon preform is infiltrated at room temperature with liquid sols and afterwards oxidized to render the cellular ceramic. Table 9.1 shows examples of reactants used for infiltration and the resulting composition of the wood-derived macroporous ceramic.

Ota et al. were probably the first to deliberately use wood as a biomorphic template to produce cellular ceramics. By impregnating the carbon preforms with alkoxide solutions and applying standard sol-gel chemistry, various metal oxide macroporous ceramics have been produced using this approach. SiC-based cellular ceramics of diverse compositions were fabricated by Greil et al. via the infiltration and reaction of liquid or gaseous silicon metal with the carbon preform. Other gaseous metals and metal precursors, preceramic polymers, ceramic suspensions and salt solutions have recently been employed to infiltrate the carbon cellular structure and obtain oxide, carbide, phosphate and zeolite-containing macroporous ceramics through the wood-derived replica technique.

The pore size distribution of wood-derived porous ceramics is determined by the microstructure of the original wood template employed. Since wood structures may exhibit cell sizes down to a few micrometers, porous ceramics obtained from wood templates display pore sizes markedly lower than those achieved with the polymer replica technique, typically within the range 10 to 300 μm (Figure 1.2). The porosity of these structures is predominantly open and can vary from 25 up to 95% depending on the amount of material impregnated into the template, as illustrated in Figure 1.2.
The anisotropic nature of cellular ceramics produced using wood as template might be very advantageous in applications that require open and highly oriented porous structures, such as in catalysis and in the filtration of liquids and hot gases. As a result of their highly oriented structures, the mechanical properties of wood-derived ceramics are markedly anisotropic. The mechanical strength in the axial direction (along the oriented pores) is considerably higher than that in the tangential/perpendicular direction, as indicated in Figure 1.3. As in the case of the sponge replica method, the walls of the wood-derived structures might contain flaws/pores generated from the pyrolysis of residual carbon in oxidizing environments. Such pores degrade the mechanical strength of the cellular structure, particularly at high porosity levels (Figure 1.3). Structures with high mechanical strength can only be achieved when the carbon preform is totally converted into the ceramic phase. Another disadvantage of the wood-replica approach is the several time-consuming steps involved, which might add considerable costs to the process.

Numerous other approaches using synthetic or natural biomorphic templates such as plants, egg shell membrane, bacteria and bioclastic structures formed by aquatic organisms (e.g. diatoms) have also been applied in the last years to fabricate meso- and macroporous particles, films and unique 3D porous structures up to 100 μm in size. Although a detailed description of these porous materials go beyond the scope of this article, the references cited above might be useful for the interested reader.

1.3 Sacrificial template method

The sacrificial template technique usually consists of the preparation of a biphasic composite comprising a continuous matrix of ceramic particles or ceramic
precursors and a dispersed sacrificial phase that is initially homogeneously distributed throughout the matrix and is ultimately extracted to generate pores within the microstructure (Figure 1.1(b)). This method leads to porous materials displaying a negative replica of the original sacrificial template, as opposed to the positive morphology obtained from the replica technique described above.

The biphasic composite is commonly prepared by (a) pressing a powder mixture of the two components, (b) forming a two-phase suspension that is subsequently processed by wet colloidal routes such as slip, tape or direct casting, or (c) impregnating previously consolidated preforms of the sacrificial material with a preceramic polymer or ceramic suspension.

The way that the sacrificial material is extracted from the consolidated composite depends primarily on the type of pore former employed. A wide variety of sacrificial materials have been used as pore formers, including natural and synthetic organics, salts, liquids, metals and ceramic compounds. Table 9.2 illustrates some examples from the recent literature of possible sacrificial templates.

Synthetic and natural organics are often extracted through pyrolysis by applying long thermal treatments at temperatures between 200 and 600 °C. The long periods required for complete pyrolysis of the organic component and the extensive amount of gaseous by-products generated during this process are the main disadvantage of using organic materials as sacrificial phase. Lyckfeldt and Ferreira reported that the burnout rate has to be limited to only 20 mg/min in order to avoid cracking of relatively thin ceramic plates (3 – 4 cm) during pyrolysis. Under the conservative assumption that this burnout rate would also hold for larger components, the removal of the sacrificial material from an alumina brick of 5×10×23 cm³ with
aimed porosity of 50% would require a heat treatment of more than 3 weeks. The mismatch in thermal expansion coefficient between the organic and inorganic phases can also induce cracks within the porous structure during pyrolysis.

Most of these drawbacks can be partially overcome by applying liquid pore formers such as water and oils or a solid phase that can be easily sublimated (e.g. naphtalene) (Table 9.2). Even though the extraction process is also time-consuming, liquids and volatile oils can be evaporated or sublimated at milder conditions without generating undesired toxic gases and excessive stresses during removal of the pore former75-77.

Sacrificial materials such as salts, ceramic and metallic particles, on the other hand, are usually extracted by chemical rather than thermal means. The extraction of salts has been easily accomplished by repeatedly washing the composite with water72,78. Ceramic and metallic particles or fibers require more aggressive agents and are in most cases removed by acidic leaching30,79,80.

In all of these processes, the continuous matrix phase has to be partially consolidated prior to removal of the sacrificial material, so that the porous structure does not collapse during the extraction step. When the continuous phase is a suspension of colloidal ceramic particles, consolidation is usually achieved with the help of setting agents and binders8 or through the formation of a stiff attractive network of particles throughout the matrix71,82. Alternatively, sol-gel transitions based on the condensation of metal alkoxide and hydroxides in solution has also been used to consolidate the continuous phase75, 76, 81. In the case of preceramic polymers, consolidation is achieved by cross-linking the macromolecules through a curing process.
that takes place at temperatures slightly lower than that used for the pyrolysis step.

The use of relatively volatile oils as a sacrificial phase in aqueous or non-aqueous emulsions is an interesting alternative for the fabrication of porous ceramics by this template method. The main advantages of this approach are (a) the fact that the template is easily incorporated into the continuous phase by simple agitation or mixing, (b) the very small droplet/pore sizes that can be achieved when using immiscible liquids exhibiting low interfacial energy and (c) the mild conditions required for removal of the template.

![Figure 1.5: Microstructures of macroporous ceramics produced with the sacrificial template method.](image-url)

(a) TiO₂ foam exhibiting hierarchical porous structure produced via emulsion templating, (b) ordered macroporous SiO₂ obtained using polystyrene beads as templates, (c) highly oriented SiO₂ honeycomb structure achieved via the unidirectional freeze-drying of silica gels, (d) macroporous Al₂O₃ exhibiting dendrimer-like pores obtained using camphene as sacrificial template.
The emulsion template method has been recently applied in combination with sol-gel reactants and surfactants to fabricate ordered macroporous structures from monodisperse oil droplets obtained by fractionation. Materials with porosity up to 90% have also been produced from aqueous emulsions using surface modified particles to stabilize the droplet oil-water interface. The incorporation of a third phase into the emulsions, as for example water in non-aqueous systems and air in aqueous emulsions, has allowed for the fabrication of porous ceramics with a well-defined hierarchical pore size distribution (Figure 1.5(a)).

The sacrificial template technique is quite flexible with respect to the possible chemical compositions that can be used in the fabrication process. As indicated in Table 9.2, porous ceramics of various chemical compositions have been produced using this approach. A wide number of different oxides have been used to fabricate porous ceramics using starch particles as sacrificial template. The main advantages of this approach are its simplicity, the ready availability of starch particles of various morphologies and sizes (2–100 μm), and the fact that it can be applied to any material which can be dispersed in an aqueous suspension. Non-oxide porous ceramics, on the other hand, have been often produced using preceramic polymers in combination with various different template materials (Table 9.2).

One of the main advantages of the sacrificial template method in comparison to the other fabrication routes is the possibility to deliberately tailor the porosity, pore size distribution and pore morphology of the final ceramic component through the appropriate choice of the sacrificial material. Figure 1.2 shows that the range of porosity and pore sizes that can be achieved with this technique is very broad (20–90% and 1–700 μm, respectively), since they only depend on the volume fraction and size of the
sacrificial template used. Porous materials exhibiting monomodal pore size distribution at various porosity levels can for instance be easily produced using different initial amounts of monodisperse templating particles (Figure 1.5(b)).

Porous ceramics with long anisotropic pores and channels have been produced with this method by orienting nickel wires in a magnetic field⁷⁹, by aligning ceramic-coated cotton threads⁸⁰ or by casting a ceramic suspension into a sacrificial mold displaying long and thin (0.5 mm) polymeric rods⁸¹. Pores with special morphologies have also been produced by a freeze casting approach using water or a high-melting point oil as sacrificial material. By tuning the growth of ice/oil crystals during the unidirectional freezing of suspensions, dendritic or highly oriented porous structures has been obtained after sublimation of the templating crystals (Figure 1.5(c))⁷⁷,⁸⁸,⁹¹,⁹²,⁹³,⁹⁴.

Since in this method the ceramic component corresponds to the negative of the original template, the removal of the sacrificial phase does not lead to flaws in the struts as in the case of the positive replica techniques described earlier. Therefore, the mechanical strength of sacrificial-templated porous structures is usually considerably higher than that of porous materials produced via positive replica, as clearly indicated in Figure 1.3. Macroporous ceramics obtained with the template method display compressive strengths typically within the range predicted for open and closed-cell structures.

### 1.4 Direct foaming methods

In direct foaming methods, porous materials are produced by incorporating air into a suspension or liquid media, which is subsequently set in order to keep the
structure of air bubbles created (Figure 1.1(c)). In most cases, the consolidated foams are afterwards sintered at high temperatures to obtain high-strength porous ceramics.

The total porosity of directly-foamed ceramics is proportional to the amount of gas incorporated into the suspension or liquid medium during the foaming process. The pore size, on the other hand, is determined by the stability of the wet foam before setting takes place.

Liquid foams are thermodynamically unstable systems due to their high gas-liquid interfacial area. Several physical processes take place in wet foams to decrease the overall system free energy, leading to foam destabilization. The main destabilization mechanisms are drainage (creaming), coalescence (film rupture) and Ostwald ripening (disproportionation).

![Figure 1.6: Foam drainage. The Plateau border and thin films formed after bubble rearrangement and distortion on the top foam layer are indicated in the magnified image (adapted from original picture after J.J. Cillier).](image)

Drainage is the physical separation between the gaseous and liquid phases of the foam due to the effect of gravity. In draining foams, light gas bubbles move upwards forming a denser foam layer on the top, while the heavier liquid phase is
concentrated on the bottom, as illustrated in Figure 1.6. Bubbles accumulated on the top usually rearrange and deform to form highly packed foams with polyhedral cells. The resulting foam exhibits a three dimensional microstructure characterized by thin films (or lamellas) between the faces of touching cells and so-called Plateau borders at the intersection of three neighboring thin films (Figure 1.6).

![Diagram](image)

Figure 1.7: Schematic dependence of the disjoining pressure among two interacting gas bubbles as a function of their distance $D$. Coalescence is favored by attractive van der Waals forces (a) and can only be hindered by providing steric and/or electrostatic repulsion among the interacting bubbles (b).

Coalescence takes place when the thin films formed after drainage are not stable enough to keep the touching cells apart, resulting in the association of
neighboring bubbles. The stability of the thin films is determined by the attractive and repulsive interactions between bubbles, as schematically illustrated in Figure 1.7. van der Waals attractive forces tend to push the bubbles against each other (negative disjoining pressure) and are thus the main driving force for thin film collapse. Coalescence can only be hindered by providing electrostatic and/or steric repulsive forces sufficiently strong to overcome the attractive van der Waals forces (Figure 1.7 (b)). This can be imparted by surfactant molecules or particles attached to the air-water interface.

Foams can be tailored to efficiently prevent drainage and coalescence processes, but seldom can they resist long-term Ostwald ripening or disproportionation. This destabilization mechanism is driven by the difference in Laplace pressure between bubbles of different sizes. The Laplace pressure inside a gas bubble arises from the curvature of the air-water interface. For spherical bubbles of radius \( R \) and gas-liquid interfacial energy \( \gamma \), the Laplace pressure \( \Delta P \) is given by \( 2\gamma/R \). The difference in Laplace pressure between bubbles of distinct sizes \( (R) \) leads to bubble disproportionation and Ostwald ripening due to the steady diffusion of gas molecules from smaller to larger bubbles over time. Surfactant and biomolecules adsorbed at the gas-liquid interface can slow down this coarsening process by decreasing the interfacial energy \( \gamma \).

The combined action of all these physical processes may collapse the foam within a few seconds after air incorporation. The foam lifetime can be increased to a few minutes or several hours by adsorbing long-chain surfactants or proteins at the air-water interface. Remarkably stable foams exhibiting lifetime of several days and
weeks have been recently prepared through the adsorption of colloidal particles on the surface of air bubbles. These destabilization processes significantly increase the size of incorporated bubbles, resulting in large pores in the final cellular microstructure. Therefore, the most critical issue on direct foaming methods is the approach used to stabilize the air bubbles incorporated within the initial suspension or liquid media. We describe below the main direct foaming methods currently available, according to the approach used for foam stabilization.

1.4.1 Stabilization with surfactants

Several long-chain amphiphilic molecules and biomolecules such as lipids and proteins can be used as surface active agents to stabilize wet aqueous foams. These molecules slow down the coalescence and disproportionation of bubbles by adsorbing at the air bubble surface and reducing the air-water interfacial energy. However, due to the low adsorption energy of surfactants at the gas-liquid interface, long-chain surfactants and biomolecules cannot prevent the long-term destabilization of foams. Wet foams stabilized with long-chain surfactants collapse within a few minutes after foaming, whereas those stabilized by proteins exhibit bubble disproportionation within a few hours. Table 9.4 depicts examples of surfactants used for the stabilization of foams in direct foaming methods.

Therefore, direct foaming based on surfactants require a setting agent to consolidate the foam microstructure before extensive coalescence and disproportionation take place. The ultimate pore size of the porous ceramic depends on a balance between the kinetics of bubble disproportionation and the speed of
liquid/suspension setting. Small pore sizes (~50 μm) can only be achieved by using efficient surfactants and by rapidly setting the wet foam.

Numerous processing routes have been developed in the last decades to prepare porous ceramics using direct foaming methods based on surfactants. Several methods have been addressed in previous review articles by Sepulveda and Saggio-Woyansky et al. Here, we focus mainly on techniques which are flexible in terms of possible chemical compositions and which can be deliberately tuned to control the final porosity, pore morphology and size distribution. Table 9.3 depicts the main techniques that fulfill these conditions and have been thus extensively investigated in recent years. The fabrication processes differ mainly with respect to the method of air incorporation, foam setting and possible chemical compositions (Table 9.3).

Some of these direct foaming methods were adapted from conventional techniques used for the production of polymer foams. Following the success of the polymer replica approach, Wood et al. patented a process in 1974 where ceramic particles are not used to impregnate already formed polymer foams, but are instead incorporated into organic solutions containing precursors of a polyurethane foam. The obtained ceramic/organic mixtures are foamed by in-situ air incorporation in the presence of surfactants (Table 9.3) and finally consolidated by the thermosetting condensation reaction between polyols and polyisocyanates (polyurethane precursors). The in-situ incorporation of air occurs through the nucleation and growth of air bubbles upon heating (physical blowing) or chemical reaction (chemical blowing) (Table 9.3). By this method, the ceramic particles are distributed within the polymeric phase, avoiding the formation of hollow struts that usually degrade the foam final mechanical strength after pyrolysis (Figure 1.3). Porous ceramics of various chemical
compositions were produced by Minnear, Evans and co-workers using the above mentioned approach (Table 9.3).

Recently, Colombo et al. developed a method where the ceramic particles from Wood's technique are replaced by preceramic silicone-based polymers, enabling the production of porous ceramics based on amorphous SiC, SiOC, SiNC compositions of enhanced high temperature properties. Porous ceramics with these compositions have also been produced without polyurethane precursors using solely the thermosetting properties of silicone-based polymers in combination with in-situ blowing agents, either in the presence of surfactants or by applying a pressure-drop technique. The well-established polymer technology used for the production of thermoplastic polystyrene foams was also recently applied by Williams and Evans to fabricate ceramic foams with up to 84% porosity, as illustrated in Table 9.3.

Foam consolidation has not been restricted only to polymeric setting systems, but has been imparted also by inorganic materials exhibiting sol-gel phase transitions in liquid medium. This approach was used by Fujiu et al. to prepare silica foams using Freon for gas incorporation during the condensation reaction of colloidal silica. Tomita et al. have recently reported a similar method to prepare silica foams, where air is incorporated by mechanical frothing with surfactants in order to avoid the harmful effects of chlorofluorocarbons. A sol-gel method using metal alkoxide solutions that lead to biocompatible SiO$_2$-based compositions has also been developed for the production of porous scaffolds for bone replacement and tissue repair. Recently, Santos et al. applied the sol-gel technique to produce ZrO$_2$ porous ceramics from the condensation reaction of zirconium oxychloride in combination with Freon and surfactants. A special sol-gel based method for the production of Al$_2$O$_3$ ultralight foams
was recently developed by Grader et al\textsuperscript{9} using metal organic crystals as precursors. Even though the preparation of porous ceramics by sol-gel can in principle be extended to many other chemical compositions, the technique has been predominantly applied to silica-based systems.

In order to produce porous ceramics with a wider chemical compositional range, several techniques using polymeric setting systems instead of the silica-based sol-gel transitions have been developed since the 1990s. The amount of organics applied in these so-called gelcasting methods is, however, significantly lower than that used in previous polymer blowing techniques (Table 9.3), reducing the need of an extensive pyrolysis step prior to sintering and allowing for the formation of porous ceramics with controlled degree of pore interconnectivity\textsuperscript{17}.

The in-situ free radical polymerization of acrylamide monomers, originally developed for dense ceramics, was successfully used for setting ceramic foams of various compositions by Binner and co-workers\textsuperscript{14,15}. The toxicity of the monomers originally used and the need of oxygen-free environments to accomplish the polymerization reaction are the main disadvantages of this method.

The drawbacks of the first gelcasting system were partially\textsuperscript{109} or totally\textsuperscript{14,16} overcome by replacing the original organic additives by less harmful polymerizable monomers\textsuperscript{109} or by applying non-toxic cross-linking reactants which do not require oxygen-free atmosphere\textsuperscript{14,16}. In the last years, several alternative methods that apply environmental-friendly setting agents from the food industry have been developed to circumvent the shortcomings of the original gelcasting technique. The temperature or pH-induced gelation of gelatine\textsuperscript{16}, ovalbumin\textsuperscript{17,19} and bovine serum albumin\textsuperscript{20}, for instance, have been successfully used for setting the foam wet structure. A similar
approach relying on the temperature-induced gelling of polysaccharides such as sucrose\textsuperscript{121}, agar\textsuperscript{122} and carrageenan gum\textsuperscript{119} has been recently applied as non-toxic processing route for the fabrication of porous ceramics. Many of these alternative setting methods are considerably slower than the original polymerization reaction. Consequently, the speed of the setting reaction is another important criterion, besides toxicity and atmosphere sensitivity, when selecting direct foaming methods for fabrication of porous ceramics of small pore size (< 200 \textmu m).

By controlling the foam stability and the setting kinetics, pore sizes within the range of 35 \textmu m to 1.2 mm have been achieved using the above surfactant-based direct foaming methods (Figure 1.2). This wide pore size range lies between the lower size limit of the polymer replica technique and the upper limit that can be achieved with the wood replica method, as indicated in Figure 1.2. This figure also shows that the porosity of cellular structures produced via surfactant-based direct foaming can be tuned from approximately 40 up to 97%. The pores obtained with this method are typically spherical and can be either closed or opened depending on the foam wet processing (Figure 1.8).
Chapter 1

Figure 1.8: Microstructures of macroporous ceramics produced by direct foaming with long-chain surfactants as foam stabilizers. Figure a shows a closed-cell foam produced from preceramic polymers and polyurethane precursors, highlighting the dense struts typically obtained with direct foaming methods. Figure b depicts an open-cell ceramic foam produced through the in-situ polymerization of monomers shortly after air incorporation.

Open pores exhibiting interconnecting windows (Figure 1.8(b)) are obtained if particles segregate at the plateau borders of the foam due to bubble disproportionation. Closed pores, on the other hand, are typically achieved when the particles are distributed uniformly around the gas bubbles upon setting (Figure 1.8(a)). These conditions can be controlled in the process by adjusting the foam stability, air content, particle concentration and setting kinetics.
As opposed to the replica techniques, the direct foaming methods usually lead to dense flawless struts after sintering (Figure 1.8(a)), which markedly increase the mechanical strength of the porous ceramic in comparison to the replica-derived structures (Figure 1.3). For porosities higher than 90% (relative density < 10%) the cell walls are markedly thin, leading to lower mechanical strength than that theoretically estimated for open-cell structures (Figure 1.3). However, by decreasing the porosity (increasing density) pores gradually change from a highly open to a completely closed morphology, increasing the strength towards the level predicted for closed-cell structures.

1.4.2 Stabilization with particles

Colloidal particles have been used to stabilize high energy interfaces for more than a century in so-called Pickering emulsions\textsuperscript{23}. This concept has also been applied for many decades in flotation technology\textsuperscript{24} and has been recently exploited for the preparation of ultrastable wet foams\textsuperscript{26,97-99,105-107}.

The attachment of particles at gas-liquid interfaces occurs when particles are not completely wetted in the liquid phase or, in other words, are partially lyophobic (hydrophobic if the liquid is water). Under this condition, it is energetically favorable to replace part of the high energy solid-liquid area by a solid-gas area through particle attachment at the gas-liquid interface (Figure 1.9). The position of the particles at the interface is ultimately determined by a balance between the gas-liquid, gas-solid and solid-liquid interfacial tensions, as depicted in Figure 1.9. A simple way to describe the particle position at the interface is through the contact angle formed at equilibrium through the liquid phase (Figure 1.9). Slightly lyophobic particles remain predominantly
in the liquid phase and exhibit a contact angle $< 90^\circ$, whereas extensively lyophobic particles are positioned primarily in the gaseous phase with a contact angle $> 90^\circ$.

Similar to the hydrophile-lypophile balance (HLB) used for surfactants, the contact angle of particles determines the dispersed and continuous phases of the mixture\textsuperscript{26}. For equal amounts of gas and liquid (1:1 mixtures), contact angles $< 90^\circ$ lead to the formation of air in water mixtures (foams), while contact angles $> 90^\circ$ result in the formation of water in air mixtures (mists), as illustrated in Figure 1.9.
Particles attached to the gas-liquid interfaces of foams and mists lower the overall system free energy by replacing part of the gas-liquid interfacial area rather than reducing the interfacial tension as in the case of surfactants. The energy of attachment or free energy gained \( G \) by the adsorption of a particle of radius \( r \) at the interface can thus be calculated using simple geometrical arguments, which lead to the following equations:

**Eq. 1.1** \[ G = \pi r^2 \gamma_{LG} (1 - \cos \theta)^2 \text{ for } \theta < 90^\circ \]

and

**Eq. 1.2** \[ G = \pi r^2 \gamma_{LG} (1 + \cos \theta)^2 \text{ for } \theta > 90^\circ \]

where \( \theta \) is the contact angle and \( \gamma_{LG} \) is the gas-liquid interfacial tension.

![Energy of attachment of colloidal particles at an air-water interface](image)

**Figure 1.10:** Energy of attachment of colloidal particles at an air-water interface \( \gamma_{LG} = 72.8 \text{ mN/m} \) as a function of the contact angle for different particle radius.
Figure 1.10 shows the predicted energy of particle attachment $G$ as a function of the contact angle $\theta$ for three different particle sizes. Remarkably, the attachment energy of particles can amount to several thousands or millions of $kT$s for contact angles within the range $30^\circ < \theta < 150^\circ$ and particle radius larger than 20 nm ($k$ is the Boltzmann constant and $T$ is the temperature). Even though the maximum energy gain is only achieved at $\theta = 90^\circ$, contact angles as low as $20^\circ$ are enough to render attachment energies on the order of $10^3 \, kT$ in the case of 100 nm particles.

![Diagram of foams](image)

Figure 1.11: a) Foam film stabilized by solid particles. $P_c = P_1 - P_2$ is the capillary pressure. The case of $P_c > 0$ is depicted in b) (adapted from Denkov et al\(^{19}\)).

However, not only the adsorption energy of particles to the air-water interface, but also the stability of the thin liquid film between the air bubbles plays an important role in stabilizing foams. The thin liquid film usually decreases in thickness and eventually ruptures due to foam drainage or to collision between bubbles. If particles are adsorbed at the air-water interface, thinning of the liquid film can be counterbalanced by the development of a capillary pressure across the gas-liquid interface between two adjacent particles.
The capillary pressure arises from the deformation of the air-liquid interface between the particles (Figure 1.11) and can be described by the following equations\textsuperscript{18,19}.

\begin{equation}
P_{c}^{\text{max}} = +p \frac{2 \gamma_{LG}}{r} \cos \theta \text{ for } \theta < 90^\circ
\end{equation}

and

\begin{equation}
P_{c}^{\text{max}} = -p \frac{2 \gamma_{LG}}{r} \cos \theta \text{ for } \theta > 90^\circ
\end{equation}

where $\theta$ is the contact angle, $\gamma_{LG}$ is the gas-liquid interfacial tension and $p$ a parameter that depends on the coverage of particles and particle arrangements within the liquid film. Contrary to the adsorption energy of particles (Eq. 1.1 and Eq. 1.2), the maximum capillary pressure is maximized at 0° contact angle and becomes zero at 90°. These two opposite trends have to be taken into account in order to understand the optimum conditions for the stabilization of an air-water interface with particles.

These aspects have been considered in the literature by Denkov \textit{et al.}\textsuperscript{18} and more recently by Kaptay\textsuperscript{29,30}. Kaptay proposed a combined analysis of the adsorption energy (Eq. 1.1 and Eq. 1.2) and the maximum capillary pressure (Eq. 1.3 and Eq. 1.4) in order to understand the stability of emulsions and foams. The analysis is based on the estimation of the probability of particle adsorption at the interface and the probability of film stabilization by the adsorbed particles. The probability $e_{\text{particle adsorption}}$ that a particle is stable at the air-water interface is assumed to be equal to the term $(\pm \cos \theta)$ from Eq. 1.1 and Eq. 1.2, whereas the probability of film stabilization by particles $e_{\text{stable liquid film}}$ is assumed to be equal to the term $\pm \cos \theta$ from Eq. 1.3 and Eq. 1.4. Figure 1.11a and 1.11b show the dependence of these probability factors on the equilibrium contact angle of particles at the interface. The terms $e_{\text{particle adsorption}}$ and $e_{\text{stable liquid film}}$ show opposite dependences on the equilibrium contact angle. Assuming that stable foams require
particle adsorption at the air-water interface and stable thin liquid film, one can estimate the probability of foam stabilization $\varepsilon_{\text{stabilized foam/mist}}$ by multiplying the terms $\varepsilon_{\text{particle adsorption}}$ and $\varepsilon_{\text{stable liquid film}}$. Figure 1.12c shows the dependence of the calculated $\varepsilon_{\text{stabilized foam/mist}}$ on the equilibrium contact angle. An optimum contact angle for foam formation around 70° is found, whereas mists would be most stable at a contact angle around 110°. Based on these findings, a foam stability diagram can be established as depicted in Figure 1.12d. This diagram shows the contact angle values required to obtain stable foams and mists. According to Figure 1.11d, foams can be stabilized by single particle layers with contact angles ranging from 15 to 90°, while mists would be stable at contact angles between 90 and 175°.

The surprisingly high energy associated with the adsorption of particles at interfaces contrasts to the extremely lower adsorption energies of surfactants, typically a few $kT$. For that reason, colloidal particles tend to adsorb irreversibly on interfaces, as opposed to the continuous adsorption and desorption of surfactants. This high adsorption energy combined with the high stability of thin films containing particles at the interface explains the outstanding stability exhibited by particle-stabilized foams in comparison to surfactant-based systems. In addition to the steric layer and capillary pressure provided against coalescence, particles attached to the air-water interface form a network (coating) that strongly hinders the shrinkage and expansion of bubbles, minimizing Ostwald ripening for very long periods of time.
Figure 1.12: The probabilities that a) particles are stabilized at the air-water interface, b) that the liquid films are stabilized by a single layer of particles and c) that the foam/mist are stabilized. The foam/mist stability diagram is shown in d) (adapted from Kaptay99).
In literature, there are several examples of particle-stabilized bubbles and foams. Dickinson et al.\(^9\) and Du et al.\(^6\) demonstrated the stabilization of single bubbles with hydrophobized silica particles. These particles initially contained surface silanol groups which reacted with silanizing agents to impart hydrophobicity. The latter is quantified in terms of the residual content of SiOH. Binks et al.\(^8\) used hydrophobized silica particles with hydrophobicities ranging from 100 to 14 % SiOH. It was found that no foam was formed for hydrophilic (> 70 % SiOH) and very hydrophobic (14 % SiOH) particles. Particles with intermediate hydrophobicity were able to stabilize foams which were completely stable to collapse, coalescence and disproportionation. However, due to the low particle concentration used in these examples, the foams underwent extensive drainage after aeration which could not be prevented by using particles as foam stabilizers. Alargova et al.\(^5\) stabilized foams with hydrophobic polymer microrods. Similar to the results of Binks et al, these foams were stable for long times after extensive drainage occurred. Sun et al.\(^7\) studied the stabilization of liquid metal foams with ceramic particles. The objective of this work was to determine the optimal wetting angle for liquid foam stability. They used polytetrafluorethylene (PTFE), polyethylene (PE) and polyvinylchloride (PVC) particles in water-ethanol mixtures to mimic ceramic particles in liquid metals and found that foam stabilization was most effective for wetting angles between 75 and 85 °. Although these particles could prevent coalescence and disproportionation, they were not able to prevent drainage of the wet foams.
1.5 Summary

Several processing routes using replica, sacrificial template or direct foaming methods are nowadays available for the production of macroporous ceramics. The techniques differ greatly in terms of processing features and final microstructures and properties achieved.

The polymer replica technique is an easy and well-established method to prepare open cellular structures with pore sizes ranging from 200 µm to 3 mm at porosity levels between 40 and 95%. The rheology of the impregnating suspension and its adhesion on the polymeric sponge are the most crucial steps in this method. Despite the overall simplicity of the technique, the mechanical strength of cellular structures produced with this route can be substantially degraded by the formation of cracked struts during pyrolysis of the polymeric sponge.

A novel replica approach that uses wood structures as positive templates was developed in recent years. Highly oriented open pores ranging from 10 to 300 µm can be produced with this method at porosities between 25 and 95%. The most important processing step in this route is the conversion of the wood-derived carbon preform into a ceramic phase. The availability of templates exhibiting the aimed microstructure is also crucial in this method. The mechanical strength of wood-derived ceramics is highly anisotropic and often suffers from the presence of pores on the cell walls due to incomplete or inefficient conversion. The several steps required to convert the wood structures into the macroporous ceramic might also excessively increase the cost of the process.

Sacrificial templating methods provide a straightforward alternative for the fabrication of macroporous ceramics with porosities and average pore sizes ranging
from 20 to 90% and 1 to 700 μm, respectively. Predominantly open pores of various different morphologies can be produced with this method. The most crucial step in this technique is the removal of the sacrificial phase by pyrolysis, evaporation or sublimation. These processes might involve the release of an excessive amount of gases and have to be carried out at sufficiently slow rates in order to avoid cracking of the cellular structure. The slow removal of the sacrificial phase may considerably increase the processing time in the case of large components. The mechanical strength of cellular structures produced with this method is often substantially higher than that achieved with the positive replica techniques mentioned above.

Direct foaming methods offer an easy, cheap and fast way to prepare macroporous ceramics with open or closed porosities from 40 to 97%. The pores produced with this approach result from the direct incorporation of air bubbles into a ceramic suspension, eliminating the need for extensive pyrolysis steps prior to sintering. The stabilization and setting of the wet foams is the decisive step in direct foaming methods. Foams stabilized with surfactants lead to porous ceramics exhibiting average pore sizes from 35 μm to 1.2 mm. Cellular structures prepared by direct foaming usually exhibit mechanical strengths considerably higher than that of replica techniques due mainly to the absence of flaws in the cell struts.

It has been demonstrated that not only surfactants but also particles are able to stabilize single air bubbles and foams. Due to the irreversible adsorption of particles to the air-water interface and the high foam film stability, these foams were completely stable to coalescence and disproportionation, but drainage could not be avoided. Additionally, most examples of particle-stabilized foams were restricted to polymeric particles or hydrophobized silica. The preparation of wet foams which show neither
bubble growth nor drainage has not been reported so far. Such foams would be advantageous for many applications in areas ranging from cosmetics and food to materials manufacturing.

1.6 References


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Ultrastable Particle-Stabilized Foams


Abstract

Wet foams are used either as end or intermediate product in a variety of applications ranging from food and cosmetics to materials manufacturing. We present a novel direct foaming method to produce ultrastable wet foams which show no bubble growth and drainage over days. The method is base on an in-situ hydrophobization of colloidal particles which adsorb to the air-water interface upon mechanical frothing of the suspension. The obtained foams exhibit a pronounced yield stress which allows for shaping of parts using extrusion, injection moulding or related techniques. The outstanding stability of the wet foams has made it possible to fabricate bulk macroporous structures upon drying and heat treatment or hollow capsules upon dilution of the wet foam. A large variety of ceramic, polymeric or metallic particles can be used which makes this method very versatile compared to other methods that use particles as foam stabilizers.
2.1 Introduction

Aqueous foams are important in a variety of different applications ranging from food and cosmetics to oil recovery, blast mitigation and fire extinguishing. Well-established and emerging applications that use foams as an intermediate structure to produce macroporous materials are also widely spread in the engineering field to fabricate thermal insulating materials and low-weight structures, as well as in medicine to produce artificial implants and scaffolds for drug delivery and tissue engineering. The thermodynamically unstable nature of liquid foams is a critical issue in all these applications. Foam instability arises from the high energy associated to the gas-liquid interface. This constitutes a driving force for decreasing the foam total interfacial area through the coalescence and disproportionation (Ostwald ripening) of bubbles. Such processes can be partially hindered using long-chain surfactants or biomolecules such as lipids and proteins to adsorb at the air bubble surface and reduce the gas-liquid interfacial energy. In addition to surfactants and biomolecules, colloidal particles have long been exploited to stabilize oil droplets in Pickering emulsions. However, it was only recently recognized that partially-hydrophobic particles can also attach to gas-liquid interfaces and stabilize air bubbles in surfactant-free diluted suspensions. The attachment of particles at the gas-liquid interface requires an optimum balance between the solid-liquid, solid-gas and liquid-gas interfacial tensions and is therefore dependent on the wetting behavior at the particle surface (Figure 2.1(a,b)).

A number of approaches have been described in the literature to change the lyophobicity and wetting properties of solid particles in order to favor their attachment
at gas-liquid interfaces. In the flotation industry, for instance, wetting is usually controlled through the adsorption of long-chain surfactants on the particle surface (typically > 10 carbons). Hydrophobic silane species have also been deliberately grafted on the surface of silica nanoparticles to perform model investigations in the absence of surfactants. However, in all the particle-stabilized foams reported so far, the concentration of modified particles in the liquid medium is not sufficiently high to stabilize a high amount of gas-liquid interfacial area. Therefore, the initially aerated suspension undergoes extensive drainage and creaming before a stable floating foam is achieved above the liquid phase. The stabilization of a high concentration of sub-millimeter-sized air bubbles that do not undergo drainage or creaming would however be highly advantageous in many foam applications.

We report here a simple and versatile approach to prepare ultra-stable particle-stabilized foams that percolate throughout the entire liquid phase and exhibit no drainage or creaming effects. The novelty of our method is the fact that it enables the surface modification of a high concentration of colloidal particles in the liquid phase, allowing for the stabilization of a high gas-liquid interfacial area against disproportionation, coalescence, drainage and creaming. In this article we describe and discuss (1) our approach to surface modify a large concentration of particles in the liquid phase, (2) the resulting attachment of lyophilized particles at a gas-liquid interface, (3) the foaming behavior after surface modification, and finally (4) the foam stability achieved. The examples herein described illustrate the universal nature of the method, which in principle can be extended to any type of oxide or non-oxide particles regardless their initial wetting behavior.
2.2 Experimental

The colloidal particles used in this study were acquired from the following suppliers: δ-Al₂O₃, $d_{so} \approx 70$ nm, Nanophase Technologies Co. (Romeoville, IL, USA); α-Al₂O₃, $d_{so} \approx 200$ nm (grade Ceralox HPA-0.5), Sasol North America Inc. (Tucson, AZ, USA); α-Al₂O₃, $d_{so} \approx 1800$ nm (grade CL 2500 SG), Alcoa Co. (Ludwigshafen, Germany); ZrO₂, $d_{so} \approx 50$ nm (grade TZ-3Y-E), Tosoh Corporation (Tokyo, Japan); β-Ca₃(PO₄)₂, $d_{so} \approx 50$ nm, Flame Powders AG (Schlieren, Switzerland); SiO₂, $d_{so} \approx 80$ nm (grade Snowtex ZL), Nissan Chemical (Houston, TX, USA). All other chemicals were purchased from Fluka AG (Buchs, Switzerland). Prior to foaming, colloidal suspensions were prepared by adding the dry powders to the liquid solvent upon steady mixing. The suspension solids concentration varied between 15 and 45 vol%, depending on the powder, solvent and short amphiphiles used. Surface lyophobization of initially hydrophilic particles was carried out by first de-agglomerating the powder through a standard ball-milling process, followed by the gradual addition of aqueous solutions containing the short amphiphiles. Concentrated 2M HCl or 1M NaOH solutions (Titrisol, Fluka AG, Buchs, Switzerland) were used for pH adjustments. The adsorption of amphiphiles on the particle surface was indirectly determined by measuring the concentration of amphiphiles left in the bulk liquid media after 2 h mixing of the powder with the amphiphile. The bulk concentration was determined by removing the particles in a two-step centrifugation process (Z513K, Hermle Labortechnik GmbH, 4500 rpm, 1 h; 5417R, Eppendorf AG, 15000 rpm, 20 min) and subsequently measuring the amphiphilic concentration in the supernatant solutions by potentiometric titration (DT-1200, Dispersion Technology, Inc., Mount Kisco, NY, USA). The suspension surface tension was assessed with the pendant drop method (PATI, Sinterface Technologies GmbH, Berlin,
Germany), using 15-35 mm³ suspension droplets pending in air. Foams were produced by thoroughly mixing the concentrated suspensions with a planetary mixer (Major Classic, Kenwood Ltd, Havant, UK) for 3 minutes at full speed. The whipped cream and egg white foams used for comparison were also prepared by mechanical frothing for 3 minutes. The shaving foam (Gillette Foam, Regular, Gillette Co, London) was taken directly from the product container and was not submitted to any further processing. The foamability was measured from the weight and volume of the foam obtained. Transmitted light microscopy (Polyvar MET, Reichert-Jung, Austria) was used to investigate foam stability by monitoring the bubble size distribution of wet foams over time. Fluorescent silica particles and hexyl amine was used for the confocal laser scanning microscopy images. The labeled silica particles (d₅₀ ~ 500 nm) were synthesized following the procedure described in reference²² and consisted of a silica core (~ 400 nm), a fluorescent layer around the core (~ 10 nm) and an outer silica rim (~ 100 nm). Concentrated silica foams (15 vol%) were prepared with a hand-mixer at pH 10.2 with 30 mM of hexyl amine. Hollow colloidosomes were obtained by diluting (20x) the concentrated foams and were subsequently harvested for imaging in the confocal microscope.

2.3 Results and discussion

Colloidal particles of various chemical compositions (Figure 2.1(c)) were surface lyophilobized through the adsorption of short-chain amphiphilic molecules on the particle surface. A key feature of our approach is the use of short amphiphiles (typically < 8 carbons) which exhibit high solubility and high critical micelle concentrations in the aqueous phase. This is a primary requisite to enable the surface modification of a high
concentration of colloidal particles in the liquid phase. By choosing appropriate anchoring groups and pH conditions (Figure 2.1(c)), particles were surface lyophobized through the adsorption of short amphiphiles via electrostatic interactions (carboxylates and amines) and ligand exchange reactions (gallates).23

Figure 2.1: Possible approaches to attach colloidal particles at gas-liquid interfaces by tuning their surface wetting properties. The stabilization of gas bubbles with colloidal particles is schematically illustrated in (a) (the particle size was exaggerated for clarity). The adsorption of partially lyophobic particles at the gas-liquid interface is shown in (b), illustrating the tension (γ) balance responsible for particle attachment. The approaches we used to tune the wetting properties of originally hydrophilic particles are shown in (c) to illustrate the universality of the foaming method developed. The same principles can be easily extended to other types of particles, using different surface modifiers, liquid and gaseous phases.

Figure 2.2(a) shows an example of the electrostatic-driven adsorption of anionic carboxylate amphiphiles onto positively-charged alumina particles in a suspension at acidic pH conditions (Figure 2.1(c)). The lyophobization achieved via amphiphile adsorption was confirmed by contact angle measurements of valeric acid aqueous solutions (0.05 mol/L; pH = 4.75) deposited on polycrystalline alumina substrates,
which rendered angles of approximately 60° measured through the aqueous phase. Lyophobicization occurs due to the relatively strong interaction between the anchoring group and the particle surface, leaving the amphiphile's hydrophobic tail in contact with the aqueous solution.

![Graphs showing surface lyophobicization and foaming behaviour using alumina particles and short fatty acids as amphiphiles (□: Propionic acid, C₃; O: Butyric acid, C₄; △: Valeric acid, C₅; ▽: Enanthic acid, C₇). Figure (a) shows the surface lyophobicization of colloidal particles accomplished through the electrostatic-driven adsorption of negatively-charged carboxylic acids on ]

Figure 2.2: Example of surface lyophobicization and foaming behaviour using alumina particles and short fatty acids as amphiphiles (□: Propionic acid, C₃; O: Butyric acid, C₄; △: Valeric acid, C₅; ▽: Enanthic acid, C₇). Figure (a) shows the surface lyophobicization of colloidal particles accomplished through the electrostatic-driven adsorption of negatively-charged carboxylic acids on
positively-charged alumina particles. The symbols \( I \) and \( C \) denote the amount of amphiphile adsorbed per unit surface area of alumina and the initial concentration of amphiphile added to the suspension, respectively. The ability of lyophobicized particles to attach at air-water interfaces results in a significant decrease in the surface tension of colloidal suspensions (\( \gamma_{\text{sw}} \)), as illustrated in (b). The asterisks (*) indicate the critical concentration at which the particles are supposed to attach at the gas-liquid interface. The decrease in surface tension resulted in remarkably high foamability upon high mechanical shearing, as indicated in (c). \( R \) is the foam expansion ratio given by the volume of foam divided by the volume of initial suspension. The volume percentage of air incorporated in the foams is also indicated in the right y-axis in graph (c). All data were obtained from 35 vol% alumina suspensions at pH 4.75.

In the case of the example shown in Figure 2.2(a), the adsorption of negatively-charged carboxylate ions on the alumina surface was observed to screen the surface positive charge at acidic pHs, reducing the particle zeta potential in water. Therefore, additions of carboxylate amphiphiles beyond the concentrations depicted in Figure 2.2(a) led to strong particle coagulation due to van der Waals and hydrophobic attractive forces.

The attachment of the resulting partially lyophobic particles at the air-water interface was indirectly evidenced by surface tension measurements of a suspension droplet at various concentrations of added amphiphilic molecules (Figure 2.2(b)). A relatively abrupt decrease in surface tension was observed for amphiphile additions above a certain critical concentration, as indicated in Figure 2.2(b). Since a fraction of the added amphiphiles does not adsorb at the particle surface (Figure 2.2(a)), part of the surface tension reduction observed was caused by the adsorption of free amphiphilic molecules at the air-water interface. In order to investigate this issue, the individual
contributions of the free amphiphiles and of the partially lyophobic particles to the reduction in the overall surface tension was measured and plotted in Figure 2.3 for the case of suspensions with butyric acid as an example. The contribution of the amphiphile alone was evaluated by measuring the surface tension of aqueous solutions containing amphiphile concentrations corresponding to the fraction of non-adsorbed molecules given in Figure 2.2(a).

Figure 2.3: Surface tension reduction caused by free amphiphiles (open symbols) and by the combined effect of surface modified particles and free amphiphiles (full symbols). Butyric acid is the amphiphile used in this example. The graph illustrates the individual contribution of the free non-adsorbed amphiphiles ($\Delta \gamma_{\text{amph}}$) and that of the modified particles ($\Delta \gamma_{\text{part}}$) to the overall decrease in the suspension surface tension. All data were obtained at pH 4.75, either from 35 vol% alumina suspensions (full symbols) or butyric acid aqueous solutions containing the concentration of non-adsorbed amphiphiles depicted in Figure 2.2(a) (open symbols).
The results shown in Figure 2.3 indicate that below the critical amphiphile concentration, the contribution of amphiphiles (Δγ_{amph}) to the overall surface tension increases steadily, whereas the contribution of modified particles (Δγ_{part}) remains constant. On the other hand, for amphiphile concentrations above the critical point, a drastic increase in the contribution of modified particles to the overall surface tension is observed. This indicates that a significant fraction of modified particles attach to the air-water interface for amphiphile concentrations beyond the critical condition. This was also evidenced by the formation of a thin stiff skin on the surface of suspensions prepared with amphiphiles above this critical concentration.

The presence of partially lyophobicized particles in the suspension enabled the preparation of foams by simply incorporating air bubbles through mechanical frothing. Foams prepared by vigorous mechanical shearing of concentrated alumina suspensions (35 vol% solids) showed a five- to sixfold increase in volume at optimum concentrations of carboxylic acid, as illustrated in Figure 2.2(c). This volume increase corresponds to an amount of incorporated air of approximately 85% with respect to the total foam volume. A bubble size distribution ranging typically from 10 to 100 μm is formed via this foaming process at maximum foamability conditions. Narrower bubble size distributions are achieved by increasing the particle lyophobicity. Further increase of the surface lyophobicity leads however to strong coagulation between particles within the liquid media, hindering the attachment of particles at the gas-liquid interface and thus the foaming process.

In general, foam formation was favored by increasing the particle concentration or decreasing the particle size in the initial suspension. Such trends are explained by the fact that an increase in particle concentration and a decrease in particle size reduce
the time required for the modified particles to diffuse and adsorb on the air bubble surface. For the particle size used in the example reported in Figure 2.2 (diameter ~ 200 nm), a minimum colloid concentration of 15 vol% was necessary to obtain relatively stable high-volume foams. However, this lower concentration limit could be reduced to approximately 5 vol% by using highly mobile partially lyophobized nanoparticles (diameter ~ 70 nm) as foam stabilizers. The production of fresh bubbles at very high rates during air incorporation was also observed to be crucial for the preparation of foams that can percolate throughout the entire volume of the initial suspension. The aforementioned general foaming behavior was observed for all the examples outlined in Figure 2.1(c).

The adsorption of lyophobic particles at the air-water interface of our foams was also confirmed by confocal microscopy images of air bubbles obtained from the dilution of concentrated fluorescent silica foams. An enormous number of extremely stable air bubbles or hollow colloidosomes were produced upon foam dilution, as shown in Figure 2.4. Small clusters of particles were adsorbed at the air-water interface, suggesting the existence of an attractive colloidal network around the air bubbles.

The stability of our high-volume particle-stabilized foams was compared to that of foams known to be very stable in cosmetic and food applications. No liquid drainage, creaming and bubble disproportionation was observed in particle-stabilized foams within more than 4 days after foam preparation. Highly stable foams were actually only produced for amphiphile additions higher than the critical concentrations depicted in Figure 2.2(b) and Figure 2.3, indicating that the stable foams prepared in this work are indeed stabilized by partially lyophobized colloidal particles. The outstanding stability of the particle-stabilized foams contrasts to the markedly higher drainage and
disproportionation rates of food and cosmetic wet foams. Liquid foams containing conventional long-chain surfactants adsorbed at the air-water interface collapse much faster than the foams investigated here, typically within a couple of minutes. The remarkable resistance of our particle-stabilized foams against coalescence and disproportionation is most likely imparted by the strong attachment of particles at the air-water interface (Figure 2.4) and by the formation of an attractive particle network at the interface and throughout the foam lamella.

Figure 2.4: Hierarchical features of the particle-stabilized foams containing short amphiphilic molecules. High-volume macroscopic foams (a) with bubble sizes within the range 10 – 50 μm (b) are formed through the adsorption of submicron-sized colloidal particles at the air-liquid interface (c). Particles attach at the air-water interface due to the surface hydrophobicity imparted by the adsorbed amphiphilic molecules, as schematically indicated in (d). The confocal images shown in (b) and (c) were obtained after dilution of concentrated foams (inset in b) containing fluorescently-labelled silica particles and hexyl amine as amphiphile.

The unique colloidal architecture responsible for the long-term stability of the foam depicted in Figure 2.4 is based on the sequential assembly of amphiphiles on the
surface of particles and of particles on the surface of air bubbles, which leads to a
hierarchical structure spanning over more than 5 orders of magnitude in length scale.
Foam assembly involves a great extent of synergism between the individual
components at different length scales, leading ultimately to the intricate hierarchical
structure depicted in Figure 2.4.

2.4 Conclusions

High-volume wet foams with remarkable long-term stability and bubble size as
small as 10-100 μm can be prepared for cosmetic and food applications using the
described method. The strong attachment of particles at the air-water interface also
enables the fabrication of an enormous number of hollow colloidosomes (Figure 2.4(b))
for a variety of emerging applications31. Additionally, the outstanding foam stability has
allowed us to fabricate bulk macroporous structures with a variety of different ceramic,
polymeric and metallic materials by drying and heat treating the wet foams.
Macroporous materials prepared by this simple and straightforward method can be
used as low-weight structural components, porous media for chemical and biological
separation, thermal and electrical insulating materials, catalyst supports, refractory
filters for molten metals, and scaffolds for tissue engineering and medical implants34.
Therefore, we expect this novel technique to open new opportunities in a wide number
of areas, including food, cosmetics, engineering, biology and medicine.

2.5 References

MACROPOROUS CERAMICS FROM PARTICLE-STABILIZED FOAMS


Abstract

We present a novel direct foaming method to produce macroporous ceramics using particles instead of surfactants as stabilizers of the wet foams. This method allows for the fabrication of ultra-stable wet foams which resist coarsening upon drying and sintering. Macroporous ceramics of various chemical compositions with open or closed cells, average cell sizes ranging from 10 to 300 μm and porosities within 45 and 95% can be easily prepared using this new approach. The sintered foams show high compressive strengths of up to 16 MPa in case of alumina foams with porosities of 88%.
3.1 Introduction

Porous ceramics are of great interest due to their numerous potential applications in catalysis, adsorption and separation, filtration of molten metals or hot gases, refractory insulation of furnaces, as well as hard tissue repair and engineering. The three main processing routes for the fabrication of macroporous ceramics are the replica technique, the sacrificial template method and the direct-foaming technique. The processing route ultimately determines the microstructure of the final macroporous ceramic. Therefore, the selection of a given processing method depends strongly on the microstructure needed in the end application, as well as on the inherent features of the process such as cost, simplicity and versatility.

The direct foaming technique is particularly suitable for the fabrication of open and closed porous structures with porosities ranging from 45 to 97% and cell sizes between 30 μm and 1 mm. Direct foaming methods involve the incorporation of a gaseous phase into a ceramic suspension consisting of ceramic powder, solvent, dispersants, surfactants, polymeric binder and gelling agents. The incorporation of the gaseous phase is carried out either by mechanical frothing, injection of a gas stream, gas-releasing chemical reactions or solvent evaporation.

The liquid foams obtained upon gas incorporation are thermodynamically unstable due to their large interfacial area. Therefore, gas bubbles which initially nucleated as spheres grow as polyhedral cells. There are mainly three processes responsible for coarsening: drainage and coalescence and Ostwald ripening. Drainage of the liquid from the lamellas between the bubbles results in a close approach of bubble surfaces which can lead to their coalescence and to foam collapse. Additionally,
due to different Laplace pressures of bubbles with different sizes, gas diffusion occurs from smaller to larger bubbles. This migration of gas between bubbles leads to coarsening of the foam and to a broadening of the bubble size distribution. Eventually, the liquid foam collapses due to the combined action of these destabilization mechanisms. Additives are often used to avoid foam collapse by setting the foam structure shortly after air incorporation. This usually occurs by gelling or cross-linking organic compounds added to the suspension liquid medium. A drawback of these methods is the fact that they cannot avoid rapid bubble growth before the setting reaction takes place, which leads to large average bubble sizes (30 μm to 1 mm) and a wide bubble size distribution.

We have recently shown that ultra-stable wet foams can be produced by using particles instead of surfactants as foam stabilizers in the direct foaming method. The energy gain upon adsorption of a particle to the air-water interface of fresh gas bubbles can be as high as thousands of $kT$, as opposed to the adsorption energy of a few $kT$ in the case of surfactants ($k$ is the Boltzmann constant and $T$ is the temperature). Therefore, particles can irreversibly adsorb at the surface of gas bubbles, in contrast to surfactants which adsorb and desorb at relatively short time scales at the interface.

The formation of ultra-stable wet foams requires the adsorption of partially hydrophobic particles to the air-water interface. Partial hydrophobization can be achieved through the physical or chemical adsorption of short-chain amphiphilic molecules on the particle surface. The short molecules adsorb with their polar head group onto the particle, leaving the hydrophobic tail in contact with the aqueous solution. Due to their surface hydrophobicity, particles adsorb onto air-water interfaces.
and reduce the foam overall free energy by removing part of the highly energetic gas-liquid interfacial area. Foam formation is therefore based on two consecutive assembly processes, namely the adsorption of short-chain amphiphilic molecules on the particle surface and the adsorption of these partially hydrophobized particles onto the air-water interface of freshly incorporated bubbles. Through these assembly processes, a three-level hierarchical structure is formed, containing short-chain amphiphilic molecules in the molecular scale, partially hydrophobized particles in the colloidal scale and finally air bubbles in the macroscopic scale.

The aim of this work is to investigate the stabilization of foams with colloidal particles and the development of a processing route for the fabrication of solid macroporous ceramics with tailored microstructure. In order to illustrate the main features of this new process, we used mainly alumina powder and short-chain carboxylic acids as particles and amphiphiles, respectively, for foam stabilization. These molecules show a high solubility in water and are thus suitable for the surface modification of a high concentration of particles in the initial suspension. In this article, the entire processing route to obtain the macroporous ceramics is outlined and the final microstructure and mechanical properties of the porous structures produced are described.

3.2 Materials and methods

3.2.1 Materials

Experiments were carried out using high-purity \( \alpha-\text{Al}_2\text{O}_3 \) powder (Ceralox, HPA-0.5 w/MgO, Tucson, Arizona, USA) with an average particle diameter \( d_p \) of 200 nm, a specific surface area of 10 m\(^2\)/g and a density of 3.98 g/cm\(^3\). Other chemicals used in the
experiments were deionized water, hydrochloric acid (2 N, Titrisol, Merck, Germany) and sodium hydroxide (1 N, Titrisol, Merck, Germany). The short-chain carboxylic acids were propionic, butyric, valeric and enanthic acids (Fluka, Buchs, Switzerland). Table 3.1 shows the chemical formulas as well as the pKₐ values of these amphiphiles. At a pH equal to the pKₐ, 50% of the dissolved molecules are deprotonated. The amphiphile propyl gallate, as well as the gelling agents hydroxyaluminum diacetate (dₐ ~ 0.7 µm) and sodium alginate (Fluka AG Buchs, Switzerland) were later used in this study to produce open-cell macroporous structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propionic acid</td>
<td>CH₃CH₂-COOH</td>
<td>4.86</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>CH₃(CH₂)₂-COOH</td>
<td>4.83</td>
</tr>
<tr>
<td>Valeric acid</td>
<td>CH₃(CH₂)₃-COOH</td>
<td>4.84</td>
</tr>
<tr>
<td>Enanthic acid</td>
<td>CH₃(CH₂)₅-COOH</td>
<td>4.89</td>
</tr>
</tbody>
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### 3.2.2 Suspension preparation

Suspensions containing carboxylic acids were produced as follows: alumina powder was stepwise added to water containing hydrochloric acid (0.7 wt% to alumina) to obtain a suspension with a solids loading of 50 vol%. Homogenization and deagglomeration was carried out on a ballmill for at least 18 h using polyethylene milling pots and alumina balls (10mm diameter, ratio balls:powder ~ 2:1). An aqueous solution containing the amphiphile and if necessary pH-adjusting agents was then slowly and drop wise added to the ballmilled suspension under slight stirring to avoid
local particle agglomeration and coagulation. Afterwards, the pH was set to its desired value and the amount of water needed to achieve certain solids contents was added.

Suspensions containing propyl gallate as amphiphile were prepared by stepwise adding alumina powder to water containing 506 mmol/l NaOH and 29 mmol/l propyl gallate. The suspension solids loading and pH were initially fixed to 50 vol% and 9.8, respectively. Homogenization of the suspensions was carried out as described above. Afterwards, the propyl gallate needed to adjust the amphiphile concentration in the final suspension to 100 mmol/l was dissolved in a NaOH aqueous solution displaying pH higher than 10. This solution was then slowly and drop wise added to the ballmilled suspension under slight stirring to avoid local particle agglomeration. Finally, the pH was set to 9.9 and the solids loading to 20 vol% by adding water to the suspension.

3.2.3 Adsorption measurements

For the adsorption measurements, alumina suspensions were prepared as described above. After ball-milling, the carboxylic acid was drop wise added to the suspension, the pH was set to 4.75 and the solids loading to 35 vol% alumina. The suspensions were stirred for 2 h to achieve equilibrium conditions. Two tubes, each filled with 45 ml of suspension, were then centrifuged (Hermle, Z 513 K, Wehingen, Germany) for 1 h at a speed of 4500 rpm. The supernatant obtained was again centrifuged (5417R, Eppendorf, Leipzig, Germany) using 16 small tubes, each containing 1.5 ml of supernatant. In this case, the centrifugation time was set to 20 min and the rotation speed was 15000 rpm. The pH of the resulting supernatant was set to a value higher than 10 to ensure complete deprotonation of the amphiphilic molecules. The amphiphile concentration in the supernatant was measured by titrating the solution to
a pH lower than 2 using either 1 N or 0.1 N HNO₃. An automatic titration unit (DT1200, Dispersion Technologies Inc., Mount Cisco, New York, USA) was used for these measurements.

3.2.4 Zeta-potential analysis

Zeta-potential measurements (DT1200, Dispersion Technologies Inc., Mount Cisco, New York, USA) were conducted in 2 vol% alumina suspensions at pH 4.75 to assess the effect of the amphiphilic molecules on the surface charge of the alumina particles. For each amphiphile concentration, a new suspension was prepared and ultrasonicated for 5 min prior to the measurement.

3.2.5 Rheological tests

The rheological behavior of the suspensions was evaluated using a vane configuration in a stress-controlled rheometer (Model CS-50, Bohlin Instruments, Cirencester, U.K.). The measurements were performed under steady-shear conditions by applying a step-wise stress increase until a shear rate of about 200 s⁻¹ was reached. The solids loading of the suspension was 35 vol% alumina at pH 4.75.

3.2.6 Surface tension measurements

The surface tension of the suspensions was measured using the pendant drop method (PAT1, Sinterface Technologies, Berlin, Germany). Alumina suspensions were prepared as mentioned above, by drop wise adding the carboxylic acid, setting the pH to 4.75 and diluting the suspension to a solids loading of 35 vol% alumina. Depending on the surface tension of the suspension, the drop volume was set to a constant value within the range 12 - 35 mm³.
3.2.7 Foaming and foam characterization

Foaming of 150 ml suspensions was carried out using a household mixer (Kenwood Major Classic; Kenwood Schumpf AG, Baar, Switzerland) at full power (800 W) for 3 min. The foam density was measured with a custom-built tool which consisted of a plastic cylindrical cup with small holes on the bottom and a massive sliding stamp on top. The foam was carefully filled into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. The volume between the bottom of the stamp and the bottom of the cylinder was kept constant. Dividing the mass of the foam by its volume resulted in the foam density. The bubble size distribution of the wet foams was evaluated using an optical microscope in transmission mode (Polyvar MET, Reichert-Jung, Austria) connected to a digital camera. The bubble sizes were measured with the linear intercept method using the software Lince (Linear Intercept, TU Darmstadt, Germany).

3.2.8 Foam setting and drying

To avoid crack formation during drying, the wet foams were strengthened prior to water evaporation by either coagulating the particles within the lamella or by chemically gelling the foam liquid phase.

In the case of wet foams containing carboxylic acid, the particles within the foam lamella were coagulated by changing the pH in-situ from 4.75 to 7.5 using the enzyme-catalyzed hydrolysis of urea (Sigma-Aldrich, Buchs, Switzerland). The urea content in the suspensions was 0.05 wt% with respect to alumina and the concentration of the enzyme urease (Roche Diagnostics GmbH, Mannheim, Germany) was 1 unit per gram alumina. The enzymatic activity of the urease used was
58000 units/(g of pure urease). One unit is defined as the amount of enzyme necessary to release 1 μmol of reaction product per minute from the substrate at 24 °C and at the pH where the enzymatic activity in water is at its maximum. Urea was added to the suspension before homogenization, whereas urease was dissolved in water and added to the suspension prior to the foaming step.

In the case of wet foams containing propyl gallate as amphiphile, the foam liquid phase was gelled using the time-delayed gelation between sodium alginate and hydroxyaluminum diacetate (HADA) as described elsewhere in the literature. In order to homogeneously distribute the gelling agent within the suspension, sodium alginate was first dissolved in water at 80 °C. After cooling to room temperature, the alginate solution was added to the suspension under stirring. The amount of alginate added corresponded to 0.25 wt% with respect to the mass of alumina in the final suspension. The pH of the suspension was then set to 9.9 and the amount of water needed to achieve a solids content of 20 vol% was added. In order to slow down the gelation process, the suspension was cooled in ice prior to foaming. HADA was then added as powder to the suspension under stirring. The weight ratio HADA:sodium alginate was 7:1. Foaming was finally conducted by mechanical frothing as described above.

The resulting wet foams were hand-shaped into cylindrical parts (diameter: 100 mm, height 50 mm) and subsequently dried in air at 22–25 °C for 24 to 48 h.

3.2.9 Sintering of the foams

Sintering of the cylindrical dried foams was performed in an electrical furnace (HT 40/16, Nabertherm, Germany) at 1575 °C for 2 h. The heating rate was set to 1 °C/min and the cooling rate to 3 °C/min.
3.2.10 Compressive strength measurements

Compressive strength measurements were performed on a universal testing machine (Instron 8562, model A1477-1003, Norwood, MA, USA). A bulk piece of ceramic foam was ground on both sides resulting in parallel opposite surfaces that ensured homogeneous sample loading during compression. Cylindrical samples with diameters of 15 mm and lengths of 30 mm were drilled out of this bulk piece of foam with a diamond core drill and crushed under a compression speed of 0.5 mm/min.

3.3 Results and discussion

3.3.1 Amphiphile adsorption and zeta potential

The formation of stable foams requires the adsorption of particles on the surface of freshly-incorporated air bubbles. In order to enable their adsorption at the gas-liquid interface, particles with a partially hydrophobized surface are needed. In case of alumina, hydrophobization can be achieved by modifying the particle surface with short-chain carboxylic acids which adsorb with the carboxylate group onto alumina, leaving the hydrophobic tail in contact with the aqueous solution. The surface properties of the resulting modified particles are mainly determined by the concentration of adsorbed amphiphilic molecules and their tail length.

Figure 3.1 shows that carboxylic acids with chain lengths of up to 6 carbons adsorb onto alumina particles at acidic conditions. All measurements were carried out in suspensions containing 35 vol% alumina at pH 4.75 and carboxylic acid concentrations typically required to obtain stable foams. Under such conditions, the dissociated carboxylic acid molecules can adsorb electrostatically as counter-ions onto
the oppositely charged alumina surface or through ligand exchange reactions with the alumina hydroxyl surface groups. We observed that the addition of competing counter-ions such as Cl⁻ into the suspension decreased the amount of adsorbed carboxylate molecules, indicating that the amphiphiles are predominantly adsorbed as counter-ions on the particle surface.

Figure 3.1: Adsorption of short-chain carboxylic acids on alumina particles: propionic acid (■), butyric acid (○), valeric acid (▲) and enanthic acid (▼). Measurements were obtained from 35 vol% alumina suspensions at pH 4.75.

The adsorption of the carboxylic acids on alumina was also influenced by the concentration of particles in the suspension. For a constant ratio of added propionic acid to particle surface area of 1.23 μmol/m², we observed a linear increase in the amount of adsorbed amphiphiles from 0.44 to 1.11 μmol/m² by increasing the suspension solids content from 5 to 35 vol%, respectively. Based on these adsorption data, we estimate an adsorbed amount of propionic acid of 0.35 μmol/m² at a solids
content of 2 vol%. This estimated value is in good agreement with the data reported by Hidber et al. for this particle concentration (0.31 μmol/m²). The increase in solids content in the above experiments was also accompanied by an increase in the ionic strength of the liquid media. As a result of the increased ionic strength, higher surface charges are developed on the particle surface and higher concentrations of counter-ions are needed for charge neutralization. Therefore, the enhanced adsorption of amphiphilic counter-ions observed at high solids content might result from the increased surface charge developed on the particles at high particle concentrations.

The surface modification accomplished through the adsorption of carboxylic acid molecules also led to a significant reduction of the particle's zeta potential (potential at the shear plane), as shown in Figure 3.2. Surprisingly, this reduction strongly depends on the tail length of the amphiphilic molecule and is far more pronounced than that achieved with equivalent amounts of the 1:1 electrolyte sodium chloride. The addition of high concentrations of carboxylic acids did not invert the zeta potential sign nor changed the alumina isoelectric point, confirming that these molecules adsorb as counter-ions rather than as specific adsorbing species around the particles. Therefore, the electrical potential on the alumina surface remains constant at 45 mV upon addition of amphiphiles or back electrolyte. On the other hand, the zeta potential is strongly influenced by the concentration and valency of counter-ions in the diffuse layer which screen the particle surface charge.
The stronger screening effect of amphiphiles as compared to a standard electrolyte (Figure 3.2) might result from the specific adsorption of additional anions onto the partially hydrophobized particle surfaces. The hydrophobicity imparted by the first layer of deprotonated amphiphiles adsorbed on the surface leads to an energetically unfavourable exposure of hydrophobic species into the aqueous phase. This favours the adsorption of additional molecules from the aqueous phase onto the particle surface to decrease the system free energy. Hydroxyl ions (OH⁻) are known to specifically adsorb on hydrophobic surfaces in contact to water. Likewise, deprotonated amphiphiles might also adsorb as a second layer on the particle surface in a configuration similar to hemi-micelles. In both cases, a negative charge would be added to the particle surface, further screening the positive charges on the particle surface. The effect is more pronounced for amphiphiles with longer hydrophobic tails.
since these can lead to an increased surface hydrophobicity at the same concentration in solution (Figure 3.1). The hydrophobic interactions between the first layer of adsorbed amphiphiles and the second layer of anions is apparently not strong enough to neither invert the particle zeta potential nor form a well-defined hemi-micelle around the surface. Most importantly, the second layer of anions does not cover all the hydrophobic surface sites, keeping the particles sufficiently hydrophobic to adsorb at the air-water interface (see section 3.3.3).

3.3.2 Rheological behavior

The screening of the particle’s surface charge upon amphiphile addition leads to an increase in the suspension viscosity, as shown in Figure 3.3. Due to the surface charge screening, the electrical diffuse layer around the particle surface is not sufficiently thick to overcome the attractive van der Waals forces between particles. The results are particle coagulation and a subsequent increase in the suspension viscosity. Figure 3.4 shows that the suspension viscosity increases suddenly above a critical concentration of adsorbed carboxylic acid molecules. This critical concentration decreases with the increase of the amphiphile tail length due to the stronger screening effect of the longer molecules (Figure 3.2). Besides van der Waals attraction, hydrophobic attractive forces\textsuperscript{20,21} might also play a role on the viscosity increase observed in Figure 3.3. This hydrophobic attraction is expected to increase upon increase of the amphiphile tail length.
3.3.3 Surface tension

The change in particle hydrophobicity upon adsorption of short-chain carboxylic acids can be monitored also by surface tension measurements. The addition of carboxylic acid molecules resulted in a decrease in the surface tension of the suspensions, as illustrated in Figure 3.4a. This decrease is in part due to the free carboxylic acid molecules present in the suspension which adsorb at the air-water interface. The concentration of these free carboxylic acid molecules was determined from the adsorption measurements (Figure 3.1) and their contribution to the total surface tension reduction was plotted in Figure 3.4b. The contribution of free amphiphiles was estimated from surface tension measurements of aqueous solutions containing carboxylic acid concentrations equivalent to that expected for free amphiphiles in the suspension.
Figure 3.4: a) Surface tension of 35 vol% alumina suspensions at pH 4.75 for different concentrations of carboxylic acids with different tail length (propionic acid (■), butyric acid (○), valeric acid (▲), enanthic acid (▼)). b) Surface tension of free carboxylic acids in water at pH 4.75. The concentration of free amphiphiles was determined from adsorption measurements of 35 vol% alumina suspensions at pH 4.75 and plotted as top x-scale for the example of propionic acid as an example.

Figure 3.4b shows that the free amphiphiles lead to a gradual and monotonic decrease of the suspension surface tension. On the other hand, Figure 3.4a indicates
that above a certain amphiphile concentration in suspension, the surface tension drops more abruptly than one would expect from the reduction given by the free amphiphilic molecules alone. At this amphiphile concentration, the particles are hydrophobic enough to adsorb to the air-water interface. The adsorbed particles replace part of the highly energetic interface area and lower the overall free energy of the system, leading to an apparent reduction in surface tension of the suspension. The amphiphile concentration needed to render the particles sufficiently hydrophobic to adsorb to the air-water interface decreases markedly with increasing tail length. This can be attributed to the more hydrophobic nature of carboxylic acids with increasing tail length.

3.3.4 Foaming and foam stability

The concentration of amphiphilic molecules in the initial suspension and the length of their hydrophobic tail can now be used to tailor the degree of surface hydrophobization of the alumina particles in water (see Figure 3.4a). By providing the proper hydrophobicity on the particle surface, suspensions were homogeneously foamed throughout the whole volume upon mechanical frothing. The mixing speed significantly influences the shear rates and shear stresses applied around the air bubbles during frothing. Even though the mixing conditions were not investigated here, an increase of the shear stresses applied during frothing should facilitate the mechanical rupture of freshly incorporated bubbles and thus lead to foams with smaller average bubble sizes and narrower bubble size distributions$^{23,24}$. 

Figure 3.5: Air content of foamed suspensions containing 35 vol% alumina at pH 4.75 and different short-chain carboxylic acids: propionic acid (■), butyric acid (○), valeric acid (▲), enanthic acid (△).

The wet foams obtained after mixing feature air contents up to 85% (Figure 3.5) and possess a high stiffness in the wet state. By increasing the concentration of a given carboxylic acid, the air content of the foam first increases rapidly and then reaches a plateau before decreasing sharply at high amphiphile additions. This sharp decrease at high amphiphile concentrations is attributed to an increase in the viscosity of the initial suspension, caused by the screening effect of counter-ions on the surface charge of the particles (section 3.3.2). An increased viscosity hinders the incorporation of air into the initial suspension and results therefore in foams with lower air contents.

The as-prepared wet foams exhibit a pronounced yield stress, which allows for shaping of parts using extrusion, injection moulding, pressure filtration or related techniques. The foams can also be sprayed or easily poured into moulds after dilution of the as-prepared foams with water. Dilution does not affect the stability of the air
bubbles and can be used to adjust the foam viscosity according to the shaping method desired.

The stability of the obtained particle-stabilized foams was compared to that of shaving foam known to be very resistant against destabilization (Gillette Foam, Regular, Gillette Co, London). Figure 3.6 shows that the particle-stabilized foams are stable against bubble growth and drainage over days, whereas the shaving foam shows a rapid bubble growth within the first hours.

The enhanced stability of the foams obtained here is based on the different mechanism used to stabilize the air-water interface compared to that applied in the conventional shaving foam. In the ceramic foams, particles are used as stabilizers whereas conventional amphiphilic surfactants are used to stabilize the air-water interface in the shaving foam. The energy required to desorb a particle from an air-water interface is orders of magnitudes higher than the few kTs needed to desorb a surfactant molecule from the interface\(^3\). The irreversible adsorption of particles to the interface results in a percolating interfacial armor that mechanically impedes bubble growth, shrinkage and coalescence\(^3\). Particles are also expected to form a network throughout the foam lamella, which further prevents bubble coarsening.
Figure 3.6: Relative average bubble size as a function of time after foaming for particle-stabilized foams containing propionic acid (176 mmol/l, ◇), butyric acid (50 mmol/l, O), valeric acid (30 mmol/l, ▲) and enanthic acid (10 mmol/l, ▽) (35 vol% alumina, pH 4.75). The relative average bubble size corresponds to the ratio between actual and initial average bubble size. All data for the particle-stabilized foams were obtained from 35 vol% alumina suspensions at pH 4.75. The stability of a surfactant-stabilized shaving foam (Gillette™) (□) is also included in the graph for comparison.

3.3.5 Microstructure and mechanical strength of sintered foams

The high stability of the wet foams allows for drying directly in air at room temperature. In order to avoid crack formation during water removal, the wet foam had to be slightly strengthened to overcome the capillary stresses developed during drying and to avoid differential shrinkage within the drying foam. In this work, the strengthening effect was achieved either by coagulating the particles within the foam
lamella or by gelling the foam liquid phase. Particles were coagulated in-situ by shifting the pH from 4.75 to 7.5 using an enzyme-catalyzed decomposition reaction of urea\(^5\), whereas the gelation of the liquid phase was achieved by cross-linking sodium alginate macromolecules with an ion-releasing agent (see section 3.2.8).

Figure 3.7a shows the microstructure of a macroporous alumina obtained after drying and sintering a wet foam prepared with butyric acid. In this case, crack formation was avoided by coagulating the particles with the internal pH-shift reaction. The macroporous structure obtained exhibit a total porosity of 88%. Cells are mostly closed with average size of approximately 35 \(\mu\)m and standard deviation of 15 \(\mu\)m. Single cells are separated by walls with minimum thicknesses below 1 \(\mu\)m (inset Figure 3.7a). The foam cells are in this case predominantly closed due to the fact that the air bubbles of the original wet foams are completely covered with the surface modified particles. Such coverage remains through the gelling, drying and sintering procedure, resulting in the closed cells depicted in Figure 3.7a.

Alternatively, the particle layer that covers the air bubbles of wet foams can also be disrupted during the gelling process to produce macroporous structures with interconnected cells, as shown in Figure 3.7b. Here, the average cell size is in the range of 100 to 150 \(\mu\)m. In this case, the foam was prepared with propyl gallate and gelled with sodium alginate. The gelation process led to a significant shrinkage of the wet foam. Cell interconnectivity is most likely formed by a local differential shrinkage of the particle layer around the air bubbles during the gelation process. This shrinkage favors the rupture of the particle coating around the bubbles, leading to interconnecting cells after drying and sintering.
Figure 3.7: Microstructures of (a) a close cell particle-stabilized foam, (b) an open cell particle-stabilized foam, (c) a surfactant-stabilized foam prepared with the direct foaming technique (after Green and Colombo)\textsuperscript{a}, and (d) a reticulated foam prepared with the replica technique (after Green and Colombo)\textsuperscript{b}. The inset in (a), (d) and (e) show single struts which are dense in case of the direct foaming technique and hollow in case of the replica technique.

The microstructure of our particle-stabilized foams can be tailored to render average cell sizes within the range of 10 to 300 $\mu$m at porosities between 40 and 95\%\textsuperscript{\textit{c}}.
Compared to surfactant stabilized foams, our foams can reach smaller average cell sizes and exhibit either open or closed cells even at high porosities\(^3\). The smaller cell sizes result from the high stability of the foams in the wet state which impedes bubble coarsening.

Due to the possibility to have a closed-cell structure, the maximum compressive strength of our particle-stabilized foams can be higher than that of surfactant-stabilized foams at similar porosities (Figure 3.8).

Figure 3.8: Compressive strength of our particle stabilized foams (●, particle network strengthened during drying), compared to foams made by other techniques such as direct foaming with surfactants, replica technique or sacrificial templating\(^1\). The relative strength corresponds to the ratio between the strength of the porous and the dense materials. The strength data for the particle stabilized foams were obtained from samples exhibiting predominantly closed cells.
In case of surfactant-stabilized foams, the openings between the cells (Figure 3.7c) are responsible for the lower compressive strength. Such openings arise from the instability of the wet foams before the setting reaction takes place. Foams made by the replica method show an even lower compressive strength due to their highly open cell structure (Figure 3.7d) and the presence of cracks and defects in the struts which derive from the burnout of the polymeric material. Additionally, the triangular shape of these defects leads to stress concentrations at the thin edges of the ceramic struts.

The interconnectivity of the cells in case of particle-stabilized foams (Figure 3.7b) is comparable to that achieved with surfactant-stabilized foams (Figure 3.7c), but lower than that of foams produced by the replica technique (Figure 3.7d). However, it is important to note that the preparation of open-cell structures from particle-stabilized foams has not been fully exploited yet and should be thoroughly investigated in future work.

3.4 Conclusions

The in-situ hydrophobization of colloidal particles in concentrated suspensions allowed for the preparation of high-volume wet foams with air contents up to 85\% and bubble sizes between 10 and 300 µm. These foams showed neither bubble growth nor drainage over days. Short-chain carboxylic acids were used to in-situ hydrophobize the alumina particles used in this work. The degree of particle hydrophobization can be adjusted with the concentration and the tail length of the carboxylic acid molecules added to the suspension. Upon adsorption of these modified particles to the air-water interface, the surface tension of the suspension is significantly lowered. By providing enough hydrophobicity to the particle surface, suspensions were foamed
homogeneously throughout the whole volume. Due to their high stability, these wet foams can be dried in air without bubble coarsening and crack formation. The macroporous ceramics obtained after sintering exhibit porosities of up to 95%, with either open or closed cells between 10 and 300 μm. The mechanical strengths of the sintered foams with closed cells are significantly higher compared to those produced from surfactant-stabilized foams and from polymer replica and sacrificial template techniques. The principles outlined here can also be applied to other ceramic powders, allowing for the preparation of macroporous ceramics with various chemical compositions and tailored final microstructure.

3.5 Acknowledgment

The authors would like to thank Philip Sturzenegger, Rahel Nägeli, Claudia Strehler and Andreas Bihl for their contribution to the experimental work.

3.6 References

TAILORING THE MICROSTRUCTURE OF PARTICLE-STABILIZED WET FOAMS


Abstract

Inorganic particles which are in-situ hydrophobized upon adsorption of short-chain amphiphilic molecules can be used as foam stabilizers. In this study, we tailor the microstructure of particle-stabilized wet foams, namely the foam air content, average bubble size and bubble size distribution by changing the composition of the initial suspension. Wet foams featuring average bubble sizes between 10 and 200\,\mu m and air contents between 45 and 95\% were obtained by adjusting the amphiphile and particle concentration, pH, ionic strength and particle size in the initial suspension. The influence of these parameters on the bubble size was satisfactorily described in terms of a balance between the shear stress applied during mixing and the counteracting Laplace pressure of the air bubbles. This model, originally developed for oil droplets in emulsions, can therefore be used to deliberately tailor the microstructure of particle-stabilized wet foams.
4.1 Introduction

Wet aqueous foams are used in numerous different applications ranging from food and cosmetics to oil recovery and fire extinguishing\(^1\). Additionally, wet foams can be used as intermediate products to fabricate solid porous materials applied as thermal insulators, low weight structures, scaffolds for drug delivery and tissue engineering, among others\(^3\).

However, wet foams are thermodynamically unstable and show limited resistance against bubble coarsening as a result of their high internal interfacial area. To improve the stability of wet foams, surfactants are used to lower the surface tension of the gas-liquid interface and thus increase the lifetime of gas bubbles. However, these surfactants are not able to completely avoid bubble growth due to their low energy of attachment to the gas-liquid interface, which is only a few \(kT\)s for a single surfactant molecule (\(k\) being the Boltzmann constant and \(T\) the temperature).

In order to improve the stability of wet foams, the original observation of Pickering\(^4\) and Ramsden\(^5\) was in recent years extended to gas-liquid systems and particles have been used to adsorb on the surface of gas bubbles to stabilize the gas-liquid interface\(^6\text{-}^n\). Upon adsorption, particles lower the overall free energy of the system by replacing part of the high-energetic gas-liquid interfacial area with less energetic interfaces. As opposed to surfactants, the energy of attachment of a particle at a gas-liquid interface can reach thousands of \(kT\)s\(^6\text{-}^n\). Therefore, particles can irreversibly adsorb at gas-liquid interfaces, in contrast to the constant adsorption and desorption of surfactants. Particles adsorbed at the interface impede bubble coalescence and form an interfacial armor that resists the low pressures arising from gas diffusion outwards the
bubble (Ostwald ripening). As a result, particle-stabilized foams exhibit enhanced
stability in comparison to foams stabilized by surfactants.

Recently, we developed a very versatile method to prepare high-volume wet
foams stabilized by partially hydrophobized particles\textsuperscript{11-13}. In-situ hydrophobization of
initially hydrophilic particles enabled the attachment of particles to the gas-liquid
interface. Short amphiphilic molecules containing less than 8 carbons in the
hydrocarbon tail were adsorbed on the particles to impart surface hydrophobicity.
Particles of various surface chemistry have been used as foam stabilizers by deliberately
choosing the anchoring group of the adsorbing amphiphiles\textsuperscript{13}. The surface
hydrophobization of a high concentration of particles and their adsorption to air-water
interfaces enabled the stabilization of high-volume wet foams. These wet foams
showed neither bubble growth nor drainage over more than four days\textsuperscript{11,12}.

The formation of stable wet foams using modified particles as stabilizing agents
opens many opportunities in a number of areas where foams are used either as an
intermediate or end product, including food, pharmaceutics, cosmetics, oil recovery,
textile manufacture and materials fabrication. In these applications, microstructural
features of the wet foam such as the average bubble size, the bubble size distribution
and the air content are of major importance, since they determine the rheological
behaviour of the wet foam and the functional properties of the final product. The size
and content of gas bubbles in food foams, for example, have a marked effect on the
sensorial quality and texture of the final food product\textsuperscript{14,15}. Likewise, the air content,
bubble size and bubble size distribution of wet foams used to produce porous materials
also have a remarkable influence on the final mechanical and physical properties of
porous solid structures\textsuperscript{16,17}. 
Given the importance of the foam microstructure in various applications, we evaluate here the effect of the composition of the foam precursor suspension on the final microstructure of particle-stabilized wet foams. The concentration of surface modifier, salt and particles, as well as the particle size and the pH of the initial precursor suspension are the main parameters investigated. These parameters are expected to change some of the factors that control foam formation, such as the viscosity and surface tension of the suspension. A deliberate control of these parameters should therefore enable one to tailor the final microstructure of particle-stabilized wet foams.

4.2 Materials and methods

4.2.1 Materials

Sub-micron alumina powders were used as model colloidal particles in this study. The powders were acquired from the following suppliers: \( \text{Al}_2\text{O}_3, d_{50} \sim 28 \text{ nm} \), Nanotechnologies (Austin, Texas, USA); \( \delta\text{-Al}_2\text{O}_3, d_{50} \sim 70 \text{ nm} \), Nanophase Technologies Co. (Romeoville, IL, USA); \( \alpha\text{-Al}_2\text{O}_3, d_{50} \sim 116 \text{ nm} \) (grade TM-DAR) Taimei Chemicals Co. (Tokyo, Japan); \( \alpha\text{-Al}_2\text{O}_3, d_{50} \sim 200 \text{ nm} \) (grade Ceralox HPA-0.5), Sasol North America Inc. (Tucson, AZ, USA); \( \alpha\text{-Al}_2\text{O}_3, d_{50} \sim 1800 \text{ nm} \) (grade CL2500SG), Alcoa (Ludwigshafen, Germany). Table 4.1 depicts the physical properties of these powders. If not supplied by the manufacturer, the particle size was measured on an X-ray Disk Centrifuge Sedigraph (XDC, Brookhaven Instruments, Worcestershire, Great Britain) and confirmed by scanning electron microscopy. The specific surface area was obtained by BET adsorption measurements (Nova 1000 Series, Quantachrome, Odelzhausen, Germany).
The short-chain amphiphilic molecules used in this work were propionic acid and valeric acid (Fluka AG, Buchs, Switzerland). Other chemicals used in the experiments were delonized water, hydrochloric acid (2 N, Titrisol, Merck, Germany), sodium hydroxide (1 N, Titrisol, Merck, Germany) and sodium chloride (Fluka AG, Buchs, Switzerland).

Table 4.1: Properties of the alumina powders used in this study

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>Specific surface area (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>28*</td>
<td>54.80*</td>
<td>3.90*</td>
<td>Nanotechnologies</td>
</tr>
<tr>
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<td>3.98</td>
<td>Sasol</td>
</tr>
<tr>
<td>1800</td>
<td>0.95*</td>
<td>3.98*</td>
<td>Alcoa</td>
</tr>
</tbody>
</table>

* data supplied by the manufacturer

4.2.2 Suspension preparation

Suspensions were prepared by adding the dry powder step-wise to water upon continuous stirring. During powder addition, the pH was kept at values below 5 using 2 N HCl in order to electrostatically stabilize the alumina particles. The initial solids content of suspensions prepared with 28, 60, 120, 200 and 1800 nm sized particles was set to 25, 30, 20, 50 and 45 vol% respectively, before ball-milling. In case of 60 and 28 nm particles, 20 mM NaCl was also added to the initial suspension to partially screen the particles surface charge and enable the addition of powder until the above-mentioned solids content. Homogenization was carried out on a ballmill for at least
18 h using polyethylene milling pots and alumina balls (10 mm diameter, ratio balls:powder ~ 2:1). An aqueous solution containing the amphiphile and if necessary pH-adjusting agents was then slowly and dropwise added to the ballmilled suspension under slight stirring to avoid local particle agglomeration. Afterwards, the pH was set to its desired value and the amount of water needed to achieve the target solids content was added.

4.2.3 Foaming and foam characterization

Foaming of 150 ml suspensions was carried out using a household mixer (Kenwood, Major Classic) at full power (800 W) for 3 min.

The foam density was measured with a custom-built tool which consisted of a plastic cylindrical cup with small holes on the bottom and a massive sliding stamp on top. The foam was carefully filled into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. The volume between the bottom of the stamp and the bottom of the cylinder was kept constant. Dividing the mass of the foam by its volume resulted in the foam density.

The bubble size distribution of the wet foams was evaluated using an optical microscope in transmission mode (Polyvar MET, Reichert-Jung, Austria) connected to a digital camera. The bubble sizes were measured with the linear intercept method using the software Linear Intercept (TU Darmstadt, Germany). The average bubble size ($d_{50}$) was determined from the resulting cumulative bubble size distribution, as the size corresponding to a number cumulative percentage of 50%.
4.2.4 Surface tension measurements

The surface tension of the suspensions was measured using the pendant drop method (PAT1, Sinterface Technologies, Berlin, Germany). Suspensions were prepared as mentioned above by drop wise adding the carboxylic acid, adjusting the pH to 4.75 and diluting the suspension to the desired solids content. Depending on the surface tension, the drop volume was set to a constant value within the range 12 – 35 mm³.

4.2.5 Foam rheology

Foam rheology was evaluated in a stress-controlled rheometer (Model CS-50, Bohlin Instruments, Cirencester, U.K.) using profiled parallel plates (diameter: 25mm) with a gap of 1mm. Measurements were performed under steady-shear conditions by applying a step-wise stress increase until a shear rate of at least 500 s⁻¹ was reached.

4.3 Results and discussion

The influence of the composition of the initial suspension on the microstructure of wet foams was investigated by characterizing the foams with regards to air content, average bubble size and bubble size distribution. Figure 4.1 shows two typical wet foam microstructures, one with small average bubble sizes and a narrow bubble size distribution (Figure 4.1a) and the other with large bubble sizes and a wide size distribution (Figure 4.1b). The parameters evaluated were the amphiphile concentration, pH, ionic strength, particle concentration in the initial suspension and particle size. Valeric acid was used as amphiphile to hydrophobize the alumina particles’ surface in most experiments, except for the study concerning the influence of ionic strength where propionic acid was used. Trends similar to the ones described here
were observed for several other short-chain amphiphilic molecules with hydrocarbon
tails containing 3 to 8 carbon atoms.

Figure 4.1: Typical microstructure of wet foams showing a) small average bubble
size and narrow bubble size distribution and b) large average bubble size and
wide bubble size distribution.

4.3.1 Initial amphiphile concentration

The amphiphile concentration in the initial suspension directly affects the
hydrophobicity of the colloidal particles. An increase in the initial amphiphile
concentration leads to a higher adsorption onto the particles, enhancing the surface
hydrophobicity. Above a critical concentration of absorbed amphiphiles, the particles
are sufficiently hydrophobic to adsorb to air-water interfaces and to stabilize freshly
introduced air bubbles. Therefore, foam formation and their resulting microstructure
depends strongly on the initial amphiphile concentration in the suspension.
Figure 4.2a shows the effect of the initial valeric acid concentration on the air content and average bubble size of suspensions containing 35 vol% of 200 nm alumina particles at pH 4.75. The discrete bubble size distribution of wet foams prepared with 10 and 40 mmol/l of valeric acid is depicted in Figure 4.2b. No stable foam is formed below the critical valeric acid concentration of 5 mmol/l (Figure 4.2a). At this concentration, the particles are not sufficiently hydrophobic to adsorb to the air-water interface. With increasing valeric acid concentration, the particles become hydrophobic enough to attach to the surface of air bubbles, resulting in stable wet foams (Figure 4.2a). The air content in the wet foam remains nearly constant at approximately 80 % for valeric acid contents between 10 and 40 mmol/l. The addition of valeric acid concentrations higher than 40 mmol/l leads to a considerable increase in the suspension viscosity (> 2 Pa s at 100 s⁻¹), hindering the incorporation of air and foam formation (Figure 4.2a). This viscosity increase is caused by the enhanced screening of the particles’ surface charge resulting from the high amphiphile concentrations (section 4.3.3).¹ ¹

Even though the air content of the wet foams remained nearly constant at 80 %, the average bubble size decreases from 108 to 16 μm with increasing the valeric acid concentration from 10 to 40 mmol/l. Foams with lower average bubble size also exhibited a narrower bubble size distribution, as shown in Figure 4.2b.
Figure 4.2: a) Effect of the valeric acid concentration in the suspension (35 vol% 200 nm α-alumina, pH 4.75) on the air content (■) and the average bubble size (□) of the achieved foams. b) Bubble size distribution of foams from suspensions (35 vol% 200 nm α-alumina, pH 4.75) containing 10 (■), and 40 mmol/l (□) valeric acid.
4.3.2 Suspension pH

Besides the amphiphile concentration, the pH of the suspension also influences significantly the wet foam microstructure. Figure 4.3 shows the effect of pH on the air content, average bubble size and bubble size distribution of wet foams prepared from suspensions containing 35 vol% of 200 nm alumina particles and a constant valeric acid concentration of 30 mmol/l.

The results show a constant air content in the wet foam of approximately 82% between pH 2.5 and 7 of the initial suspension. Below pH 2.5, no stable foam was formed and above pH 7, the air content decreases due to an increase in the viscosity of the initial suspension as the pH approaches the isoelectric point of alumina (pH 9.4).

The pH has also a pronounced effect on the average bubble size and the bubble size distribution (Figure 4.3). Interestingly, highly aerated foams with small average bubble size and narrow bubble size distributions were achieved at a pH-range between 3.5 and 5. For pH-values in the range 5 – 7 and below 3, foams feature relatively large bubbles (Figure 4.3a) and a wide bubble size distribution (Figure 4.3b).
Figure 4.3: a) Effect of the pH of the suspension (35 vol% 200 nm alumina, 30 mmol/l valeric acid) on the air content (■) and the average bubble size (○) of the achieved foams. b) Bubble size distribution of foams from suspensions (35 vol% 200 nm alumina, 30 mmol/l valeric acid) at pH 4.75 (■), and pH 2.5 (○).
4.3.3 Ionic strength

The concentration of salt in the initial suspensions directly affects the interactions between the partially hydrophobized colloidal particles and is therefore also expected to affect the microstructure of wet foams. The addition of salt to the suspension increases the medium ionic strength, screens the particle surface charge and reduces the electrostatic repulsive forces between particles. In order to investigate the influence of ionic strength on the foam properties, suspensions with different NaCl concentrations were prepared. In this case, the particle concentration was set to 35 vol% and 176 mmol/l propionic acid were added to hydrophobize the particles at a pH of 4.1.

Figure 4.4 shows the effect of the salt concentration in the initial suspension on the microstructural features of the resulting wet foams. An increase in NaCl concentration from 1 to 500 mmol/l decreases the average bubble size from 65 to 20 μm and narrows the foam bubble size distribution. These effects were accompanied by an increase in the suspension initial viscosity from 0.013 Pa s to 1.92 Pa s (at 100 s⁻¹). The air content in the wet foam remains constant at a level slightly above 80 % up to a salt concentration of 100 mmol/l which corresponds to a viscosity of 0.18 Pa s. The addition of more NaCl leads to a strong decrease in the air content of the foam, as a result of an increased initial viscosity of up to 2 Pa s (at 100 s⁻¹).
Figure 4.4: Effect of salt concentration in the suspension (35 vol% 200 nm alumina, 176 mmol/l propionic acid, pH 4.1) on a) the air content (●) and the average bubble size (○) of the achieved foam, and b) Bubble size distribution of foams containing 1 mmol/l (●) and 200 mmol/l (○) NaCl.
4.3.4 Particle concentration

The microstructure of the wet foams can also be tailored by the particle concentration in the suspension. The influence of particle concentration on the microstructure of wet foams was determined by varying the solids content in an alumina suspension containing 200 nm particles at pH 4.75 and a valeric acid concentration of 1.40 μmol/m³ (Figure 4.5). This condition corresponds to an amphiphile concentration of 30 mmol/l in a suspension containing 35 vol% alumina.

The results depicted in Figure 4.5a show a strong decrease in average bubble size from 161 to 16 μm upon increasing the suspension solids content from 10 to 50 vol% alumina. On the other hand, the foam air content changes only from 85 to 71% within this range of solids concentration. The drop in air content above a solids content of 50 vol% results from the strong increase in the viscosity of the initial suspension. The minimum particle concentration required for the formation of stable foams is 5 vol% in this case. The bubble size distribution in the foam is wide at low solids content and becomes narrower with increasing particle concentration (Figure 4.5b).
Figure 4.5: a) Effect of the concentration of 200nm alumina particles in the suspension (1.40 \textmu mol/m$^3$ valeric acid, pH 4.75) on the air content (●) and the average bubble size (□) of the achieved foam. b) Bubble size distribution of foams obtained from suspensions (1.40 \textmu mol/m$^3$ valeric acid, pH 4.75) containing 20 (●), and 40 vol% (□) of 200 nm alumina particles.
4.3.5 Particle size

Figure 4.6 shows the effect of particle size on the average bubble size, air content and bubble size distribution of foams prepared from 15 vol% alumina suspensions containing particle sizes ranging from 28 to 1800 nm. In this case, valeric acid concentrations resulting in stable foams with high air content (> 80 %) combined with small average bubble size (< 60 µm) were chosen for foam preparation. Valeric acid contents of 1.59, 1.50, 1.44, 1.40 and 15.81 µmol/m² were used in suspensions containing 28, 60, 116, 200 and 1800 nm particles, respectively. Air contents of approximately 90% were obtained for all the foams prepared with different particle sizes (Figure 4.6a) except for the foam which was stabilized with 1800 nm particles. This foam showed an air content slightly below 80%. With increasing the particle size from 28 to 1800 nm, the average bubble size in the foam increases from 56 to 140 µm (Figure 4.6a). Additionally, the use of smaller particles as foam stabilizers leads to wet foams with slightly narrower bubble size distributions, as indicated in Figure 4.6b.

It is important to note that in case of 1800 nm particles, the valeric acid concentration per surface area needed to obtain stable foams was considerably higher compared to that required for smaller particles. Even though foam formation with 1800 nm particles was also observed at lower amphiphile concentrations, coalescence and drainage could not be prevented at these conditions. These results suggest that the preparation of wet foams that are stable against bubble coarsening and drainage requires particle sizes not larger than a few microns in diameter. Theoretical calculations based on the adsorption energy of particles at the gas-liquid interface and the resultant maximum capillary pressure showed that particles larger than ~3 µm are
not able to stabilize foams for long periods of time$^{18-32}$. These results are in the same order of magnitude as our experimental findings.

Figure 4.6: a) Effect of the particle size on the air content (■) and the average bubble size (○) of foams prepared from 15 vol% suspension at pH 4.75. Valeric acid concentrations of 1.59, 1.50, 1.44, 1.40 and 1.58 μmol/m$^2$ were used for the preparation of suspensions containing 28, 60, 116, 200 and 1800 nm particles, respectively. b) Bubble size distribution of foams obtained from suspensions (15 vol%, pH 4.75) containing 28 (○) and 200 nm (■) alumina particles.
4.3.6 Influence of mechanical shearing on the wet foam microstructures

In order to understand the influence of the investigated parameters on the final microstructure of the wet foams, one has to consider in detail the influence of mechanical shearing on the development of the foam microstructure. The bubble size, in particular, is significantly influenced by the stresses applied on the bubble surface during shearing. Even though qualitative predictions of foam bubble sizes are rather scarce in the literature, a number of models have been suggested to describe the influence of mechanical shearing on the size of oil droplets in emulsions\textsuperscript{21,23}. In the 1930s, Taylor introduced a model to predict the final droplet size of a viscous fluid dispersed in a second immiscible fluid\textsuperscript{24,25}. According to this model, the final droplet size is achieved through a series of break-up steps of larger droplets during shearing. To understand this model, let us consider an isolated spherical droplet of radius $R$, viscosity $\eta$, and surface tension $\sigma$ that deforms into an ellipsoid or an elongated cylinder when sheared in a fluid of viscosity $\eta_c$. Droplet deformation only takes place if the applied shear stress $\tau_{\text{applied}}$ overcomes the interfacial stress $\tau_{\text{interface}}$. The ratio between these two counteracting stresses is defined as the Capillary number $Ca$ ($Ca = \tau_{\text{applied}} / \tau_{\text{interface}}$). When $Ca$ exceeds a critical value $Ca_{\text{crit}}$, the elongated droplet ruptures into smaller droplets. $Ca_{\text{crit}}$ depends on the viscosity ratio $\rho$ between the dispersed and the continuous phase ($\rho = \eta / \eta_c$) as well as on the type of flow\textsuperscript{26,27}. By assuming the interfacial stress $\tau_{\text{interface}}$ to be equal to the Laplace pressure $\sigma R$ of the droplet, one can estimate the droplet size $R$ at the critical condition as follows:

$$R \propto \frac{Ca_{\text{crit}} \cdot \sigma}{\tau_{\text{applied}}} = \frac{Ca_{\text{crit}} \cdot \sigma}{\eta_c \gamma}$$

Eq. 4.1
where $\gamma$ is the shear rate applied during mixing.

In order to use Eq. 4.1 to describe the shearing rupture of oil droplets in concentrated emulsions, several authors have suggested that the viscosity of the continuous fluid $\eta_c$ has to be replaced by the effective viscosity of the concentrated emulsion itself, $\eta_{ef}$. Even though this simple equation does not take into account the complex mechanisms involved at the microscopic level, it indicates the key physical parameters that control the final droplet size. Thus, this model was used here to understand the effect of the initial suspension composition on the final bubble size of the investigated foams. For that purpose, we assumed the effective viscosity $\eta_{ef}$ to be equal to the final viscosity of the foam after mixing.

The surface tension of the initial suspension ($\sigma$) and the apparent viscosity of the wet foams ($\eta_{ap}$) were thus measured for compositions containing different valeric acid and particle concentrations. The rheological measurements showed that the wet foams are viscoelastic materials with a strong yielding behavior. Foam fracturing was observed for stresses higher than the yield point, leading to inhomogeneous flow patterns. Bubble rupture was assumed to occur predominantly before the fracturing phenomenon. Therefore, the effective viscosity that leads to bubble rupture ($\eta_{ef}$) was assumed to be equal to the foam apparent viscosity before the yielding point. Since no yielding was observed at a shear rate of 0.01 s$^{-1}$ for all the evaluated compositions, the apparent viscosity at this shearing condition was arbitrarily taken as $\eta_{ap}$.

Figure 4.7a and b show the influence of the suspension initial amphiphile concentration on the surface tension, effective viscosity and critical Capillary number of wet foams prepared with 35 vol% of 200 nm alumina particles.
Figure 4.7: Effect of valeric acid concentration in the initial suspension on a) suspension surface tension (O), b) foam apparent viscosity (■) and critical Capillary number (□) and c) average bubble size (*) and Ca_{crt} o / η ratio (O). All measurements were obtained from suspension containing 35 vol% alumina particles (200 nm) at pH 4.75.
The increase in amphiphile concentration from 10 to 40 mmol/l led to a
decrease of the suspension surface tension from 72 mN/m to approximately 54 mN/m
(Figure 4.7a). This decrease in surface tension is mainly due to an enhanced adsorption
of the partially hydrophobic particles at the air-water interface. Higher amphiphile
concentrations in the initial suspension result in a higher amount of adsorbed
molecules on the particle surface, increasing the hydrophobicity of particles and
favoring their adsorption at the air-water interface. The surface tension is also
decreased by the adsorption of free amphphilic molecules at the air-water interface. 
This effect also increases for higher amphiphile concentrations.

Figure 4.7b shows that the foam viscosity increases with increasing amphiphile
concentration in the initial suspension. This increase is due to the more pronounced
screening of the particle surface charge achieved for higher concentrations of
amphphilic molecules adsorbed on the particle surface or free in the liquid medium.
As a result of this screening effect, the thickness of the electrical double layer around
the particles is reduced, decreasing the repulsive forces between them. The
interparticle attraction due to van der Waals forces is thus favored, leading to an
increase in foam viscosity.

The critical Capillary number $Ca_{cm}$ depicted in Figure 4.7b was calculated based
on the viscosity of the foam ($\eta_f = \eta_{foam}$) and the viscosity of air ($\eta_a$), assuming simple
shearing conditions and an air viscosity of $1.85 \times 10^{-5}$ Pa s as shown in the Appendix. The
$Ca_{cm}$ value increases for a lower viscosity ratio $p = \eta_f/\eta_a$. Since the viscosity of air
remains constant, $Ca_{cm}$ increases as a function of the amphiphile concentration due to
the increase in foam viscosity and a resulting decrease in the viscosity ratio $p = \eta_f/\eta_a$. 
According to Eq. 4.1, the final bubble size \( R \) should be proportional to the ratio \( \frac{Ca_{crit} \cdot \sigma}{\eta_{eff}} \). This ratio was therefore calculated from the rheology and surface tension data shown above and compared in Figure 4.7c with the experimentally measured average bubble size \( R \) obtained at different amphiphile concentrations. The results show a remarkably good agreement between the measured bubble size and the ratio \( \frac{Ca_{crit} \cdot \sigma}{\eta_{eff}} \) for wet foams containing different initial amphiphile concentrations. Based on this analysis, we conclude that the average bubble size decreases with increasing amphiphile concentration as a result of the decrease in surface tension (Figure 4.7a) and the increase in foam viscosity (Figure 4.7b). These two effects compensate for the less pronounced increase in the critical Capillary number obtained for increasing amphiphile concentrations (Figure 4.7b).

The effect of the particle concentration on the average bubble size can also be interpreted on the basis of Eq. 4.1. Figure 4.8 shows the influence of the particle concentration on the surface tension, foam viscosity and critical capillary number.
Figure 4.8: Effect of solids content in the initial suspension on a) suspension surface tension (○), b) foam apparent viscosity (■) and critical Capillary number (□) and c) average bubble size (●) and Ca<sub>crit</sub>σ/η ratio (○). All measurements were taken from suspensions at pH 4.75 containing 0.134wt% valeric acid with respect to alumina.
The surface tension of the initial suspension decreases with increasing particle concentrations (Figure 4.8a). This can be explained by an increase in surface hydrophobicity of particles with increasing particle concentration. Earlier investigations have shown that the adsorption of propionic acid on alumina particles increases from 0.50 to 1.11 μmol/m² by changing the suspension particle concentration from 10 to 35 vol%12. A similar behavior can be expected for valeric acid. The higher amount of amphiphiles adsorbed on the surface enhances the particle hydrophobicity and thus their adsorption to the air-water interface, leading to a lower surface tension. The amphiphilic molecules that do not adsorb on the particle surface and remain free in the liquid medium might also decrease the suspension surface tension. However, this effect is believed to be of minor importance due to the low concentrations of free amphiphiles in the suspension for the valeric acid concentrations evaluated here13.

Figure 4.8b shows that higher particle concentrations in the initial suspension also increase the viscosity of the foams, as would be expected for any colloidal suspension. This increase in foam viscosity leads to higher critical capillary numbers, as indicated in Figure 4.8b.

The experimentally measured bubble size R and the calculated ratio $Ca_{crit} \cdot \sigma/\eta_{eff}$ for foams with different solids content are compared in Figure 4.8c. The results show that the decrease in average bubble size for higher particle concentrations is accompanied by a decrease of the ratio $Ca_{crit} \cdot \sigma/\eta_{eff}$, confirming the good agreement between the experimentally measured data and the predictions from the model. As in the case of the effect of amphiphile concentration, the decrease in average bubble size with increasing particle concentration is caused by a decrease in the suspension surface tension and an increase in foam viscosity.
The effect of pH, ionic strength and particle size on the average bubble size can also be interpreted on the basis of this model. Even though not shown here, an excellent agreement between the average bubble size and the ratio $\frac{Ca_{\text{crit}} \cdot \sigma}{\eta_{\text{eff}}}$ was also obtained for these parameters.

From the results shown here, we conclude that the final average bubble size of wet foams is indeed controlled by shearing and rupture of single bubbles during the frothing process. The suspension surface tension, the foam viscosity before yielding and the critical Capillary number were the main factors determining the final bubble size of the wet foams. Even though it was not subject of this work, the shear rate should also influence the final bubble size as predicted in Eq. 4.1. Besides the parameters investigated here, other changes in the composition of the initial precursor suspension would also affect the final bubble size of wet foams by influencing the factors depicted in Eq. 4.1. Therefore, this simple physical model can be a powerful tool for tailoring the microstructure of particle-stabilized wet foams.

### 4.3.7 Tailoring the wet foam microstructure

Figure 4.9 shows the average bubble size and the air content of wet foams prepared by changing the parameters investigated in this study (light grey area). The results obtained here are compared to those observed for foams stabilized with long-chain surfactants\textsuperscript{16} (dark grey area).

The use of partially hydrophobic particles as stabilizing agents enables the preparation of wet foams with smaller average bubble sizes than those achieved using conventional long-chain surfactants. This can be attributed to the enhanced stability of particle-stabilized foams against bubble coalescence and Ostwald ripening\textsuperscript{6-13}. 
Figure 4.9: Bubble size and air content range for foams prepared by direct foaming with surfactants (+, dark grey) and with particles (from this work, light grey). For the particle-stabilized foams, the microstructure can be tailored by changing the amphiphile concentration in suspension (▲), pH of the suspension (□), ionic strength (○), particle concentration (△) and particle size (▼). Foams prepared using long-chain surfactants were set by a number of different gelling reactions described in the literature.

According to Figure 4.9, the microstructure of particle-stabilized foams can be tailored in a wide range by adjusting some of the experimental parameters investigated here such as amphiphile concentration, pH, ionic strength, particle concentration and particle size. The air content of the resulting foams can vary between 45 and 90%, whereas the average bubble size can be tailored within the range from 10 to 200 μm.
4.4 Conclusions

We showed that the microstructure of wet particle-stabilized foams can be tailored in a wide range by adjusting the composition of the initial colloidal suspension, namely the short amphiphile content, particle concentration, pH, ionic strength and particle size. In order to form stable high-volume foams, the particles need to be sufficiently hydrophobic to adsorb to the surface of air bubbles. Foam formation also requires suspensions with initial viscosities lower than approximately 2 Pa s (at 100 s\(^{-1}\)) to allow for the incorporation of air during mechanical frothing. The effect of the suspension composition on the final bubble size of the wet foam was interpreted with the help of a model that describes the rupture of bubbles as a balance between interfacial stresses and shearing stresses applied during the mixing process. According to this model, the final bubble size can be tailored by changing the suspension surface tension, the foam viscosity and the shearing rate applied during mixing. An increase of the amphiphile content and particle concentration led to foams with smaller average bubbles mainly due to a decrease in the suspension surface tension and an increase in the effective foam viscosity. The ability to control the microstructure of wet foams in a wide range combined with the high stability in the wet state opens the possibility to use these foams in many different areas ranging from pharmaceutical, food and cosmetics to health care, medicine and materials' manufacture.

4.5 Acknowledgment

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4.6 References

STABILIZATION OF FOAMS WITH INORGANIC COLLOIDAL PARTICLES


Abstract

The stabilization of wet foams is important in various applications and can be drastically improved by adsorbing particles instead of surfactants to the gas-liquid interface. Interfacial adsorption is favored through the surface hydrophobization of initially hydrophilic particles. In this work, we use short amphiphilic molecules to partially hydrophobize the surface of various inorganic particles in order to produce ultra-stable particle-stabilized foams of different chemical compositions. For that purpose, the functional group of the amphiphilic molecule was tailored according to the surface chemistry of the particles to be used as foam stabilizers. Short-chain carboxylic acids, alkyl gallates and alkyl amines were shown to be appropriate amphiphiles to in-situ hydrophobize the surface of different inorganic particles. The simplicity and versatility of this approach is expected to aid the formulation of stable wet foams with air contents up to 95% and bubble sizes between 10 and 300 μm for a variety of applications.
5.1 Introduction

Wet foams are routinely used as end or intermediate products in many different areas ranging from cosmetics and food to oil recovery and materials manufacture\textsuperscript{1}. However, wet foams are thermodynamically unstable because of their large air-water interfacial area and thus high overall free energy. Surfactants or proteins\textsuperscript{2-4} are often used to reduce the free energy of wet foams by lowering the air-water interfaceal energy. Nevertheless, surfactants can be easily desorbed from the interface due to the fact that their energy of attachment to the interface is comparable to thermal energy (few $kT$s, $k$ being Boltzmann's constant and $T$ the temperature). As a result, destabilization mechanisms such as bubble coalescence and disproportionation (Ostwald ripening) cannot be completely prevented and drainage is observed on short time scales in surfactant-stabilized foams. This leads to bubble coarsening over time\textsuperscript{2-4}.

To improve the stability of wet foams, particles have been used to adsorb at the air-water interface\textsuperscript{5-10}. The adsorption of particles reduces the highly-energetic interfacial area and lowers therefore the free energy of the system. Due to their energy of attachment in the order of $10^3 - 10^5 kT$, particles tend to adsorb irreversibly at the interface\textsuperscript{5}. Attempts to deliberately adsorb particles at an air-water interface resulted in foams remarkably more resistant against coalescence and disproportionation than foams stabilized by surfactants and proteins. However, in these studies, stable foams were only achieved after extensive drainage and creaming of the initially aerated suspension\textsuperscript{5,9,11}.

Recently, we reported a simple method for the preparation of high-volume particle-stabilized foams which show neither bubble growth nor drainage over several
days$^{10,12}$. The method is based on aqueous suspensions in which the in-situ hydrophobization of initially hydrophilic particles occurs through the adsorption of short-chain amphiphiles on the particle surface. The short amphiphiles exhibit high solubility and high critical micelle concentrations in water and can therefore modify high concentrations of particles in the initial suspension of typically 5 to 45 vol% solids content. This allows for the stabilization of a large air-water interfacial area, leading to high-volume particle-stabilized foams. This foaming method has been extensively described using alumina as model colloidal particles for foam stabilization$^{10}$. In fact, the approach used for the surface hydrophobization of alumina particles can be easily extended to colloidal particles of different chemical compositions$^{10}$. This imparts versatility to the method and allows one to add specific functionalities to the wet or dried foams, widening the number of applications where particle-stabilized foams can be used.

The aim of this work is to investigate the use of this novel approach for the modification of colloid particles with different surface chemistries in order to prepare high-volume stable foams of various chemical compositions. The approach used for the modification of oxide particles of various surface chemistries is described below and is subsequently exemplified using three different types of amphiphilic molecules.

### 5.2 Surface chemistry and modification of oxide particles in water

The formation of high-volume particle-stabilized foams is based on the adsorption of partially hydrophobized particles to the air-water interface. In our previous work, we have shown that alumina particles can be in-situ hydrophobized upon surface adsorption of short-chain carboxylic acids at acidic pH conditions$^{10,12}$. 
These molecules adsorb electrostatically with their hydrophilic head group onto the particle surface\(^4\), leaving the hydrophobic tail in contact with the aqueous medium. The degree of particle hydrophobization depends on the amount of adsorbed carboxylic acid and the length of the hydrophobic tail as has been shown earlier\(^5\).

In order to extend this approach to different types of inorganic particles, one has to deliberately select amphiphilic molecules exhibiting a short hydrophobic tail (2 – 7 carbons) combined with a head group that is able to adsorb on each specific particle surface. Therefore, the choice of the amphiphile head group highly depends on the surface chemistry of the particle involved.

The surface chemistry of oxide particles in water is determined by the protonation and deprotonation reactions of surface hydroxyl groups (-OH) with H\(_3\)O\(^+\) and OH\(^-\) ions from the aqueous medium (Figure 5.1). The reactivity of the hydroxyl groups is strongly influenced by the charge-to-size ratio of the underlying metal ion of the solid oxide\(^4\). Oxides of metals with high charge-to-size ratio (e.g. Si\(^{4+}\)) tend to have predominantly deprotonated hydroxyl groups on the surface (-O\(^-\)), whereas oxides consisting of metals with low charge-to-size ratio (e.g. Mg\(^{2+}\)) display mainly protonated hydroxyl groups on the surface (-OH\(^+\)). Such trends are valid in aqueous media containing equal concentrations of H\(_3\)O\(^+\) and OH\(^-\) ions (pH = 7)\(^4\). By changing the pH and thus the concentration of H\(_3\)O\(^+\) and OH\(^-\) ions in the aqueous phase, one can affect the relative density of surface protonated (-OH\(^+\)) and deprotonated (-O\(^-\)) groups.
Figure 5.1: a) Predominant state of the surface hydroxyl groups at pH 7 for particles with different isoelectric points. b) Possible surface modifiers for predominantly positive, neutral or negative surfaces: carboxylic acids or alkyl gallates, alkyl gallates, and alkyl amines, respectively. c) Modified surfaces highlighting the electrostatic-driven adsorption of carboxylic acids and alkyl amines, as well as the ligand exchange reaction of alkyl gallates on the oxide surface. It is important to note that the adsorption of alkyl gallates onto positively charged surfaces is favoured over the adsorption onto neutral surfaces ($k_i < k_j$).

The adsorption of molecules from the aqueous medium onto the surface of oxide particles can be driven by (1) electrostatic interactions between the particle surface charge and ionized molecules, or (2) specific chemical reactions between the
molecule and the surface hydroxyl groups. In case of oxides exhibiting predominantly positive or negative charges on the surface (high and low IEPs, respectively), the electrostatic adsorption of amphiphilic molecules is a convenient approach for surface hydrophobization. Therefore, protonated amines and deprotonated carboxylic acid groups can be used for the surface modification of oxides exhibiting low and high IEPs, respectively (Figure 5.1).

For oxides with intermediate IEPs and zero net charge, surface hydrophobization can be accomplished by choosing amphiphiles with functional groups that react with the surface hydroxyl groups. Pyrogallol groups are known to efficiently adsorb on oxide surfaces via ligand exchange reactions and thus can be used in combination with a short hydrocarbon tail as surface modifiers of particles with intermediate IEP (Figure 5.1). In this case, the adsorption on positively charged surfaces is favoured over the adsorption on neutral surfaces ($k_1 < k_2$) since the protonated hydroxyl group ($\text{-OH}_2^+$) is a better leaving group compared to the neutral hydroxyl group ($\text{-OH}$).

With this simple and versatile approach based on the selection of amphiphiles with suitable head groups and tail lengths, one should be able to impart surface hydrophobicity on particles of various chemical compositions. In the following sections, we illustrate the versatility of this approach using the three selected amphiphiles outlined in Figure 5.1.

5.3 Materials and methods

5.3.1 Materials

The colloidal particles used in this study were acquired from the following suppliers: Al$_2$O$_3$, $d_{50} \sim 30$ nm, Nanotechnologies Inc. (Austin, TX, USA); $\delta$-Al$_2$O$_3$, $d_{50} \sim$
Stabilization of Foams with Inorganic Colloidal Particles

70 nm, Nanophase Technologies Co. (Romeoville, IL, USA); \( \alpha\text{-Al}_2\text{O}_3 \), \( d_{p_0} \approx 200 \) nm (grade Ceralox HPA-0.5), Sasol North America Inc. (Tucson, AZ, USA); \( \alpha\text{-Al}_2\text{O}_3 \), \( d_{p_0} \approx 1800 \) nm (grade CL 2500 SG), Alcoa Co. (Ludwigshafen, Germany); \( \text{ZrO}_2 \), \( d_{p_0} \approx 50 \) nm (grade TZ-3Y-E), Tosoh Corporation (Tokyo, Japan); \( \beta\text{-Ca}_3(\text{PO}_4)_2 \), \( d_{p_0} \approx 50 \) nm, Flame Powders AG (Schlieren, Switzerland); \( \text{SiO}_2 \), \( d_{p_0} \approx 80 \) nm (grade Snowtex ZL), Nissan Chemical (Houston, TX, USA); Portland cement (grade CEM I 32.5R, Lugato Chemie, Hamburg, Germany); Ti, \( d_{p_0} \approx 600 \) nm (Melorium Technologies, Inc., Rochester, NY, USA).

The short-chain amphiphilic molecules investigated were butyric acid, valeric acid, propyl gallate, butyl gallate and hexyl amine (Fluka AG, Buchs, Switzerland). Other chemicals used in the experiments were deionized water, hydrochloric acid (2 N, Titrisol, Merck, Germany) and sodium hydroxide (1 N, Titrisol, Merck, Germany).

5.3.2 Suspension preparation

Suspensions were prepared by step-wise adding the dry powder to deionized water upon continuous stirring with a standard laboratory mixer. The pH of all suspensions was either adjusted or monitored in order to electrostatically stabilize the particles. In case of alumina suspensions containing carboxylic acids, the pH was set to values below 5 by adding small aliquots of a 2 N HCl aqueous solution. For the alumina suspensions with propyl gallate, the powder was added into an aqueous solution already containing 506 mmol/l NaOH and 29 mmol/l propyl gallate resulting in a suspension with pH ~ 9.8. In case of silica suspensions, the powder was added to pure water and no further pH adjustment was needed. The solids loading of the alumina and silica suspensions was set to 50 and 45 vol%, respectively. In a typical formulation
for alumina suspensions using carboxylic acids as surface modifiers, 270 g α-Al₂O₃ (Ceralox) was added to 65.94 g of water containing 1.898 ml 2 N HCl.

Homogenization and powder deagglomerations was carried out on a ballmill for at least 18 h using polyethylene milling pots and alumina balls in case of alumina particles or zirconia balls in case of silica particles (ball diameter: 10 mm). A mass ratio balls:powder of approximately 2:1 was used in both cases. After the ball-milling procedure, the pH of the suspensions was ~5.5, ~9.5 and ~8.5 in case of alumina to be coated with carboxylic acids, alumina with propyl gallate and silica, respectively. A diluted aqueous solution containing the amphiphile and pH-adjusting agents, was then slowly and drop wise added to the ballmilled suspension under gentle magnetic stirring to avoid local particle coagulation. Afterwards, the pH was set to its desired value and the amount of water needed to achieve a certain solids content was added.

5.3.3 Zeta-potential measurements

Zeta-potential measurements (DT1200, Dispersion Technologies Inc., Mount Cisco, New York, USA) were conducted in 2 vol% suspensions to determine the surface charge and the isoelectric point of the particles. Prior to each experiment, the suspensions were ultrasonicated for 5 min to obtain a homogeneous suspension. The pH of the suspension was initially set to values above 10 using a 1 N NaOH solution and was afterwards gradually decreased using a 1 N HNO₃ solution while acquiring the zeta potential data.
5.3.4 Surface tension measurements

The surface tension of the suspensions was assessed using the pendant drop method (PAT1, Sinterface Technologies, Berlin, Germany)\(^5\). Suspensions were prepared using the ball-milling procedure mentioned above. The amphiphile was added drop wise upon magnetic stirring and the solids loading was set to 35 vol\%. The drop volume was fixed at a constant value within the range 12 – 35 mm\(^3\), depending on the surface tension of the suspension.

5.3.5 Foaming and foam characterization

Foaming of 150ml suspension was carried out using a household mixer (Kenwood, Major Classic) at full power (800 W) for 3 min.

The foam density was measured with a custom-built tool which consisted of a cylindrical plastic cup with small holes on the bottom and a massive sliding stamp on top. The foam was carefully filled into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. During this procedure, a fraction of the foam is expelled through the small holes on the bottom of the cup, avoiding an excessive compression of the foam inside the cylinder. The volume between the bottom of the stamp and the bottom of the cylinder was kept constant. Dividing the mass of the foam by its volume resulted in the foam density.

The bubble size distribution of the wet foam was evaluated using an optical microscope in transmission mode (Polyvar MET, Reichert-Jung, Austria) connected to a digital camera. For each sample, 5 pictures were taken and a minimum of 150 bubbles were evaluated. The bubble sizes were measured with the linear intercept method using the software Linear Intercept (TU Darmstadt, Germany).
5.4 Results and discussion

5.4.1 In-situ hydrophobization

The in-situ hydrophobization of particles with different surface chemistries was accomplished using butyric acid, propyl gallate and hexyl amine as amphiphiles (Table 5.1). Colloidal particles containing predominantly –OH, –OH and –O groups on the surface were selected in order to represent the possible surface chemistries typically encountered in oxide surfaces.

Table 5.1: Amphiphiles used to surface modify particles with different surface chemistries and the conditions under which the experiments were carried out.

<table>
<thead>
<tr>
<th>Predominant state of surface hydroxyl groups</th>
<th>Amphiphile</th>
<th>Particles / IEP</th>
<th>Solvent / pH</th>
<th>Solids content (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–OH, –OH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Butyric acid</td>
<td>Al₂O₃ / 9.4</td>
<td>Water / pH 4.75</td>
<td>35</td>
</tr>
<tr>
<td>–OH, –OH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Propyl gallate</td>
<td>Al₂O₃ / 9.4</td>
<td>Water / pH 9.9</td>
<td>35</td>
</tr>
<tr>
<td>–O&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Hexyl amine</td>
<td>SiO₂ / 1.5</td>
<td>Water / pH 10.6</td>
<td>35</td>
</tr>
</tbody>
</table>
Surfaces with predominantly $-\text{OH}_2^+$ and $-\text{OH}$ groups were provided using alumina particles at acidic (pH 4.75) and slightly alkaline conditions (pH 9.9), respectively (Table 5.1). The zeta potential data shown in Figure 5.2 for bare alumina particles confirm that the surface exhibits mainly $-\text{OH}_2^+$ (positive net charge) and $-\text{OH}$ (neutral net charge) groups at these pH conditions. Surfaces displaying mostly $-\text{O}^-$ groups, on the other hand, were obtained using silica particles in alkaline solutions (pH...
10.6), as indicated in Table 5.1. The negative zeta potential obtained for bare silica at alkaline pHs (Figure 2) confirms the predominance of $-\mathrm{O}^-$ groups on the silica surface at this condition.

The amphiphiles butyric acid and hexyl amine are expected to adsorb onto the alumina and silica particles, respectively, through electrostatic interactions between the charged surfaces and the oppositely ionized amphiphilic molecules (Figure 5.1). Ionization of the amphiphiles occurs via deprotonation and protonation reactions of the carboxylate and amine groups, respectively, in aqueous solution. The deprotonation of the carboxylate group takes place at pH values in the vicinity or higher than the pK$_a$ value of this functional group which is equal to 4.63 \cite{16}. On the other hand, the protonation of the amine group occurs at pH values close to or lower than the pK$_a$ value of this functional group which is equal to 10.66 \cite{17}. Surface modification of particles using these amphiphiles was carried out at pHs close to the molecules' pK$_a$ values (Table 5.1). Under this condition, approximately half of the amphiphilic molecules present in the aqueous medium are ionized and capable of adsorbing on the oppositely charged particle surface. The adsorption of propyl gallate on oxide surfaces, on the other hand, occurs via a ligand exchange reaction \cite{13} where the surface hydroxyl groups ($\cdot\mathrm{OH}$ or $\cdot\mathrm{OH}^+$) are replaced by one or more of the molecule's hydroxyl groups ($\cdot\mathrm{OH}$ or $-\mathrm{O}$). Therefore, the adsorption of gallate molecules does not necessarily require oppositely charged surfaces and amphiphiles, and can even occur at pH values where the groups on the surface and on the molecules exhibit the same charge sign.

Figure 5.2 shows that the electrostatic adsorption of butyric acid on alumina and hexyl amine on silica does not change the IEP of the particles, suggesting a non-specific adsorption of these amphiphiles on the particle surface. Conversely, the adsorption of
propyl gallate shifts the IEP of alumina to more acidic values, indicating that additional negative charges are incorporated on the surface upon adsorption. These additional negative charges might result from (1) the coordination of two of the molecule’s –OH groups to a surface metal ion that was originally bond to only one –OH group (Figure 5.1), or (2) the exchange of a positively charged -OH$_2^+$ group on the surface by at least one of the molecule’s –OH groups$^{13}$.

5.4.2 Suspension surface tension

The degree of particle hydrophobization achieved through the surface adsorption of amphiphiles was investigated with the help of surface tension measurements. The surface tension of suspensions containing 35 vol% particles and different initial concentrations of amphiphiles is shown in Figure 5.3. A decrease in surface tension upon increasing the initial amphiphile concentration in solution is observed for all the evaluated suspensions. For alumina hydrophobized with carboxylic acids, it has been shown$^{10,12}$ that part of the total reduction in surface tension results from the adsorption of free amphiphilic molecules to the air-water interface. However, above a critical amphiphile concentration (marked by * in the graph), a relatively strong decrease in surface tension is observed due to the adsorption of the partially hydrophobized particles to the air-water interface. As a result of this particle adsorption, the total area of the highly-energetic air-water interface is reduced, decreasing the overall surface tension of the suspension. Particle adsorption to the air-water interface for amphiphile additions higher than the critical concentration (*) was directly confirmed by confocal laser scanning microscopy images of air bubbles covered with fluorescent partially-hydrophobized silica particles$^{10}$. 
The surface tension exhibits a similar behaviour in the case of suspensions containing alumina particles coated with propyl gallate (Figure 5.3b) and silica particles modified with hexyl amine (Figure 5.3c).

It is interesting to note that the critical amphiphile concentration is markedly different for the different amphiphilic molecules investigated here. In general, it has been observed that the critical amphiphile concentration is lower for amphiphiles with longer hydrophobic tails. This observation results from the fact that for amphiphiles with a longer hydrocarbon tail, a lower concentration in solution is required to impart sufficient hydrophobicity on the particle surface. This trend explains the lower critical concentration observed for silica particles coated with the relatively long amphiphile hexyl amine, as compared to the alumina particles modified with the shorter butyric acid and propyl gallate molecules (Figure 5.3).

Surprisingly, the critical amphiphile concentration in the case of butyric acid and propyl gallate adsorbed on alumina are quite different (Figure 5.3), in spite of the similar length of their hydrophobic tail. This might be attributed to the fact that alkyl gallates can be oxidized and form trimers at alkaline pHs. These trimers are insoluble in water and precipitate out of the liquid phase. This has also been observed by aging a solution of propyl gallate in water at pH > 10. Due to this precipitation, the concentration of dissolved propyl gallate in suspension decreases. Therefore, a higher concentration of propyl gallate is needed to achieve the same particle hydrophobicity as with butyric acid.
Figure 5.3: Surface tension of a) alumina suspensions at pH 4.75 containing different initial amounts of butyric acid (■), b) alumina suspensions at pH 9.9 containing different initial amounts of propyl gallate (▲) and c) silica suspensions at pH 10.6 containing different initial amounts of hexyl amine (●). All suspensions contained 35 vol% of particles.
5.4.3 Foaming

The attachment of particles to the air-water interface enables the stabilization of air bubbles and consequently the formation of high-volume foams upon mechanical frothing. The air content and the average bubble size of the resulting foams strongly depend on the degree of particle hydrophobization and therefore on the initial concentration of amphiphile in the suspension, as shown in Figure 5.4.

For all investigated suspensions, the amount of incorporated air increases strongly above a certain amphiphile concentration in the suspension. Below this concentration, the particles are not sufficiently hydrophobic to adsorb to the air-water interface and are therefore not able to stabilize air bubbles. With increasing amphiphile concentration, particles become sufficiently hydrophobic to adsorb at the surface of freshly incorporated air bubbles, resulting in foams with up to 85% air content. On the other hand, the average bubble size decreases with increasing amphiphile concentration and particle hydrophobicity. This we attribute to the decrease in surface tension and increase in foam viscosity obtained for higher amphiphile concentrations. These conditions decrease the resistance of air bubbles against rupture and enhance the shear stresses around the bubbles during the mechanical mixing of the suspension. As a result, the mechanical rupture of freshly incorporated bubbles is facilitated, leading to foams with smaller average bubble sizes.

The decrease in the foam air content at high amphiphile concentrations can be attributed to an increase in the suspension viscosity that ultimately hinders air incorporation by mechanical frothing. In case of electrostatically adsorbed amphiphiles (e.g. carboxylic acids, alkyl amines), the observed increase in viscosity arises from the screening of the particle surface charges by the oppositely charged amphiphiles in
solution. Such screening effect leads to particle coagulation by van der Waals and hydrophobic attractive forces. On the other hand, alkyl gallates adsorbed by ligand exchange reactions on the surface do not act as oppositely-charged counter ions in solution. Therefore, the viscosity increase in this case is caused by the screening effect of the other counter-ions used to adjust the suspension pH. The amount of NaOH required to control the suspension pH was observed to increase linearly with the increase in amphiphile concentration. Therefore, a pronounced screening effect and a significant increase in the suspension viscosity was observed at high alkyl gallate concentrations.
Figure 5.4: Air content (full symbols) and average bubble size (open symbols) of a) alumina suspensions at pH 4.75 containing different initial amounts of butyric acid (■), b) alumina suspensions at pH 9.9 containing different initial amounts of propyl gallate (▲) and c) silica suspensions at pH 10.6 containing different initial amounts of hexyl amine (▲). All suspensions contained 35 vol% of particles.
5.4.4 Foam stability

The stability of the particle-stabilized foams prepared with different amphiphilic molecules is compared in Figure 5.5 to that of a standard shaving foam stabilized by surfactants. The particle-stabilized foams show no significant bubble growth for more than 4 days, as opposed to the remarkable coarsening observed in the surfactant-stabilized foams within the first 4 h after foaming (Figure 5.5). In contrast to other particle-stabilized foams, our foams percolate throughout the whole liquid phase and exhibit no drainage over days. This results from the high concentration of modified particles in the initial suspension, which allows for the stabilization of an enormous total air-water interfacial area. The remarkable resistance of the particle-stabilized foams against coarsening has been attributed to the irreversible adsorption of the partially hydrophobic particles at the air-water interface. Apparently, the adsorbed particles form a percolating armour along the air-water interface which mechanically withstands the low pressures caused by gas diffusion outwards the small bubbles during Ostwald ripening. The formation of a particle network between the air bubbles is also expected to hinder foam coarsening. This might explain the fact that foams stabilized with partially hydrophobized silica were more prone to coarsening than those stabilized with alumina particles. Due to their lower Hamaker constant (0.83 x 10^{-20} J as compared to 5.3 x 10^{-20} J for alumina), silica particles are expected to form a weaker colloidal network within the foam lamella decreasing the long-term stability of the foam (Figure 5.5).
5.4.5 Versatility of the method

The high air content and stability of foams prepared with three different short amphiphiles illustrate the versatility of the foaming approach outlined here. Table 5.2 depicts additional examples of other colloidal particles that have been surface modified using similar short amphiphiles to produce ultra-stable particle-stabilized foams. The IEPs of these powders range from 9 to 2 and the average particle sizes from 2 μm to 30 nm. All foams prepared at the conditions shown in Table 5.2 were stable over more than 1 day and featured air contents between 45 and 90 % and average bubble sizes down to 20 μm.
Table 5.2: Particle-stabilized foams produced from a variety of oxide and non-oxide particles using the approach shown in Figure 5.1.

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Size, $d_{10}$ (nm)</th>
<th>IEP</th>
<th>Amphiphile Type</th>
<th>Conc. (mmol/l)</th>
<th>Solvent</th>
<th>Solids content (vol%)</th>
<th>Air content (%)</th>
<th>Average bubble size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particles with basic IEP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portland Cement</td>
<td>na</td>
<td>na+</td>
<td>Propyl gallate</td>
<td>112</td>
<td>Water, pH &gt;10</td>
<td>45</td>
<td>&gt;80</td>
<td>na</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>30</td>
<td>9</td>
<td></td>
<td>60</td>
<td>Water, pH &gt;10</td>
<td>15</td>
<td>90</td>
<td>56</td>
</tr>
<tr>
<td>δ-Al$_2$O$_3$</td>
<td>70</td>
<td>9</td>
<td>Valeric acid</td>
<td>50</td>
<td>Water, pH &gt;4.75</td>
<td>20</td>
<td>90</td>
<td>47</td>
</tr>
<tr>
<td>α-Al$_2$O$_3$</td>
<td>200</td>
<td>9.4</td>
<td></td>
<td>30</td>
<td>Water, pH &gt;4.75</td>
<td>35</td>
<td>80</td>
<td>26</td>
</tr>
<tr>
<td>α-Al$_2$O$_3$</td>
<td>1800</td>
<td>9</td>
<td>Propyl gallate</td>
<td>20</td>
<td></td>
<td>25</td>
<td>66</td>
<td>40</td>
</tr>
<tr>
<td>α-Al$_2$O$_3$</td>
<td>200</td>
<td>9.4</td>
<td></td>
<td>100</td>
<td>Water, pH &gt;9.9</td>
<td>35</td>
<td>83</td>
<td>30</td>
</tr>
<tr>
<td><strong>Particles with intermediate IEP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>50</td>
<td>~7</td>
<td>Propyl gallate</td>
<td>80</td>
<td>Water, pH &gt;9.9</td>
<td>22</td>
<td>79</td>
<td>70</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>50</td>
<td>~7</td>
<td>Butyl gallate</td>
<td>40</td>
<td>Water, pH &gt;9.9</td>
<td>17</td>
<td>86</td>
<td>45</td>
</tr>
<tr>
<td>Ti</td>
<td>~600</td>
<td>4.5</td>
<td>Propyl gallate</td>
<td>316</td>
<td>Water, pH &gt;9.9</td>
<td>19</td>
<td>91</td>
<td>na</td>
</tr>
<tr>
<td><strong>Particles with acidic IEP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>80</td>
<td>~1</td>
<td>Hexyl amine</td>
<td>65</td>
<td>Water, pH &gt;10</td>
<td>35</td>
<td>82</td>
<td>30</td>
</tr>
</tbody>
</table>

na: not available
In the case of cement, the IEP is poorly defined due to the continuous reaction between the particle surface and the aqueous phase. Under alkaline pHs, Portland cement particles are positively charged due to the specific adsorption of Ca\(^+\) ions on the surface.

5.5 Conclusions

We showed that inorganic colloidal particles of various surface chemistries can be partially hydrophobized in water with tailored amphiphiles to produce wet foams exhibiting high air contents and remarkable stability. Foams were stabilized through the adsorption of such partially hydrophobized particles at the air-water interface. Particle hydrophobization is achieved through the adsorption of amphiphiles exhibiting a functional group that efficiently anchors on the particle surface and a short hydrophobic tail which remains in contact with the aqueous phase. Short-chain carboxylic acids, alkyl gallates and alkyl amines were used as amphiphiles that can \textit{in-situ} hydrophobize the surface of different oxide and non-oxide particles. Other amphiphilic molecules can be envisaged based on the concepts outlined here.

High concentrations of such modified particles (35 vol\%) in the initial suspension enabled the stabilization of an enormous air-water interfacial area and therefore the formation of high-volume foams. Air contents between 45 and 90\% and average bubble sizes between 20 and 80\,\mu m were achieved via mechanical frothing of the initial suspension. All foams were stable against bubble growth and drainage over days due to the irreversible adsorption of the partially hydrophobized particles at the air-water interface. The adsorbed particles form an interfacial armour around the bubble surface that mechanically impedes bubble shrinkage and coalescence. The simplicity and versatility of this approach combined with the possibility to tailor the foam properties in a wide range is expected to open new opportunities in various areas,
including cosmetics, flotation in mining industry, pharmaceutics, food and materials manufacturing.

5.6 Acknowledgment

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5.7 References

PROCESSING OF PARTICLE-STABILIZED WET FOAMS TO POROUS CERAMICS


Abstract

In this work, we illustrate the processing of particle-stabilized wet foams into crack-free macroporous ceramics. The processing steps are discussed with particular emphasis on the consolidation and drying process of wet foams. Macroporous alumina ceramics prepared using different consolidation and drying methods are compared in terms of their final microstructure, porosity and compressive strength. Consolidation of the wet foam by particle coagulation prior to drying resulted in porous alumina with closed-cell structure, porosity of 88.7%, average cell size of 35 μm and a remarkable compressive strength of 16.3 MPa. On the other hand, wet foams consolidated via gelation of the liquid within the foam lamella led to porous structures with interconnected-cells in the size range of 100 to 150 μm. The tailored microstructural features and high mechanical strength of the macroporous ceramics may be of interest for the manufacturer of bio-scaffolds, thermal insulators, impact absorbers and light-weight ceramics among others.
6.1 Introduction

Compared to their dense counterparts, porous ceramics feature enhanced thermal insulation properties, good resistance against crack propagation, low weight, as well as high permeability and high surface area in case of open-cell structures. Porous ceramics are therefore used as refractory insulators, catalyst carriers, filters for molten metals and materials for hard tissue repair. Among the several methods used to produce macroporous ceramics, the direct foaming technique is of particular interest due to its simplicity, versatility and low cost. In this method, air bubbles are incorporated into a ceramic suspension to produce a wet foam, which is subsequently consolidated by a setting reaction, dried and finally sintered into a porous structure. Air incorporation is often accomplished by mechanical frothing of the initial suspension in the presence of long-chain surfactants.

We recently developed a direct foaming technique which allows for the fabrication of ultrastable particle-stabilized wet foams. This method is based on the adsorption of in-situ hydrophobized colloidal particles to the air-water interface of freshly generated air bubbles. Particles of a wide variety of compositions ranging from basic materials such as cement to acidic materials like silica have been used as foam stabilizers. All foams show neither bubble growth nor drainage over days and feature average bubble sizes in the range of 10 to 300 μm, combined with air contents between 40 and 95% in the wet state. The high stability in the wet state is attributed to the irreversible adsorption of partially hydrophobic particles to the air-water interface, as opposed to surfactants which adsorb and desorb on relatively short time scales.

The high stability of particle-stabilized foams does not require a setting reaction to prevent bubble coarsening, in contrast to the rapid consolidation needed in the case
of surfactant-stabilized foams. Yet, in order to fabricate solid porous ceramics from particle-stabilized wet foams, shaping, drying and sintering have to be accomplished. Due to the low strength of the wet foams and the high stresses involved during the process of drying, this step proofs to be very critical in the fabrication of crack-free parts. The driving force for crack formation during drying is mainly the gradient of the capillary pressure that develops inside the pores of the foam lamella during the evaporation of the liquid phase. If liquid evaporation were to expose the solid surface of the particles within the lamella, a solid/liquid interface would be replaced by a higher energetic solid/vapour interface. To prevent such an increase in the system’s energy, the liquid tends to spread from the inside of the body to cover the exposed interface. This process sets the liquid under a pressure which is counterbalanced by compressive stresses in the particle network within the lamella. As a result, the particle network densifies and undergoes shrinkage. These stresses are proportional to the thickness of the part and the evaporation rate, and can easily amount up to several hundred kPa.

Crack formation occurs due to these capillary stresses which act on the particle network and vary locally depending on the pore diameter. In order to avoid the formation of differential stresses leading to cracks, the capillary stresses and their gradients can be reduced by performing a slow drying process such as drying under controlled ambient conditions. Using the freeze drying method completely prevents capillary stresses via the solidification of the liquid phase followed by its direct sublimation into vapor. Besides these approaches, there exist other procedures which reduce the internal stresses and allow for fabrication of monoliths of reasonable sizes. Among them is the use of chemical additives such as drying control chemical additives (DCCA). DCCA are used in sol-gel processing to diminish the internal stresses and
reduce the shrinkage by reducing the interfacial energy and therefore the capillary stresses itself. Further, they reduce the pressure gradient within the gel and provide the path for liquid diffusion. Starch might be a good candidate as DCCA due to its water retention capabilities and binder function in granular matter.

Alternatively, the wet foam can be consolidated into a stronger structure by strengthening the foam lamella in order to resist the capillary drying stresses and reduce differential shrinkage. Several consolidation methods have been proposed in recent years for the processing of porous or near-net-shape dense ceramics. Strengthening can either be achieved by addition of a binder to the liquid phase or by gelation of the foam lamella. The gelling methods can be generally divided into physical or chemical methods, depending on the type of gel formed during consolidation. Physical gels are formed when particles are attracted to each other to form a rigid particle network. This can be accomplished by reducing the electrostatic or steric repulsive forces between particles, so that attractive van der Waals forces prevail. In case of alumina for example, attractive particle networks can be created through the enzyme-catalyzed hydrolysis of urea in water. The decomposition of urea induces an in-situ pH-shift in the suspension towards the isoelectric point of alumina at pH 9, thereby reducing the repulsive electrostatic forces between the particles. Even though physical gelation is usually not sufficiently fast to enable the consolidation of surfactant-stabilized foams, it can in principle be easily applied for the gelation of foams exhibiting enhanced stability.

Besides physical gelation, several other approaches rely on the gelation of the suspension’s liquid medium around the particles. These methods are often triggered by chemical reactions in the liquid phase and have thus been referred to as chemical gelation. The in-situ free radical polymerization of acrylamide monomers for example,
is a gelation method that was originally developed for dense ceramics and has been later on applied to ceramic foams\(^\text{16 - 19}\). The main drawbacks of this method are the toxicity of the monomers and the need of oxygen-free environments to accomplish the polymerization reaction. These disadvantages were partially or fully overcome by using less harmful monomers\(^\text{16}\) or non-toxic cross-linking reactants without the need of oxygen-free atmospheres\(^\text{17 - 18}\). Other environmentally-friendly setting agents such as the pH- or temperature-induced gelation of gelatine\(^\text{19}\), ovalbumin\(^\text{20 - 21}\) and bovine serum albumin\(^\text{22}\) have also been recently developed. Polysacharides such as starch has also been used as gelling agent as well as pore former due to its swelling properties in water at elevated temperatures\(^\text{23 - 25}\). Alternatively, alginic acid salt in combination with hydroxyaluminium diacetate (HADA) was used as a time-delayed physicochemical gelation process to prepare wet green bodies with enhanced mechanical properties\(^\text{26}\).

In this paper, we describe the processing of particle-stabilized wet foams into porous structures with particular emphasis on the evaluation of suitable approaches to avoid crack formation during drying. Therefore, several methods are investigated including controlled drying techniques, chemically aided methods and gelation methods. The controlled drying techniques investigated were drying under controlled environmental conditions, unidirectional drying and freeze-drying. Among the gelation methods, physical gelation was accomplished by an in-situ pH shift towards the IEP of the particles, whereas physicochemical gelation was carried out by the gradual release of aluminium ions from HADA combined with the cross-linking of sodium alginate. Additionally, starch was used as drying control chemical additive and binder to facilitate drying and strengthen the foam lamella. These different methods are compared with respect to the porosity, cell size, cell morphology and compressive strength of the final macroporous structures.
6.2 Materials and methods

6.2.1 Materials

The colloidal $\alpha$-Al$_2$O$_3$ particles used in this study ($d_{so} \sim 200$ nm, specific surface area $\sim 10$ m$^2$/g, density $3.98$ g/cm$^3$, grade Ceralox HPA-0.5) were acquired from Sasol North America Inc. (Tucson, AZ, USA).

The short-chain amphiphilic molecules used to hydrophobize the particle surface were butyric acid and propyl gallate (Fluka AG, Buchs, Switzerland). Other chemicals used in the experiments were deionized water, hydrochloric acid (2 N, Titrisol, Merck, Germany), sodium hydroxide (1 N, Titrisol, Merck, Germany), hydroxyaluminium diacetat ($d_{so} \sim 0.7$ µm, Fluka AG, Buchs, Switzerland), sodium alginate (Fluka AG, Buchs, Switzerland), native wheat starch (MioColl, Migros, Switzerland), urea (Sigma-Aldrich, Buchs, Switzerland) and urease (Roche Diagnostics GmbH, Mannheim, Germany). The enzymatic activity of the urease used was 58000 Units/(g of pure urease). One unit is defined as the amount of enzyme necessary to release 1 mol of reaction product per minute from the substrate at 24 °C and at the pH where the enzymatic activity in water is at its maximum.

6.2.2 Processing overview

Figure 6.1 displays the processing flow chart used for the preparation of particle-stabilized foams and porous ceramics using different drying and strengthening methods. The methods are subdivided into (1) controlled drying methods using a climate chamber, unidirectional drying and freeze drying, (2) chemically aided drying methods and (3) gelling methods based on physical and physiochemical gelation. All steps indicated in the flow chart are explained in detail within the following sections.
(1) Controlled drying
a) Climate chamber
b) Unidirectional drying
c) Freeze drying

Suspension: 50vol% alumina in water 0.7wt% HCl (to alumina)
homogenize
add butyric acid
adjust pH and solids content

Suspension: 35vol% alumina in water 50mM butyric acid pH 4.75
add starch

Figure 6.1: Processing flow chart for the preparation of particle-stabilized foams using (1) controlled drying, (2) chemically aided drying and (3) gelation methods: 1a) climate chamber, 1b) unidirectional drying, 1c) freeze drying, 2) drying control chemical additive, 3a) physical gelation and 3b) physiochemical gelation.
6.2.3 Suspension preparation

**Controlled drying methods:**

Suspensions used for the controlled drying experiments were prepared as follows: alumina powder was stepwise added to water containing hydrochloric acid (0.7 wt% to alumina) to obtain a suspension with 50 vol% solids content and a pH-value around pH 5. Homogenization of the suspensions was conducted on a ballmill for at least 18 h using polyethylene milling pots and alumina balls (10 mm diameter, ratio balls:powder ~ 2:1). Afterwards, an aqueous solution containing butyric acid and if necessary pH-adjusting agents (NaOH or HCl) was then slowly and drop wise added to the ballmilled suspension under slight stirring to avoid local particle agglomeration and coagulation. The amount of butyric acid added corresponded to a concentration of 50mmol/l in the final suspension. The pH was set to 4.75 by using a 1 N NaOH solution. Finally, the amount of water needed to adjust the solids content to 35 vol% was added.

**Chemically aided drying method:**

Suspensions were prepared similarly to the ones for the controlled drying methods. Additionally, different amounts of starch (up to 4.75 wt% to the liquid) were added in powder form to the final suspension. In order to homogeneously distribute the starch particles, the suspension was magnetically stirred for 1 min before foaming. Starch is supposed to act as drying control chemical additive and additionally as binder in order to strengthen the lamella of the wet foam.
Gelation methods:

Physical gelation

Suspensions used for the physical gelation method were prepared similarly to those described above for the controlled drying tests. In this case, however, urea (0.05 wt% to alumina) was also added to the water phase prior to the addition of alumina. The further processing (homogenization and adjustment of the amphiphile concentration and pH) followed the one described above. It is important to note that adjusting the solids content to 35 vol% will be performed later one.

Physicochemical gelation

Suspensions used for the experiments on the physicochemical gelation method were prepared in the following way: alumina powder was stepwise added to water containing 506 mmol/l NaOH and 29 mmol/l propyl gallate to obtain a suspension with a solids content of 50 vol% and a pH value around 9.8. Homogenization of the suspensions was carried out on a ballmill for at least 18 h using the same conditions described above. Afterwards, the propyl gallate needed to adjust the amphiphile concentration in the final suspension to 47 mmol/l was dissolved in a NaOH aqueous solution displaying pH higher than 10. This solution was then slowly and drop wise added to the ballmilled suspension under slight stirring to avoid local particle agglomeration. Meanwhile, different amounts of sodium alginate were dissolved in water at 80 °C. After cooling to room temperature, the alginate solution was also added to the suspension under stirring. The pH of the suspension was then set to 9.9 and finally the amount of water needed to achieve a solids content of 20 vol% was added.
6.2.4 Gelation of the wet foams

The gelation of the wet foams was triggered by adding specific additives to the initial suspension shortly before the foaming step, as described below:

**Physical gelation**

In this case, the gelation process was triggered by the addition of urease into the suspension. Urease (1 unit per gram alumina) was dissolved in the amount of remaining water (~5 ml) necessary to set the suspension solids content to 35 vol%. After addition of the urease solution, the suspension was magnetically stirred for 30 s prior to foaming.

**Physiochemical gelation**

The gelation process in this case was initiated through the addition of hydroxyaluminum diacetate (HADA) to the initial suspension. In order to slow down the gelation process, the suspension was first cooled down in ice. HADA was then added as powder to the suspension. In order to distribute the particles homogeneously, the suspension was mechanically stirred after HADA addition.

6.2.5 Foaming and foam characterization

Foaming of 150 ml suspension was carried out using a household mixer (Kenwood, Major Classic) at full power (800 W) for 3 min.

The foam density was measured with a custom-built tool which consisted of a plastic cylindrical cup with small holes on the bottom and a massive sliding stamp. The foam was carefully filled into the cup and then slightly compressed with the stamp to remove possible air pockets introduced during filling. The volume between the bottom
of the stamp and the bottom of the cylinder was kept constant. Dividing the mass of the foam by its volume resulted in the foam density.

6.2.6 Shaping and drying of the wet foams

The wet foams possess a pronounced yield stress which allows for easy shaping by extrusion, injection moulding or similar methods. Cylindrical parts (diameter: 100 mm, height 50 mm) were hand-shaped by filling the wet foam into a cardboard hollow ring placed on a glass substrate. The ring mould was removed just after shaping, leaving the cylindrical piece of foam on the glass substrate. Foam drying was subsequently carried out as follows:

**Controlled drying methods:**

*Climate chamber*

Samples were placed in a climate chamber (KBF 115, Binder, Germany) and dried at temperatures ranging from 15 to 50 °C at a relative humidity of 90%, so that the drying process was slowed in order to minimize the arising capillary stresses.

*Unidirectional drying*

Foam samples were placed on a heating plate positioned inside a climate chamber at 28 °C and 90% relative humidity. Two copper cylinders (diameter: 100 mm, height: 50 mm) were placed between the wet foam and the heating plate to work as a thermal bath and to allow for the drying of two samples simultaneously. The copper cylinders were heated to 40, 60 or 80 °C and a thermocouple was used to control the temperature of the cylinders during the drying process. The temperature gradient between the copper cylinders and the surrounding atmosphere allowed for the
Chapters

unidirectional drying of the samples. The high relative humidity inside the climatic chamber prevented the drying of the sample surface. The drying process inside the climate chamber was conducted for approximately 12 h. Samples were subsequently exposed to room temperature for another 12 h.

*Freeze drying*

Shaped wet foams were first unidirectionally frozen by placing the sample onto an aluminum cylinder (diameter: 100 mm, height: 145 mm) which was half way immersed in liquid nitrogen to assure a homogeneous temperature on the surface of the cylinder. After 30 min, the frozen foam was removed from the cylinder and placed in the freeze dryer (Alpha 2-4, 100402, Martin Christ, Osterode am Harz, Germany) for approximately 36 h at a pressure of 0.3 mbar.

*Chemically aided drying method:*

The samples were dried by direct exposure in air at 22 – 25 °C for 24 to 48 h.

*Gelation methods:*

The cylindrically shaped samples were covered with cling film to avoid drying before the gelation took place. After about 12 h, the cling film was carefully removed and the samples were dried in air at 22 – 25 °C for 24 to 48 h.

**6.2.7 Sintering of the foams**

Sintering of the cylindrical dried foams was performed in an electrical furnace (HT 40/16, Nabertherm, Germany) at 1575 °C for 2 h. The heating and cooling rates were set to 1 and 3 °C/min, respectively.
6.2.8 Microstructural analysis

The average cell size of the sintered foam was evaluated from micrographs taken with a scanning electron microscope (LEO 1530, Germany). The cell sizes were measured with the linear intercept method using the software Linear Intercept (TU Darmstadt, Germany). From the cumulative cell size distribution obtained, we determined $d_{10}$, $d_{50}$, and $d_{90}$, which correspond to the cell diameter obtained for a cumulative percentage of cells lower than 10, 50 and 90 %, respectively. In this study, the $d_{50}$ value is referred as the average cell size and the ratio $(d_{90} - d_{10})/2$ is taken as an indication of the bubble size distribution.

6.2.9 Compressive strength measurements

Compressive strength measurements were performed on a universal testing machine (Instron 8562, model A1477-1003, Norwood, USA). The sintered cylindrical parts were ground on both sides resulting in parallel opposite surfaces that ensured homogeneous sample loading during compression. Cylindrical samples with diameters of 15 mm and lengths of 30 mm were drilled out of this bulk piece of foam with a diamond core drill. The geometrical density and the compressive strength at a loading speed of 0.5 mm/min were measured for a minimum of 5 samples for each investigated composition.
6.3 Results and discussion

6.3.1 Drying, sintering and microstructure of porous ceramics

The macro- and microstructure of porous ceramics obtained by applying different drying and gelation methods are displayed in Figure 6.2 to Figure 6.4 and Figure 6.6 to Figure 6.8. The final porous structures obtained were evaluated with regards to the cell size and whether cracks are formed during water evaporation or not. The main results are summarized below for the various drying/gelation methods applied.

Controlled drying methods:

Climate chamber

In order to slow down the drying process and thus decrease the capillary stresses in the body during water removal, foam samples were dried at a relative humidity of 90\% and a temperature of either 15 or 50 °C. The high humidity applied ensured a low driving force for water evaporation, leading to drying periods as long as 48 h. The temperature, on the other hand, was changed to vary the diffusion kinetics of water from the interior of the sample to the surface.

Figure 6.2 shows that these conditions led to completely cracked samples after sintering, which prevented the preparation of samples for mechanical testing. Foams dried under such controlled ambient conditions present similar structure to those dried directly in air without temperature and humidity control. The shrinkage during drying and sintering of these specimens was typically around 25\% linear. These results suggest that the capillary stresses developed even at low drying rates are already high enough to introduce defects in the foam microstructure. We have also observed that
some of the samples displayed a higher concentration of defects in the center of the body. This indicates that the flaws may also originate from an uneven shrinkage between the surface and the core of the body. In order to minimize this differential shrinkage effect, unidirectional drying of the samples was subsequently evaluated.

![Image](image.png)

Figure 6.2: Porous ceramic which was dried in a climatic chamber under controlled atmospheric conditions (15 °C, 90 % humidity). Cracks formed inside the body during drying and aggravated during the sintering process. They could not be avoided under all conditions (temperature and humidity).

**Unidirectional drying**

Unidirectional drying of the foams from the bottom to the top should avoid uneven shrinkage and therefore reduce the stresses leading to defect formation.

The results showed that the temperature gradient between the thermal bath (copper cylinders) and the surrounding atmosphere strongly influenced the drying behavior of the wet foams. For temperature gradients lower than about 7.5 °C/cm (T_{copper} < 60 °C), the driving force for unidirectional drying was not high enough to avoid drying of the sample upper surface. This resulted in the formation of large cracks within the sample, similar to those depicted in Figure 6.2. On the other hand, temperature gradients higher than 7.5 °C/cm allowed for complete unidirectional drying of the
samples. Figure 6.3a shows the cross section of a foam which was unidirectionally dried at a temperature gradient of 13 °C/cm ($T_{\text{copper}} = 80 ^\circ\text{C}$) and subsequently sintered at 1575 °C for 2 h. The micrograph shows that the unidirectionally dried foams did not exhibit the same large defects initially observed for samples dried under controlled atmosphere (Figure 6.2). Interestingly, cells approximately one order of magnitude larger than the initial bubble size were formed throughout the whole microstructure of unidirectionally dried foams (Figure 6.3b and c). The high temperature applied during this drying process might have facilitated the coalescence of single bubbles and the formation of these unevenly shaped large pores. The walls of the large cells also showed a higher porosity in comparison to the walls of smaller cells (Figure 6.3c).

Figure 6.3: a) Cross section, b) and c) microstructure of an unidirectionally dried alumina foam subsequently sintered at 1575 °C. Large cells with slightly porous walls are distributed evenly among smaller cells originated from the bubbles.
Freeze drying

Freeze drying offers the advantage of removing the liquid from a body in the absence of capillary forces. In case of water, this is performed at low temperatures ($< 0.01$ °C) and low pressures ($< 6$ mbar) where frozen water can be directly sublimated into aqueous vapour. The gentle removal of water by freeze-drying resulted in sintered samples free of macroscopic cracks. However, Figure 6.4a and b show that the freeze-dried samples exhibited many microscopic cracks. These cracks were most likely formed during the cutting of the bodies for observation in the microscope. Since the freezing process did not lead to any shrinkage of the wet foam, the network of particles in the foam lamella did not undergo any densification during the drying process, as opposed to the increased packing achieved with the other drying approaches. Therefore, the particles are very loosely packed on the cell wall in the green state, leading to porous walls (Figure 6.4b) and weak structures after sintering. The absence of pores with dendritic morphology suggests that no ice crystals were formed during the freezing process.

![Figure 6.4: a) Microstructure of a freeze dried and sintered foam, b) detail of the porous and cracked cell wall.](image-url)
Chemically aided drying method:

Wheat starch was added to the suspension in order to act as drying control chemical additive to control water removal upon drying and as binder in order to increase the strength of the particle network in the foam lamella and thus avoiding cracking during drying. Starch is a water insoluble native polysaccharide that consists of a mixture of two D-glucose polymers: the larger and branched amylopectin and the smaller and linear amylose. Amylose gives starch its swelling properties in aqueous suspensions. Above the gelling temperature of around 55 °C, starch granules swell irreversibly by water uptake. Despite their insolubility in water below the gelling temperature, starch granules can adsorb up to 17 wt% of water at ambient temperatures. This water physically bond to the starch molecules is of advantage during drying, since it increases the water retention capability of the wet foams, leading to slower and more homogeneous drying. The binding effect of starch occurs through the physical adsorption of the polysaccharide long molecules onto the surfaces of different particles especially during the later stage of drying.

The addition of starch to the foam precursor suspension results in a decrease in the air content of the wet foam, as shown in Figure 6.5. This decrease can be explained by an increase in the suspension viscosity, which ultimately hinders the incorporation of air. Additionally, starch molecules might adversely affect the hydrophobicity of the particle surfaces and thus decrease the foam air content. Amylose is known to form complexes with fatty acids in acidic pHs at room temperature. This complex formation can decrease the concentration of free butyric acid in suspension and lead to a lower particle hydrophobicity as a result of the desorption of butyric acid molecules from the particle surface.
The samples underwent a linear drying shrinkage of approximately 5% and an additionally linear sintering shrinkage of about 20%. Starch concentrations higher than 0.64 wt% with respect to liquid enabled the preparation of crack-free foams after drying at ambient conditions. At lower concentrations, the wet foam dried inhomogeneously and cracks similar to those depicted in Figure 6.2 were observed. Figure 6.6a and c show the microstructure of samples prepared with 0.64 and 2.44 wt% of starch with respect to liquid in the suspension. In case of addition of 0.64 wt% starch, the average cell size is 34 μm with a standard deviation of 18 μm, whereas smaller cells of 24 μm (±12 μm) were achieved for foams containing 2.44 wt% starch. This can be attributed to the higher viscosity achieved at the higher starch concentration, since an increase in viscosity is known to decrease the average bubble size of mechanically frothed foams. For both starch concentrations, the cell walls are completely dense as shown in Figure 6.6b and d. It is important to note that the starch
concentrations required to avoid crack formation in particle-stabilized foams is significantly lower than that used for the preparation of porous ceramics using starch particles as sacrificial templates.\(^2\)

Figure 6.6: a) and c) Microstructure of homogeneously dried foams prepared from suspensions containing, respectively, 0.64 and 2.44 wt% starch with respect to the liquid phase. The cells are mostly closed and dense, as shown in the insets b) and d).

**Gelation methods:**

*Physical gelation*

In order to counterbalance the capillary stresses that arise during drying, the wet foam was strengthened by the in-situ coagulation of particles inside the lamella. Coagulation was achieved by shifting the pH of the suspension in the foam lamella towards the isoelectric point of the particles. At this condition, the attractive van der
Waals forces between the particles dominate over the repulsive electrostatic forces, leading to a stronger particle network.

Figure 6.7: a) Cross section, b) and c) microstructure of a foam which was physically gelled before drying. The enzyme-catalyzed decomposition reaction of urea shifted the foam pH towards the isoelectric point of alumina, resulting in a stronger particle network that prevents crack formation.

In case of alumina, the enzyme-catalyzed decomposition reaction of urea can be used to shift the pH from acidic values towards the particle isoelectric point at pH 9.4. The end-pH of this decomposition reaction is determined by the urea concentration in suspension, whereas the speed of the reaction depends on the enzyme concentration. In the case of the investigated foams, the end-pH could not exceed a value of approximately 8 in order to avoid foam collapse. Foam destabilization was observed at pHs higher than 8 probably due to the desorption of butyric acid molecules from the
particle surface and the consequent desorption of particles from the air-water interface.

The addition of 0.05 wt% urea with respect to alumina led to a pH of ~7.3, enabling the preparation of crack-free samples (Figure 6.7a) without collapsing the foam in the wet state. During drying, the shrinkage of the sample was about 7% linear, whereas it was roughly 15% during sintering. The resulting microstructure contains predominantly closed cells with an average size of approximately 35 µm and a standard deviation of 16 µm (Figure 6.7b). The cell walls are completely dense and are in most cases formed by a single layer of grains after sintering, as shown in Figure 6.7c.

**Physiochemical gelation**

The gelation of algae-derived macromolecules in the presence of multivalent ions was also used to increase the strength of wet foams and minimize cracking during drying. The combination of alginic acid salt with hydroxyaluminum diacetate (HADA) led to a gelation of the liquid phase through the cross-linking of alginate macromolecules with Al³⁺ ions, as well as a coagulation of the particle network by increasing the suspension ionic strength (ref alginate). The addition of alginic acid salt (0.25 wt%) and HADA (1.75 wt%) to the initial suspension enabled the preparation of crack-free foams after drying and sintering. Compared to other drying methods, the specimens exhibited a larger shrinkage of about 30% linear during drying, whereas during sintering, the shrinkage is comparable and roughly 20%. Interestingly, the gelation process also led to porous structures with interconnected cells in the range of 50 – 200 µm in diameter (Figure 6.8a). The large cell size is a consequence of the low solids content in the suspension (20 vol%) and agrees well with our previously published results.⁹
An increase of the alginate content to 1 wt% and the HADA concentration to 3 wt% also resulted in crack-free samples. In this case, the viscosity of the initial suspension was higher, leading to average cell sizes predominantly smaller than 100 μm (Figure 6.8b). Foaming of suspensions containing more than 1 and 3 wt% of alginate and HADA, respectively, was not feasible due to the excessively short gelling time.

Figure 6.8: Microstructure of sintered alumina foams consolidated via the physicochemical gelation method using a) 0.25 wt% and b) 1 wt% alginate. The cell size in case of 1 wt% alginate is significantly smaller due to an increase in the suspension viscosity. The open-cell structure probably results from the uneven local shrinkage that occurs during gel formation.

The cell interconnectivity observed in foams consolidated with alginate and HADA (Figure 6.8a and b) suggests that the layer of particles that initially surrounded
the gas bubbles was ruptured during the gelation process. The cross-linking of alginate macromolecules with multivalent ions is usually accompanied by a volumetric shrinkage due to solvent expulsion (syneresis). This shrinkage might be negligible for thick samples, but in case of thin foam lamellas, it is expected to be significantly high. Therefore, the rupture of the particle layer around the gas bubbles might be caused by a local uneven shrinkage of the macromolecules during the gelation process.

6.3.2 Mechanical properties

Figure 6.9 shows the geometrical density and compressive strength of the macroporous alumina monoliths prepared in this study in comparison to samples produced via other direct foaming methods. The dashed lines in the graph represent the theoretical relative strength expected for open and closed cell foams according to the model of Gibson and Ashby.

Foams consolidated via physical gelation and with starch as drying control chemical additive show the highest compressive strengths. Their mechanical strength is also significantly higher compared to porous materials prepared with other direct foaming methods at the same relative density (or porosity). A remarkably high compressive strength of 16.3 MPa at a porosity of 87% was achieved using the physical gelation of the particle network to strengthen the wet foam. The high mechanical strength of foams prepared through in-situ coagulation or with starch can be attributed to the flawless and dense closed cells obtained using these methods (Figure 6.7 and Figure 6.7).
On the other hand, the physicochemically gelled foams showed a noticeably lower mechanical strength, as a result of their interconnected cell structure (Figure 6.8). Yet, the compressive strength of these foams is comparable to that of other open-cell porous ceramics produced by direct foaming methods. It should also be noted that the preparation of interconnected structures using the approach described in this study has not been extensively explored yet. Further investigations are required to enable one
to deliberately tailor the cell interconnectivity and eventually increase the strength of these foams.

The unidirectionally dried samples featured porosities higher than 92% due to the formation of larger cells during drying (Figure 6.3a). This high overall porosity and the pores observed in the cell walls of these foams (Figure 6.3c) resulted in a low mechanical strength of 0.8 MPa. Likewise, the freeze dried foam showed a low compressive strength of 1.16 MPa at a porosity of 85.8% due to the microscopic cracks and pores formed within the cell walls of the porous structure (Figure 6.4a and b).

6.4 Conclusions

Crack formation during the preparation of bulk macroporous ceramics from particle-stabilized foams was avoided by applying different drying techniques. Methods which directly increase the wet foam strength or which assure a homogeneous drying were the most successful in respect to high mechanical strength at high porosities and avoiding crack formation. Using starch as drying control chemical additive and strengthening of the particle network are very efficient methods to avoid crack formation and resulted in porous ceramics with mainly closed cells. Strengthening the particle network was achieved by shifting the pH in-situ towards the isoelectric point of the particles. These methods led to closed-pore structures with high mechanical strengths of up to 22.9 MPa. Depending on the drying conditions, these samples featured high porosities of 80.2 – 86.5%, closed cells in the range of 24 – 35 μm and remarkably high mechanical strengths between 11.8 – 22.9 MPa.

On the other hand, the physicochemical gelation using an algae-derived polymer resulted in structures with a porosity of 79.1 - 83.5%, interconnected cells in the range of 50 – 200 μm and mechanical strength comparable to that obtained for
other open cell materials. During gel formation, there seems to be a significant shrinkage within the lamellas of the wet foam that locally ruptures the cell walls and leads to cell interconnectivity.

Controlled drying conditions were achieved drying the foams unidirectionally at high relative humidity or by applying the freeze-drying technique. In these approaches, crack formation was hindered due to the low magnitude or absence of capillary stresses in the foam during the drying process. Samples were unidirectionally dried using a temperature gradient of at least 7.5 °C/cm between the top and the bottom of the foam as driving force. As a result of the elevated temperature within the foam, a number of larger cells were formed. Most of these cells showed microporosity in the walls which lowered the mechanical strength of the samples. Finally, freeze-dried foams displayed homogeneous microstructures but excessively thin cell walls which reduced the compressive strength of the final structure. Therefore, freeze drying seems not to be a very suitable method due to the low green strength and the low mechanical properties of the sample. Drying in a climate chamber under controlled ambient conditions could not prevent crack-formation and is therefore not a suitable drying method for the preparation of macroporous ceramics.

6.5 Acknowledgment

The authors thank CIBA Specialty Chemicals for funding part of this project. The help of Marianne Dietiker and Andreas Bihl is also highly appreciated.

6.6 References

**General Conclusions**

The aim of this thesis was to develop a novel direct foaming method to produce wet foams that are stable against bubble coarsening and drainage and that can be further processed to macroporous materials. Since surfactants show only limited capability of preventing bubble growth and drainage in wet foams, particles were used as foam stabilizers. Due to the irreversible adsorption of particles to the air-water interface, such foams proved to be much more stable than surfactant-stabilized foams. However, most studies so far were restricted to either single particle-stabilized bubbles or particle-stabilized foams which underwent extensive drainage after foam formation.

In order to prepare stable high-volume foams, we developed a method which is based on an in-situ hydrophobization of initially hydrophilic particles. Hydrophobization is carried out using short-chain amphiphilic molecules as surface modifiers. This allows for the surface modification of high concentrations of particles in suspension which in turn makes the stabilization of a large interfacial area possible. Surface tension measurements have shown that the particles need to be sufficiently hydrophobized in order to adsorb to the air-water interface. The particle hydrophobicity is mainly determined by the amphiphile concentration in suspension and the suspension' pH. The obtained foams exhibit a pronounced yield stress, which allows for shaping of parts using extrusion, injection moulding, pressure filtration or related techniques. The foams can also be sprayed or easily poured into moulds after dilution of the as-prepared foams with water. Dilution does not necessarily affect the stability of the air bubbles and can be used to adjust the foam viscosity according to the shaping method.
desired. Dilution of these foams also allows for the fabrication of large numbers of hollow capsules for applications in the area of food and cosmetics as well as systems for controlled release of drugs, fragrances or dies.

The microstructure of the wet foams can be tailored within a wider range by adjusting the particle hydrophobicity, the interparticle interactions as well as the particle concentration and size. All these parameters influence the foam viscosity and yield stress as well as the surface tension of the suspension which are the main factors to control the final bubble size in foams and emulsions. It has been found that optimization of these parameters not only leads to smaller average bubble sizes, but also to narrower bubble size distributions.

By tailoring the head group of the short-chain amphiphiles, it is possible to hydrophobize particles with various surface chemistry. Particles with isoelectric points in the basic pH range are hydrophobized with short-chain carboxylic acids whereas particles with acidic isoelectric points are modified using short-chain alkyl amines. Last but not least, short-chain alkyl gallates are used for particles with isoelectric points in the intermediate pH range or for particles with low surface charges. We found that using these three amphiphilic molecules to hydrophobize particles with particle sizes between 10nm and 3μm allows for the preparation of stable foams from almost any kind of particles.

Due to the high stability of the wet foams, they can be shaped, dried in air and sintered. Several methods have been suggested and successfully applied to avoid crack-formation during drying such as the in-situ coagulation of the particle network or the gelling of the liquid phase within the foam lamella. The bulk macroporous ceramics feature porosities between 45 and 95% and either closed or interconnected pores in
the size range between 10 and 300 μm, combined with the highest ever measured compressive strength of porous ceramics.

This novel method is simple, non-toxic and very versatile in respect to materials which can be foamed. The use of high concentration of partially hydrophobized particles as foam stabilizers results in wet foams that are stable against bubble growth and drainage. Further processing of these foams leads to either bulk macroporous structures upon drying and heat treatment or to hollow capsules upon dilution of the foams. We believe this method to open new opportunities in a wide number of areas ranging from food, cosmetics and pharmaceutical to engineering, biology and medicine.
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8 OUTLOOK

The following paragraphs contain projects resulting from the work described in this thesis. Since most of these projects have already been started, this section also contains the most important preliminary results.

8.1 Porous scaffolds for hard tissue repair

Ceramics which are used for the repair or reconstruction of diseased or damaged parts of the musculo-skeletal system, need either to be inert (alumina or zirconia), resorbable (tricalcium phosphate), bioactive (hydroxyapatite, bioactive glasses, glass-ceramics) or porous for tissue ingrowth. There is a great need for bioceramics, especially since bone density decreases with age and results in a weakening of the skeletal system. This is mainly due to an unbalance cellular activity between the bone-growing cells (osteoblasts) which become progressively less productive in making new bone and repairing microfractures, and the bone-resorbing cells (osteoclasts) which maintain their normal resorbing activity, leading to an overall decrease in bone density and to structural and architectural changes.

Resorbable biomaterials are designed to degrade gradually over time and be replaced by the host tissue. One challenge is to match the resorption rate of the biomaterial to the repair rate of the body tissue and to maintain the strength and the stability of the interface during the degradation period and replacement by natural host tissue. Porous resorbable biomaterials would allow for a fast ingrowth of cells and
therefore a fast repair rate of the body tissue. Additionally, the already repaired tissue would give stability to the implanted biomaterial during its degradation.

This thesis has shown that wet foams can be produced from tricalcium phosphate (Table 5.3). However, these foams need to be further investigated to meet the following requirements in order to be used as porous bone graft material:

- interconnected pores with average pore size > 100 μm to allow cell ingrowth
- degradation rate of the material needs to be in the same range than the repair rate of the tissue

Additionally, it would be of great advantage to solidify the wet foam without sintering, similar to bone cement. This would make it possible to repair the bone defect by directly injecting the wet foam. As a result, complex shaped defects could be repaired with minimal invasion.

8.2 Hollow particle-stabilized capsules

It has been mentioned several times throughout this thesis that hollow particle-stabilized capsules can be prepared upon dilution of the wet foams (Figure 8.1 and Figure 2.4c). Such capsules can also be filled with nonpolar liquids (oils) instead of air which opens the possibility to use them for the controlled release of drugs, fragrances, dyes or similar ingredients. In order to so, the principals outlined in this thesis were applied to emulsions as well.
The following list contains some of the future challenges concerning the project of particle-stabilized capsules from foams or emulsion:

- fabrication of capsules with diameters < 1 µm
- preparation of monosized capsules
- drying of such capsules

Figure 8.1: Confocal Laser Scanning Microscopy images of a) bubbles stabilized by fluorescent silica particles and b) particles adsorbed at the air-water interface of a single bubble. The bubbles were prepared by dilution of a stable wet foam.

The fabrication of submicron-sized capsules asks for a further control of the wet foam microstructure to prepare foams with smaller average bubble sizes. We have shown that a decrease in average bubble size of the wet foam also leads to a narrower bubble size distribution which brings us further in the direction of the preparation of monosized capsules. In order to be able to dry such capsules, the particle network around the bubble needs to be strengthened which can be achieved by using specific adsorbing binders.
8.3 Particle-stabilized polymeric foams

Polymeric foams are produced on large scale for packaging, thermal insulation, mechanical and/or acoustic damping and other passive applications. Active transducer applications have emerged over the last 15 years, following the discovery that cellular polymers can be remanently electrically charged to produce foams with ferroelectric properties. These properties are the result of macroscopic dipoles created within the voids, while the underlying polymer does not need to be ferroelectric by itself. The workhorse material in this field is cellular polypropylene (PP), typically prepared by extrusion of particle filled polymer, followed by biaxial stretching and inflation processes that finally leads to thin films with flat lenslike voids. Other materials include fluoropolymers processed by solution casting followed by solvent boiling to generate the desired voids. In their thickness direction, charged cellular polymers are very soft materials with a high piezoelectric strain coefficient, whereas the in-plane piezoelectricity is virtually zero.

Stimulated by our research on particle-stabilized ceramic foams, we have also used polymeric particles such as polyvinylidene fluoride (PVDF) as foam stabilizers. In this case, the liquid phase is modified rather than the hydrophobic polymeric particles. Using the right alcohol-water mixture allows for the particles to adsorb to the air-water interface and stabilize high-volume foams (Figure 8.2). Similar to foams stabilized by ceramic particles, these foams are very stable against bubble growth and drainage over time.
Figure 8.2: Air content of foamed suspensions containing polyvinylidene fluoride particles in different alcohol-water mixtures: ethanol (■), 1-propanol (▼) and 1-butanol (▲).

Due to the enhanced thermal stability of PVDF compared to PP, these foams are interesting candidates for piezoelectric transducer materials. First results demonstrate that electrically-charged PVDF foams show indeed a piezoelectric response. However, the remanent polarization is still rather small compared to PP foams and needs to be further improved.

8.4 Particle-stabilized metallic foams

Titanium-based foams have many potential applications due to titanium's outstanding mechanical properties in combination with a low density and high chemical resistance. These foams can be used for structural applications such as sandwich cores for aerospace or submarine vehicles. Titanium's high melting point (1670 °C) also allows for the use of titanium foams at elevated temperatures as for
instance as heat exchangers or catalyst substrates. Current research concentrates on improving process control to produce higher quality materials with tailored pore morphology and homogenous pore size distribution. Tailoring the microstructure of porous materials from high-melting-point metals has been particularly challenging owing to the difficulties associated with the incorporation of controlled pores without melting the material.

In a proof-of-concept study, submicron sized titanium particles have been in-situ hydrophobized and used as foam stabilizers. The foams showed a decent stability in combination with rather small bubbles (~300 µm) and high air contents (~90%). Further work should focus on the following issues:

- improve control of foam formation and wet foam microstructure
- improve wet foam stability
- drying of the wet foams in order to avoid crack-formation
- solidification of the dried foams
This appendix contains additional tables and the corresponding references from the introduction of this thesis. In Table 9.1 to Table 9.3, examples from literature are reported for replica, sacrificial template and direct foaming methods respectively, whereas Table 9.4 consists of typical surfactants used for the stabilization of foams in direct foaming methods.

Section 9.2 contains the measured data of surface tension and foam rheology as well as the calculations for the critical Capillary number in order to apply Taylor's model.
### 9.1 Additional tables

Table 9.1: Examples of replica methods reported in the literature.

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<th>Method &amp; precursors</th>
<th>Compositions</th>
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<td>Synthetic templates</td>
<td>Impregnation with ceramic suspension</td>
<td>Al₂O₃, Reaction bonded Al₂O₃, Fiber-reinforced Al₂O₃, ZrO₂, cordierite, SiC, Si₃N₄, SiO₂, TiO₂, talc, MgO, clay, Al₂O₃-ZrO₂ composite, mullite, Li₂O-ZrO₂-SiO₂-Al₂O₃ glass ceramic, SiC-Al₂O₃-SiO₂ composites, calcium phosphate-based composites, (Ca₁₋ₓMgx)Zr₄(PO₄)₆, La₀.₈₄Sr₀.₁₆Ca₀.₀₂MnO₃</td>
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<td>Vapor infiltration and reaction with gaseous metals or metal precursors (CVI)</td>
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<td>SiC</td>
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<td></td>
<td>Impregnation with preceramic polymers</td>
<td>SiOC-C composites</td>
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<td>Liquid precipitation of precursors</td>
<td>Macroporous zeolites, Calcium phosphate-based composites</td>
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Table 9.2: Examples of sacrificial template methods reported in the literature.

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<td>PVC beads</td>
<td>Al₂O₃, PZT, (Ca₁₋ₓ,Mgₓ)Zr₄(PO₄)₆</td>
</tr>
<tr>
<td>PS beads</td>
<td>SiO₂, TiO₂, TiO₂-SiO₂, Zeolite, Al₂O₃</td>
</tr>
<tr>
<td>PEO or PVB beads</td>
<td>PZT, Hydroxyapatite</td>
</tr>
<tr>
<td>PMMA or PMMA-PEG</td>
<td>SiOC, SiC, Hydroxyapatite, PZT, Tricalcium</td>
</tr>
<tr>
<td>Synthetic organics</td>
<td>Calcium phosphate</td>
</tr>
<tr>
<td>PEO beads</td>
<td>Al₂O₃, Al₂O₃, Mullite</td>
</tr>
<tr>
<td>PS beads</td>
<td>Al₂O₃, Mullite</td>
</tr>
<tr>
<td>PMMA or PMMA-PEG</td>
<td>PZT</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>Calcium phosphates</td>
</tr>
<tr>
<td>Nylon</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>SiO₂, Al₂O₃</td>
</tr>
<tr>
<td>Polymeric gels</td>
<td>SiO₂, TiO₂</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Gelatine</td>
<td>Al₂O₃, PZT, Na₂O-CaO-MgO glass, hydroxyapatite, mullite, Si₃N₄, CaCO₃, diatomite, cordierite</td>
</tr>
<tr>
<td>Peas and seeds</td>
<td>Al₂O₃, Al₂O₃, Mullite</td>
</tr>
<tr>
<td>Cellulose / Cotton</td>
<td>Calcium phosphates</td>
</tr>
<tr>
<td>Glucose</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>Sucrose</td>
<td>PZT, Calcium phosphates</td>
</tr>
<tr>
<td>Dextrin</td>
<td>SiC</td>
</tr>
<tr>
<td>Wax</td>
<td>Hydroxyapatite</td>
</tr>
<tr>
<td>Alginate</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Starch</td>
<td>Al₂O₃, Al₂O₃, PZT, Na₂O-CaO-MgO glass, hydroxyapatite, mullite, Si₃N₄, CaCO₃, diatomite, cordierite</td>
</tr>
<tr>
<td>Freeze-drying Camphene Water</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Emulsions - Oils</td>
<td>TiO₂, Al₂O₃, Hydroxyapatite, SiO₂, CaCO₃, FeOOH, CoOOH, Mn₇O₁₃H₂O</td>
</tr>
<tr>
<td>NaCl</td>
<td>SiC</td>
</tr>
<tr>
<td>BaSO₄ and SrSO₄</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>Al₂O₃, PbTiO₃, La₁₋ₓSrₓMnO₃</td>
</tr>
<tr>
<td>Nickel</td>
<td>YSZ, Al₂O₃</td>
</tr>
<tr>
<td>Carbon (graphite, fiber, nanotubes)</td>
<td>SIC, mullite</td>
</tr>
<tr>
<td>Silica (particles, fibers)</td>
<td>SIC</td>
</tr>
<tr>
<td>ZnO</td>
<td>NiO</td>
</tr>
</tbody>
</table>
Table 9.3: Examples of direct foaming methods reported in the literature.

<table>
<thead>
<tr>
<th>Foam setting</th>
<th>Air incorporation</th>
<th>Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermosetting (condensation) of polyols and isocyanates (polyurethane precursors) in the presence of catalyst</td>
<td>Physical blowing: dichloromethane, H₂ and CH₄; Chemical blowing: CO₂ release upon reaction of isocyanate with H₂O</td>
<td>SiOC, SiC, SiNC, SiO₂ with or without fillers (Al₂O₃, TiO₂, Hydroxyapatite, MgSiO₃, BaTiO₃, ZrO₂)</td>
</tr>
<tr>
<td>Solidification of the thermoplastic polymer polystyrene upon cooling</td>
<td>Physical blowing: pentane</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Thermosetting (condensation) of preceramic silicone-based polymers</td>
<td>Physical blowing: pentane, freon, CO₂, H₂O and ethanol, azodicarbonamide</td>
<td>SiOC, SiC, SiNC, SiO₂</td>
</tr>
<tr>
<td>Surfactant-stabilized foams</td>
<td>Condensation of metal hydroxide and alkoxides species or gelling reaction between metal oxides and surfactants</td>
<td>Freon, mechanical frothing in the presence of surfactants; Evaporation of volatile compounds, Release of O₂</td>
</tr>
<tr>
<td>Sol-gel setting</td>
<td>Cross-linking of polyvinyl alcohol with organotitanates and epoxy</td>
<td>Free radical polymerization, Cross-linking of polyvinyl alcohol with organotitanates and epoxy</td>
</tr>
<tr>
<td>Temperature-induced setting of polysaccharides: sucrose, carrageenan gum, agar</td>
<td>Temperature or pH-induced setting of proteins: gelatine, ovalbumin, bovine serum albumin</td>
<td>Thermal expansion or mechanical frothing in the presence of surfactants/proteins</td>
</tr>
<tr>
<td>Cement hydration</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table 9.4: Examples of surfactants used for the stabilization of foams in direct foaming methods.

<table>
<thead>
<tr>
<th>Type</th>
<th>Molecule</th>
<th>Trade name</th>
<th>Supplier</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic</td>
<td>PEG-8 octyl phenyl ether</td>
<td>Triton X-114</td>
<td>Fluka</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>PEG-11 nonyl phenyl ether</td>
<td>Igepal CO-710</td>
<td>Rhodia</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>PEG-11 C10 oxo-alcohol</td>
<td>Lutensol ONni0</td>
<td>BASF</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>PEG-20 sorbitan oleate</td>
<td>Tween 80</td>
<td>Fluka</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>Cocoalkyldimethylamine oxide</td>
<td>Fongraminox KC-B</td>
<td>Clariant</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Poly(dimethylsiloxane) copolymer</td>
<td>Tegostab BF 2370</td>
<td>Degussa</td>
<td>103</td>
</tr>
<tr>
<td>Anionic</td>
<td>Sodium Dodecyl Sulfate (SDS)</td>
<td>-</td>
<td>Fluka</td>
<td>168</td>
</tr>
<tr>
<td>Cationic</td>
<td>Benzethonium chloride</td>
<td>-</td>
<td>Lancaster</td>
<td>188</td>
</tr>
<tr>
<td>Protein</td>
<td>Albumin</td>
<td>-</td>
<td>-</td>
<td>188, 194</td>
</tr>
</tbody>
</table>


9.2 Taylor's model

This section consists of additional information concerning Taylor's model as described in chapter 4.3.6. The critical Capillary number $Ca_{crit}$ was determined assuming simple shear. Figure 9.1 shows the dependence of the critical Capillary number on the viscosity ratio $p$ of the dispersed and the continuous phase (after Grace\textsuperscript{139} and Janssen\textsuperscript{140}). For $p < 0.12$, the data was fit according to Eq. 9.1.

![Graph showing the dependence of $Ca_{crit}$ on $p = \eta_d/\eta_c$ with a fitted line for $p < 0.12$.]

Figure 9.1: Critical Capillary number as a function of the ratio between the viscosity of the dispersed phase ($\eta_d$) and the viscosity of the continuous phase ($\eta_c$) in case of simple shear (after Grace\textsuperscript{139} and Janssen\textsuperscript{140}).

Eq. 9.1 \quad \quad Ca_{crit} = -0.54713p - 0.80247 \text{ for } p < 0.12

The data for the suspension surface tension, the effective foam viscosity, the critical Capillary number and the experimental and modeled average bubble size in the foam are given in Table 9.5 for different amphiphile or particle concentrations in suspension.
Table 9.5: Suspension surface tension, foam effective viscosity, critical Capillary number as well as experimental and modeled bubble size for different experimental conditions.

### Amphiphile concentration

<table>
<thead>
<tr>
<th>Valeric acid (mmol/l)</th>
<th>$\sigma$ (N/m)</th>
<th>$\eta_{\text{eff}}$ (Pa s)</th>
<th>$C_{\text{ac} \text{cr}}$ (•)</th>
<th>Experimental bubble size (µm)</th>
<th>$\frac{(C_{\text{ac} \text{cr}} \sigma)}{\eta_{\text{eff}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.07142</td>
<td>4.11x10³</td>
<td>5816</td>
<td>108.32</td>
<td>1.01x10⁴</td>
</tr>
<tr>
<td>20</td>
<td>0.07100</td>
<td>1.87x10⁴</td>
<td>13325</td>
<td>69.2</td>
<td>5.06x10⁴</td>
</tr>
<tr>
<td>30</td>
<td>0.06277</td>
<td>5.28x10⁴</td>
<td>23515</td>
<td>26.06</td>
<td>2.77x10⁴</td>
</tr>
<tr>
<td>40</td>
<td>0.05355</td>
<td>6.57x10⁴</td>
<td>26503</td>
<td>16.42</td>
<td>2.16x10⁴</td>
</tr>
</tbody>
</table>

### Particle concentration

<table>
<thead>
<tr>
<th>Solids content (vol%)</th>
<th>$\sigma$ (N/m)</th>
<th>$\eta_{\text{eff}}$ (Pa s)</th>
<th>$C_{\text{ac} \text{cr}}$ (•)</th>
<th>Experimental bubble size (µm)</th>
<th>$\frac{(C_{\text{ac} \text{cr}} \sigma)}{\eta_{\text{eff}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.06917</td>
<td>5.28x10³</td>
<td>6670</td>
<td>161.96</td>
<td>8.74x10⁴</td>
</tr>
<tr>
<td>15</td>
<td>0.06723</td>
<td>2.09x10⁴</td>
<td>14161</td>
<td>114.92</td>
<td>4.56x10⁴</td>
</tr>
<tr>
<td>20</td>
<td>0.06726</td>
<td>1.25x10⁴</td>
<td>10689</td>
<td>76.88</td>
<td>5.75x10⁴</td>
</tr>
<tr>
<td>25</td>
<td>0.06683</td>
<td>2.62x10⁴</td>
<td>16059</td>
<td>38.83</td>
<td>4.08x10⁴</td>
</tr>
<tr>
<td>30</td>
<td>0.06459</td>
<td>4.41x10⁴</td>
<td>21309</td>
<td>32.45</td>
<td>3.12x10⁴</td>
</tr>
<tr>
<td>35</td>
<td>0.06229</td>
<td>5.28x10⁴</td>
<td>23515</td>
<td>26.06</td>
<td>2.77x10⁴</td>
</tr>
<tr>
<td>40</td>
<td>0.05552</td>
<td>6.33x10⁴</td>
<td>25969</td>
<td>20.46</td>
<td>2.28x10⁴</td>
</tr>
</tbody>
</table>

*: bubble diameter determined from microscope imaged, **: calculated from bubble radius
9.3 References

Appendix

192 • Chapter 9


117. P. Sepulveda and L. L. Hench, Imperial College Innovations Ltd (IMCO-Non-standard) Sepulveda P and Hench LL.


CURRICULUM VITAE

Personal

Name: Urs Thomas Gonzenbach
Date of birth: December 29th, 1977, St. Gallen, Switzerland
Nationality: Swiss
Citizenship: Zürich (ZH), Pfyn (TG)
Marital status: not married

Education

2003 to present Doctoral thesis: "Particle-Stabilized Foams", Prof. Dr. Ludwig J. Gauckler; Nonmetallic Inorganic Materials, Department of Materials, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland
2003 M. Sc. degree in Material Science and Engineering, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland
1998-2002 Studies in Material Science and Engineering, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland

Research Experience

2002 Semester project: "Dynamische Rekristallisation bei der Extrusivvon Magnesium-Legierungen", Metals and Metallurgy, Prof. Dr. Peter Uggowitzer, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland
2002 Internship: “Validation of the Production Process of Zirconia and Alumina Balls for Hip Joints”, Metoxit AG, Thayngen, Switzerland
2001 Semester project: “A temperature induced gelating polymer for a forming method and a novel polymeric dispersing agent with very broad pH resistance”, Prof. Dr. Ludwig J. Gauckler; Nonmetallic
Inorganic Materials, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland

2001 Internship: "Superconduction Fault Current Limiter", ABB Corporate Research Ltd, Baden, Switzerland

2000 – 2002 Student research assistant, project: "Influence of short-chain carboxylic acids on the mechanical properties and structure of coagulated alumina suspensions", Nonmetallic Inorganic Materials, Swiss Federal Institute of Technology (ETH), Zürich, Switzerland

Publications


Oral Presentations


Poster Presentations


Patents


Awards

### Supervised Student Projects

3. M. Siegfried, “Propyl Gallate as Foaming Agent for Particle-Stabilised Al₂O₃ Foams”, Bachelor thesis, 2004
4. C. Kümin, “Drying of wet alumina foams”, student research assistant, 2004
9. A. Bardill, “Particle-Stabilized Silica Foams”, student research assistant, 2005