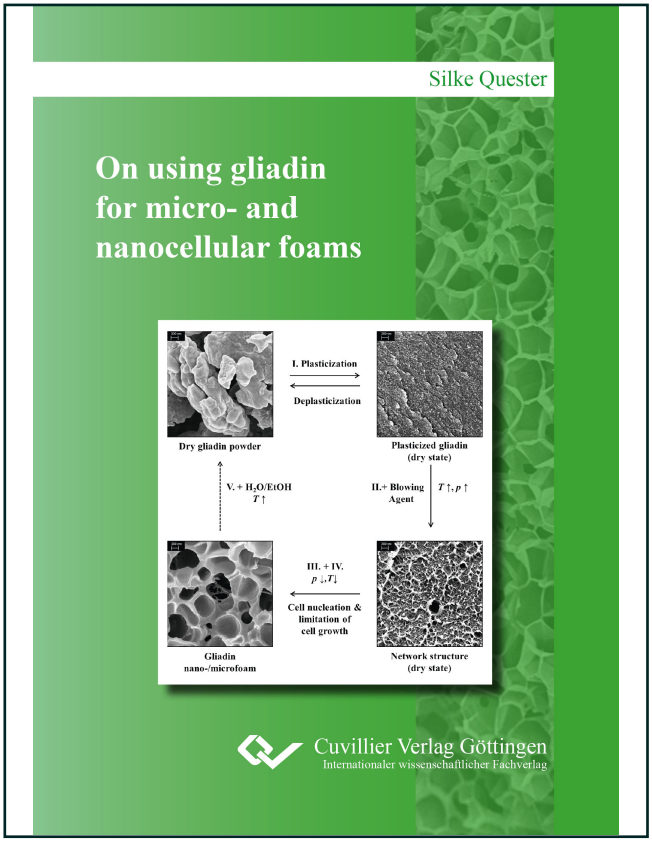
Silke Quester (Autor)

On using gliadin for micro- and nanocellular foams



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1 Introduction

1.1 Motivation

“Without natural polymers there is no life” [1]. Organic polymeric material is “as old as life itself, for DNA and RNA – the basis of life as we understand it – are natural macromolecules” [2]. In general, natural polymers or biopolymers are macromolecules including proteins, nucleic acids and polysaccharides formed by living organisms [3–6]. The first biopolymer-type macromolecules were likely to perform simple catalytic functions, possibly enhancing the self-replication of prebiotic nucleic acids [7]. The physical prerequisite for a macromolecule to serve a certain function (such as an enzyme) is a unique sufficiently rigid three dimensional structure that allows the formation of a catalytic active center by keeping functional groups in correct mutual positions and orientations [8].

In the biological world at the nano-, micro-, and macro-scale, proteins serve as the major molecular scaffold material. At the nano-scale, e.g. self-assembled actin cytoskeleton constitutes to the physical rigidity of cells, and self-assembled microtubules serve as nanoscopic protein railways that allow the transport of “cargo” within the micro-scale cell using nano-scale protein motors. Furthermore, by thermodynamically favored self-assembly of nanostructured building units, nature creates sophisticated three-dimensional structures with well-defined functions such as the tough and lightweight collagen proteins in the skin, the keratin proteins in nails and hair or silk that comprises a ratio of tensile strength to density of about five times higher than steel [9–11]. Various inorganic biological structures such as bones, teeth or animal shells are build/formed by protein templates via specific interaction of proteins and peptides, e.g. with calcium or silicon [12]. All these biopolymers are generally manufactured at environmental temperature at atmospheric pressure and were optimized by evolution. In short, nature creates intricate structures that can hardly be produced synthetically, so that skilful utilization of their unique properties such as their molecular self-assembly constitutes huge potential, especially for smart modern applications. Already being “smart function materials” by their own, proteins impart characteristics that qualifies them as potential sources to engineer “smart function materials” [13–15].

From the beginning of human history, available substances have been used to serve certain function such as nutrition, clothing and shelter [16]. The Neanderthals and Stone Age people used birch pitch as an “all-purpose glue” [17]. Plant fibers such as cotton, hemp, sisal, coir, proteinaceous fibers like silk or hair, plant and animal proteins, and natural rubber have been

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used and processed since thousands of years. Rubber for example has already been used in 1600 B.C. by the ancient Mesoamerican people for medicines, paint and other purpose [18]. No noteworthy novelty occurred until 1770, when *Priestley* recognized its use as eraser of pencil marks, and coined the term "rubber" [16], but its real story of success was settled by *Goodyear* who improved the processing of rubber, especially its durability by the vulcanization process around 1839 [19–21].

Successful conversion of pre-existing polymers into more useful products has been set in the 19th century [2], e.g. by the development of man-made fibers such as cellulose nitrate, produced by *Baronet* and *Schonbein* in 1832 and 1846, respectively [22, 23] or "Styroloxyd", discovered by *Simon*, a German apothecary [24]. Around 1870, *Parkes* and *Hyatts* developed horn-like semi-flexible products by mixing nitrocellulose solution and camphor [25–29] that were traded as "Parkesine" and "Celluloid". During this time, also plasticization of casein with formaldehyde had been discovered, e.g. as white blackboard, and is still used today for production of button [30]. Durable plastics of fully synthetic polymers had been launched at the beginning of the 20th century with the development of resinous substances, e.g. phenol-aldehyde resins [31]. In 1907, the first thermo set plastic termed as Bakelite has been invented, one year later, as the first flexible plastic by chemical modification of a polymer. The first commercial fully synthetic plastic was Bakelite, a hard, compact, insoluble and infusible condensation product of phenols and formaldehyde invented around 1909 by *Baekeland* [32–34]. The ability of formaldehyde to form resinous substances had already been developed in 1859 by *Butlerov* and in 1872 by *Bayer* [30].

These synthetic materials, significant for technical, economic, and social development and activity, had been made without knowledge on structure or composition of these materials. By the end of the 20th century, more than 50 kinds of plastics were known.

Further significant progress was set by *Staudinger*'s fundamental concept of "macromolecules" that covered both synthetic and natural polymers, claiming the existence of extremely large compounds with molecular weights exceeding 5000 atoms [35–39] - a theory which had provoked large controversy within the scientific community in the 1920's [40, 41], but was finally awarded with the Nobel Prize for chemistry in 1953 [42, 43]. The knowledge about size and bonding along with the development of structure characterization techniques such as crystallography and x-ray analysis provided insight into the structural composition, for the first time.

Thus significantly contributing to progress prerequisite for the so termed "classical" period of polymer science roughly between world war I and II [44]. After world war II, polymer

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science reached full maturity [44] by substantiating giant technological progress and development.

The success of plastics as a product has been substantial, and materials that meet almost any requirement can be produced today [45]. However, the basic materials used for making plastics are commonly extracted from oil, coal and natural gas, but these resources are finite [16]. Nonetheless, the stability and durability of plastics have been continuously improved, and plastics have become an important worldwide, multibillion-dollar industry in which a steady flow of new materials, fabrication processes, design concepts, and market demands has caused rapid and tremendous growth [46]. The molecular architectures of synthetic polymers and biopolymers can be tailored to meet the demands of modern technology. The polymers of the 21th century combine the mechanical properties and the processability of traditional polymers with the current knowledge, e.g. of electrical and optical properties, thus extending the frontiers in material science and technology [47]. Advancing plastic technologies still continues to be the top priority in the creation of expanding worldwide markets [46].

Today, more material objects are produced than ever before, constituting waste for millennia [48, 49]. The “Rasputin of modern materials (that) stubbornly refuses to die” [50] implies serious problems such as the final disposal. A dramatic increase of pollution has evoked [51], giant masses of plastics have been found in nature [52, 53], and nano-fragmentation has appeared as a serious threat for nature and humans [53–55]. Since conventional plastics have long life times (e.g. about 500 up to 1000 years for polystyrene or polyethylene [56]), the demand for bio-derived alternatives is ever-growing [57, 58].

Despite the risen demand, little knowledge exists in this novel field and further research into long-term life-cycle environmental impacts is needed. Basically, bioplastics are divided into two main categories: bio-based plastics derived from renewable resources and biodegradable ones in the sense of compostable plastics [59], so bio-based plastics can still be biodegradable or non-biodegradable. Similarly, biodegradable polymers can be petroleum-based [60, 61]. Most commercial biopolymers are still not degradable under ordinary conditions even in the presence of microorganisms and their disposal means to discard valuable raw materials [60].

Bioplastics can potentially be used for a wide range of applications [62–65], but cannot for reasons such as resistance and durability, yet replace all types of petroleum-based plastics for all applications. Additionally, aspects such as the compatibility with existing equipment and the end-of-life management have to be considered. Possibly the most important drawback is the high cost of biopolymers compared to petroleum-based ones [66]. Nevertheless, the demand of politics, consumers and retailers for “green” alternatives constantly rises and researchers all

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over the world address to the challenge regarding sustainable replacement of conventional plastics [67, 68].

Since packing materials are usually only used for a short purpose, they appear as a potentially qualified market for application of biodegradable materials. Nevertheless, the market ranges from coatings and adhesives to plastics and surfactants [69]. Besides starch, cellulose, polycaprolactone (PCL), polyvinylalcohol (PVA), and polylactic acid (PLA), also proteins have emerged as promising candidates [70]. Furthermore, also medical application appears as an interesting field of application, not at least due to the biodegradability of the proteins.

The development of bio-inspired materials for innovations has significantly expanded within the last years, and smart utilization of abundant natural potential from biological feedstock seems to imply promising potential to produce materials of superior mechanical properties. Here, gluten from wheat is an interesting candidate contemplated to replace petroleum-based packaging applications. Compared to other biopolymers, it is renewable, abundantly available, completely biodegradable and inexpensive. In virtue of the large scale industrial separation of starch from wheat [71] and from bio-fuel production, gluten has become a commodity in its own right despite from being a by-product [72–74].

Gluten comprises remarkable unique functionality and persistence of the structural integrity after cooking, thus having “no functional competitor” [75]. In the light of the awareness and constantly increasing understanding of its excellent properties, gluten has predominantly overcome its shadowy existence. Nevertheless, its effective virtue is often only noticed if the outcome of its unique function is lacking.

Besides its major role in human diets and its indispensability in the bakery industry [76, 77], its application is steadily expanding [78, 79] to (edible) packaging films [80] (wheat gluten films generally show low oxygen permeability at dry conditions due to a high content of hydrogen bonds [81]), adhesives [82–85], coatings [86], chewing gum base [87–90], meat substitute, and low-carbohydrate baked-goods [91]. In its wet state, gluten exhibits gum-like consistency. Commonly, it is traded in its dried state [75, 92, 93], but the functional properties can be regenerated by rehydration of the powder. Its enormous capacity of water-binding (up to 200% [94]) enhances product yield, softness and shelf life properties, mixing tolerance and handling properties [77]. The gas holding via formation of a continuous viscoelastic network through mixing with water (Figure 1.1-2, left) distinguishes the storage proteins of wheat from those of other cereals such as maize, rice, soybean, and others [94–96]. Unique among the cereal proteins, dough from wheat proteins exhibits the properties of viscosity and elasticity, termed as viscoelasticity and constitutes the balance that determines the suitability for different

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end-uses. In bread-making, “strong” (elastic) dough is required that is able to be stretched and to trap (carbon dioxide) gas bubbles that are produced during fermentation thus enabling bread to rise. For other purpose such as making cake and biscuits require more extensible dough. Here, too elastic dough would allow the biscuit to return to its original shape after moulding to give a smaller biscuit and too viscous dough will allow flow after shaping.

The viscoelastic properties of wheat dough are primarily determined by the major seed storage proteins, which are classified as prolamins. These proteins are present in the cells of the mature grain as a proteinaceous matrix that fills the space between the starch granules [97] and are brought together during dough mixing to form a continuous network referred to as gluten, which can be separated from dough by washing out starch, fibre and water-soluble components. The resulting fraction comprises predominantly prolamins (about 70% in dry matter) with smaller amounts of other proteins, entrapped starch granules, and lipids. The prolamins are classified on the basis of their solubility in alcohol/water mixtures, but this applies to only about half of the native gluten proteins, the monomeric gliadin fraction. The other main fraction termed as glutenin constitutes the polymeric protein assembly. These proteins are stabilized by inter-chain disulfide bonds and are therefore only soluble in alcohol-water mixtures in case these bonds are reduced to release the individual subunits [98]. It was reported that wheat gluten, gliadin and glutenin proteins without the presence of additives lack organized structural features at supramolecular and atomic level. However, using additives, organization into hierarchical assemblies, particularly at supramolecular level was reported for gliadin proteins [99]. Wheat gluten proteins have a known propensity to aggregate into a variety of forms [13], thus constituting a value potential for design of nanoscale materials utilizing the self-assembly of protein nanostructures with properties that are not easily duplicated with traditional organic molecules and other polymers [100].

Upon hydration and during processing, gliadin and glutenin undergo conformational changes and interact to form a unique viscoelastic gluten network, which is envisaged to be necessary for holding the gases and for producing light, porous products such as bread [101]. A model of the process of gas entrapment in the gluten matrix was proposed [102], based on the assumption that upon hydration and kneading wheat storage proteins unfold to form a network of “molecular slinkies”. Due to its viscoelastic nature, the network is capable to entrap air bubbles. Upon expansion of the bubbles, the “molecular slinkies” are able to stretch and thereby to entrain the bubbles from getting out of the dough. A schematic illustration is given in Figure 1.1-1.

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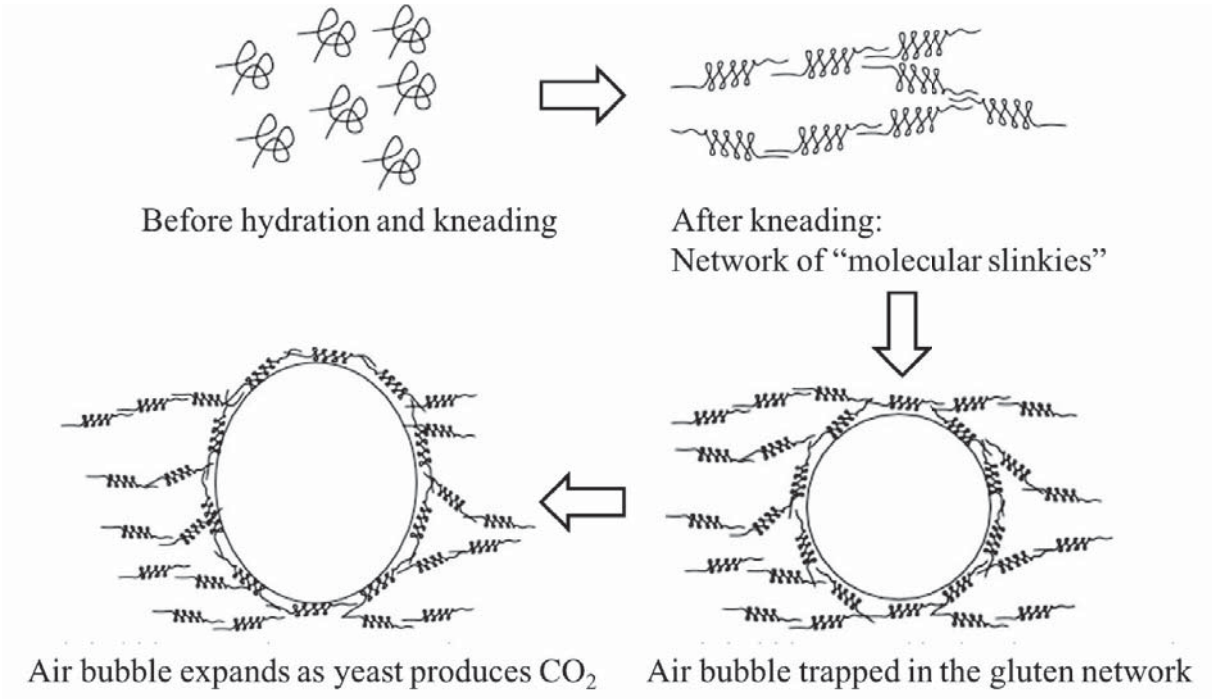

Figure 1.1-1: Schematic of the model of entrainment of gas bubbles in the viscoelastic gluten matrix. Starting from the dry gluten, the proteins unfold upon hydration and mixing to form a network of "molecular slinkies", that is, due to its unique nature capable to trap air bubbles. When the bubbles expand, e.g. due to CO_2 production by yeast, the "molecular slinkies" stretches and prevent the bubbles from getting out of the dough (slightly modified from [102]).

Of course, the real processes at the microscale during the processing of bread include numerous interactions of various components and depend on the experimental conditions and are therefor highly complex. Here, the key aspects are the film forming ability that provides gas retention and controlled expansion for improved volume, uniformity and texture, and the thermosetting properties that contribute to the structural rigidity.

Upon heat treatment, gluten proteins aggregate through the formation of new bonds between the polypeptide chains resulting in a decreased solubility and changed viscoelastic behavior. Furthermore, the compressibility is decreased while the relative elastic recovery is increased after heating [103]. At temperatures exceeding 75.0 °C, gluten proteins unfold, thereby facilitating sulfhydryl/disulfide interchange between exposed groups [104] to allow the formation of a viscoelastic matrix that can entrap small gas bubbles thus resembling excellent conditions for entrapment of small volumes of blowing agent to obtain a highly porous biopolymer foam.

Analysis of this microstructure by SEM reveals a mainly densely packed arrangement of spherical particles that constitute a continuous matrix that entraps bubbles of various sizes ranging from a few nanometers to macroscopically visible ones is found to be present in gluten that was hydrated and carefully homogenized by hand-mixing (for five minutes, Figure 1.1-2, upper row) after drying of the viscoelastic rubbery paste.

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By tempering the hydrated and thus plasticized gluten, e.g. for two hours at 95.0 °C and atmospheric pressure, a stable network structure was obtained (lower row). The SEM-micrographs displays the sample state after ethanol-soluble constituents were removed by repeated washing cycles using hot aqueous ethanol (T = 95.0 °C), unveiling a stable scaffold structure.

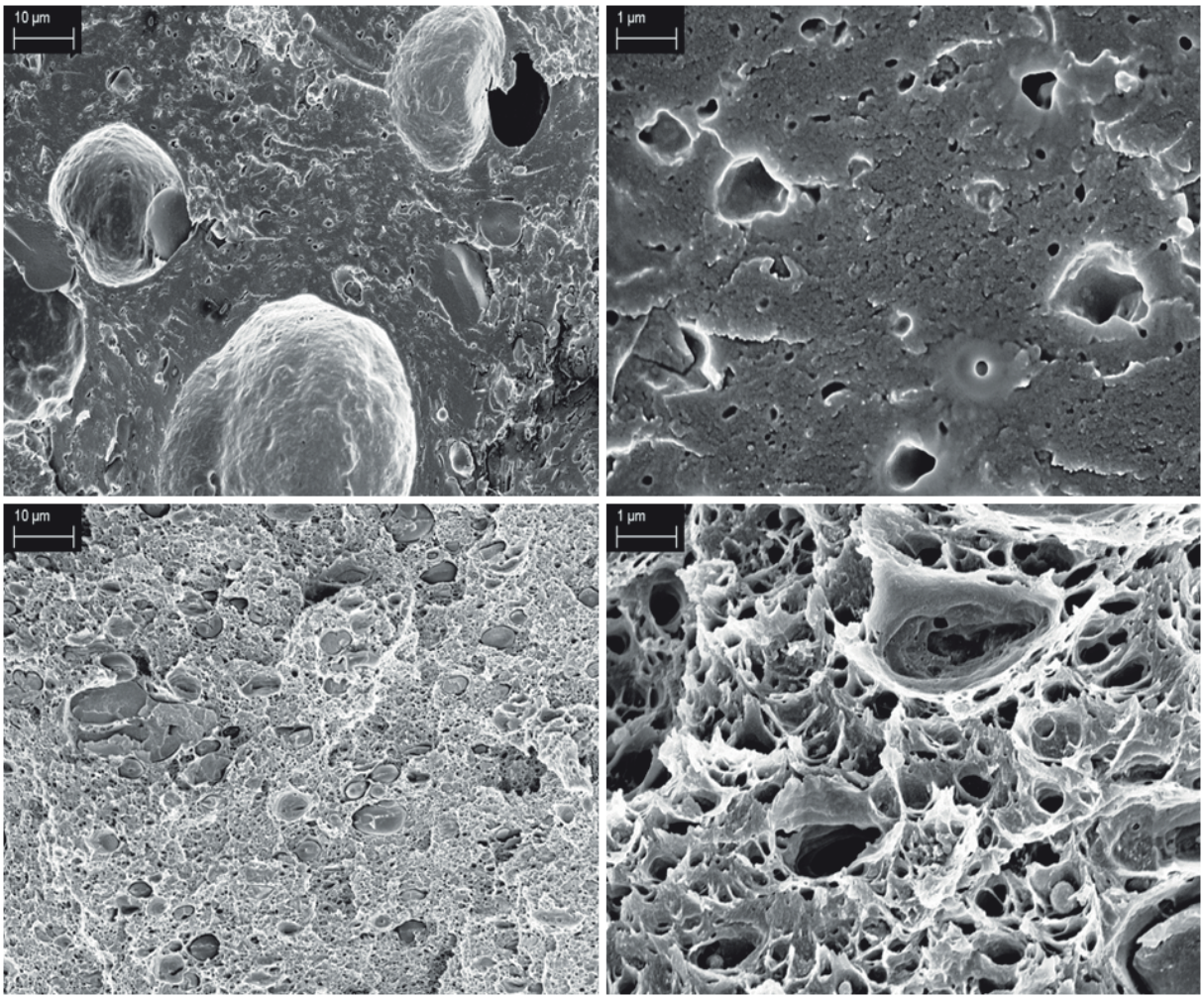

Figure 1.1-2: SEM-micrographs of the fracture surface of dried gluten paste resulting from gluten hydration and careful homogenization (upper row). Tempering for 2 hours at 95.0 °C and atmospheric pressure induced protein aggregation in network structure. The scaffold that remains after thorough removal of uncross-linked material by washing cycles using hot aqueous ethanol (T = 95.0 °C) is shown (lower row). The network structure encloses microcellular bubbles.

Nevertheless, due to the heterogeneous composition of raw gluten which was denoted as an “enigmatic complex of proteins” [73], assembly of different structural elements and geometries was detected. To prepare low-density fine-structured biopolymer foam, purification appears mandatory, for gluten is neither a pure protein nor a mixture of proteins alone, although protein is the major component usually representing about 70 - 80% on a dry weight basis, but additionally constituents such as lipid, residual starch, and other non-starch polysaccharides [104] are present, thus displaying a highly complex mixture inapplicable to study.

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Therefore, this thesis was mainly focused on studying the foaming behavior in the absence of further components of the monomeric gluten protein fraction termed as gliadin.

In the light of these facts and the quote of *Hesser* stating that “it is hoped that work by commercial, private, academic, governmental and industrial associations will continue to improve this unique and natural protein through new and improved manufacturing techniques, plant breeding and increases knowledge of cereal chemistry” [77] - this thesis is intended to contribute to such progress by systematic investigation of the possibilities to prepare micro- and nanocellular foams using the structural arrangement of proteins at the nano- or even molecular scale. As shown so far, the bubbles entrapped in the gluten matrix in baking processes are mainly macroscopic bubbles. To date, no nanofoam from gluten, gliadin or glutenin was reported nor was it addressed to the foaming behavior at the nanoscale. This thesis aims to enlighten the mechanisms involved in gliadin foaming by investigation of the unique material characteristics and their relation to the foaming characteristics.

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1.2 Objectives

In the present thesis, a procedure for sustainable but cost-effective production of biodegradable microcellular or even nanostructured foam was to be developed. Thereby, the requirement to devise an environmentally friendly and efficient method was to be met. For this reason, an abundant natural resource such as biopolymer was to be used. Due to their unique characteristics e.g. known from baking, wheat storage proteins were to be tested specifically for the possibility to utilize their nature to obtain fine-structured homogenous low density biopolymer foam. Therefore, to follow the guidelines, the starting wheat storage protein material was to be extracted from gluten in a simple procedure by using water and ethanol followed by subsequent freeze-drying or solution casting. In a further step, the required viscoelastic characteristics needed for foaming were to be adjusted via plasticization of the dry protein material with water. Here, different preparation techniques were to be tested to produce starting materials comprising different morphology, viscoelastic properties and packing to study the effect of the material character on the final foam. To this end, the degree of hydration, application of shear, swelling time, temperature and pH was to be varied. Regarding the foaming process itself, two different blowing agents, nitrogen and carbon dioxide, were to be tested and to be compared under variation of soaking time and temperature. Additionally, special focus was to be set on the expansion step, in particular on the timing, temperature and velocity of the pressure release, and the past-expansion treatment. It was to be elucidated which factors mainly govern the foam structure, cell size, and density, and which parameter constellation results in the best low-density foam with the smallest cell sizes. The effect of each processing parameter (blowing agent, pressure, temperature, pH, soaking time and temperature) was to be determined. From all performed stages, utilized materials and resultant products, scanning electron microscopy (SEM) measurements were to be performed to analyze the materials.

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2 Fundamentals

2.1 Definition of foam

According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), “foam” is a dispersion in which a large proportion of gas by volume in the form of gas bubbles is dispersed in a liquid, solid or gel. Usually, the bubble diameter is larger than 1 µm, but the thickness of the lamellae between the bubbles is often in the colloidal size range. Interchangeably with foam the term froth has been used. Froth may be distinguished from foam by the fact that the former is stabilized by solid particles while the latter is stabilized by soluble substances [105]. In general, the term “foam” refers to (spherical) gaseous voids dispersed in a dense continuum [106]. A brief overview of the terminology of typical gas/liquid and gas/solid systems is given in Table 2.1-1.

Table 2.1-1: Terminology of some two-phase systems (redrawn after [106]).

State	Terminology
Gas bubbles on top of a liquid	Froth
Gas bubbles dispersed in a liquid	Emulsion bubble
Liquid bubbles in liquid	Emulsion liquid
Liquid bubbles in solid	Gelation
Gas bubbles in solid	Foam

Foam properties strongly depend on morphological characteristics. Depending on the nature of foam cells, open and closed-cell form is distinguished. Open cells are characterized by capillaries that allow for unique adsorption and sound deadening feature. Cell size exerts great impact in disturbance distribution: small cells provide an improved energy adsorption and insulation capacity, and reduced radiation effects in the cell during heat transfer. The *Gibbs* number, a dimensionless measure of the barrier to overcome for nucleation, has been pronounced to highly impact the cellular structure of the foam [107].

Three different mechanisms of heat transfer through the foam are distinguished: conduction along the struts and cell walls of the solid polymer, conduction through the gas within the cell, and thermal radiation. Thus, the total heat transfer results as the sum of these three mechanisms [108]. Furthermore, heat transfer crucially depends on cell size and number density, as schematically shown in Figure 2.1-1.

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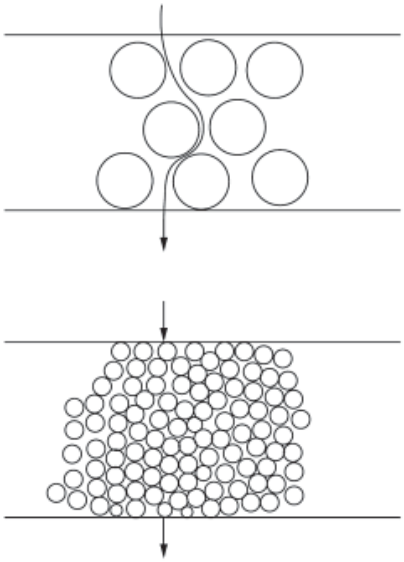

Figure 2.1-1: Schematic of heat and mass transfer through a foam at different cell size and distribution (taken from [106]).

Lee and *Rahmesh* described the foaming process from the perspective of the blowing agent as “a succession of three steps: implementation, liberation and evacuation” as a transformation from a blowing agent filled to an air filled state. The fundamental characteristic of a blowing agent is its capability to migrate through the polymer. Therefore the thermodynamic, kinetic and transport properties of the gas are of vital importance at different steps of the process [106].

2.2 Theory of foam formation

According to *Colton* and *Suh*, the term “microcellular foam” refers to polymeric foam with bubble sizes of ten microns or less, produced by saturation of a polymer with gas followed by induce of thermodynamic instability, either by temperature increase or by reduction of pressure to nucleate foam cells. The nucleation process was described to depend on the solubility, concentration, and interfacial energy of any additives present. At very low levels, additives in solution act to increase the free volume of the polymer, resulting homogeneous nucleation within the free volume. Above the solubility limit, heterogeneous nucleation dominates, as it lowers the activation energy for nucleation to levels below that for homogeneous nucleation. In the vicinity of the solubility limit of the additive, these two nucleation mechanisms compete [109].

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2.2.1 Basic principles of foaming

Basically, the foaming process itself can be divided into four stages [110]:

I. Gas dissolution,

II. Cell nucleation/bubble formation,

III. Foam growth, and

IV. Bubble stabilization.

The initial step of the foaming process is the formation of a polymer/gas-solution. Thereby, the concentration of gas solubilized in a polymer critically determines the cell morphology. The solubility of the blowing agent in a polymer (S) is determined by the saturation pressure (p_S) and saturation temperature (T_S) and can be expressed as

$$S = \int_0^{p_S} \left(\frac{\partial S}{\partial p}\right)_T dp + \int_0^{T_S} \left(\frac{\partial S}{\partial T}\right)_p dT. \tag{2-1}$$

The next step, the cell nucleation, can only occur after the solubility of the gas dissolved in the liquid is exceeded and any further increase of concentration or decrease of solubility of the gas in the liquid induces nucleation. The main driving force for this process is assumed to be the thermodynamic instability resulting from a sudden change in solubility. For bubbles formed in an initially homogeneous liquid, the process is referred to as self-nucleation or homogeneous nucleation while heterogeneous nucleation is distinguished when a second phase is initially present which allows the bubbles to form more readily at either a liquid-liquid or solid-liquid interface. In many processes without solid nucleating agents, the liquid phase actually contains many micro bubbles of air, and they serve as sites for bubble growth with the formation o f new bubbles not necessary. This can be achieved by mechanical agitation of the polymer liquid. The nucleation process is the most important step in determining the morphology of the foam, since the number and distribution of the nuclei can immensely affect the orientation and properties of the foam. It is very difficult to produce acceptable foams by a self-nucleation process. Most successful foam systems contain either nucleating agents or dispersed micro voids [111]. Normally the solubility of a polymer decreases with increasing polymer chain length [112]. Once formed, a bubble grows through diffusion of gas through the continuous matrix. For a given volume of foam, the stability is higher if a few large cells instead of many smaller ones are present. The letter would promote coalescence (see section 2.3). Interfacial tension causes a pressure difference across a (curved) surface, resulting a higher pressure on the concave side (*i.e.* to the bubble inside). Regarding the interface between a gas phase (g) in a bubble, and a liquid phase (l) surrounding the bubble, the pressures are p_g and p_l, respectively.

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For a spherical bubble of a radius r, Δp is given by (2-2):

$$\Delta p = p_g - p_l, \tag{2-2}$$

and varies with the bubble radius r (*Young-Laplace* equation):

$$\Delta p = \frac{2\sigma}{r}. \tag{2-3}$$

For $p_g > p_l$, the pressure inside the bubble exceeds the pressure from outside. For geometries that more complex, the two principal radii of curvature, r_1 and r_2, are used:

$$\Delta p = 2\sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{2-4}$$

From the *Young-Laplace* equation (2-3) it follows, that the gas pressure in a small bubble is higher than the pressure in a large bubble. Therefore, the gas will tend to diffuse from the smaller bubble into the larger one, a process which is termed as disproportion. Prerequisite for a nucleus of a radius *r* to grow is the presence of an excess gas pressure (Δp) sufficient high to overcome the surface tension σ between the gas and the bulk. If this is not reached, the nucleus shrinks and disappears. For the pressure given by the *Young-Laplace* equation (2-3), a nucleus needs a critical radius r^* to be able to grow:

$$r^* = \frac{2\sigma}{\Delta p}. \tag{2-5}$$

By transition of a single to a two-phase metastable state, e.g. by quench from a high temperature or change of pressure, a second phase nucleates, grows, and coarsens. The nucleation of the second phase is driven by the reduction of energy of the single phase system by second phase formation, thus forming nanometer-sized precipitates of the new phase. Nuclei grow due to diffusion of heat away from the nucleus into the matrix, or by mass diffusion from the matrix to the nuclei, resulting in a dispersion of second phase particles in a matrix [113].

According to *Park et al.*, to obtain the maximum number of nuclei to form, an ideal rapid pressure drop is required [114], as illustrated in Figure 2.2-1 [110]. In reality, the pressure drop proceeds over a period of time (e.g. < 2 seconds). A certain amount of nuclei forms and grows at t_1, while at t_2 more nuclei forms, but comparably less facing the competition from nucleation and growth at t_1. This illustrates the necessity of a rapid pressure drop to obtain homogeneous cell morphology based on a simultaneous nuclei development. Consequently, nuclei of various size would result in a non-homogeneous cell structure.

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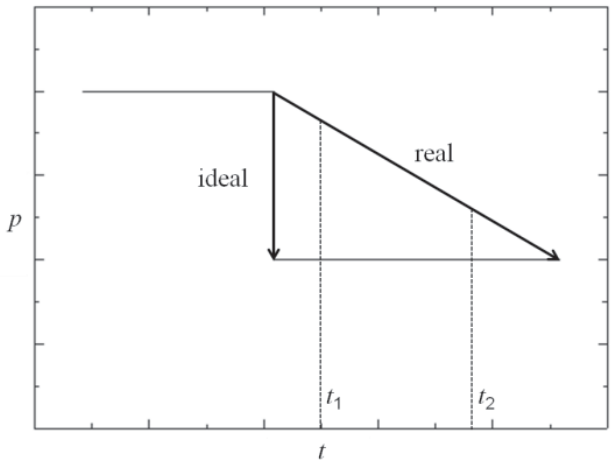

Figure 2.2-1: Schematic diagram of an ideal and a real pressure drop during the initial stage of foaming (redrawn after [110]).

In the classical nucleation theory (CNT), the cell nucleation rate (N_{nucl}) is given by (2-6):

$$N_{nucl} = f_0 C_0 \exp\left(\frac{-\Delta G_{nucl}}{kT}\right), \tag{2-6}$$

where f_0 is the frequency factor of gas molecules joining the nucleus, C_0 the concentration of gas molecules, k the *Boltzmann* constant, T the temperature in Kelvin, and ΔG_{nucl}, the *Gibbs* free energy (activation energy barrier) for homogeneous nucleation, which is defined as:

$$\Delta G_{nucl} = \frac{16\,\pi\sigma_{bp}^3}{3\Delta p^2}, \tag{2-7}$$

where σ_{bp} is the surface energy of the bubble-polymer-interface and Δp as the gas pressure used to diffuse the gas in the polymer [109].

These equations predict that for a larger pressure drop the cell nucleation rate will increase. Assuming an instantaneous pressure drop and an instantaneous nucleation, the nucleation rate and the number of nucleated cells should correspond. For a constant pressure drop with an instantaneous pressure drop rate, the cell density should therefore be constant.

In reality, the pressure drop is not performed instantaneous but proceeds over a finite time period. It is therefore expected, that the nucleation time period is affected by the time period over which the thermodynamic instability is induced in the system, and, that the pressure drop rate will affect the nucleation time period and therefore affect the nucleation rate, leading to competition between these two mechanisms [114, 115].

As bubbles grow, foam structure changes: first, small dispersed spheres in a matrix resemble a small reduction in density, which is further reduced by bubble growth, reaching lowest density when (still) spherical bubbles are arranged in a close packed structure. Thereafter, further cell growth involves formation of polyhedral cell structures. Depending on viscosity and surface

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tension, material flows towards intersecting cells to form junctions of tricuspid cross-sections. Finally, rupture of cell wall may occur, resulting in an open-cellular structure [116].

Foam stability is determined and depends on the interplay of a number of factors such as gravity drainage, capillary suction, surface elasticity, viscosity (bulk and surface), electric, double-layer repulsion, dispersion force attraction, and steric repulsion, involving bulk solution and interfacial properties [117].

Within the last years, the application of foamed plastics has significantly expanded and diversified. Apart from a low consumption of raw materials, positive product qualities such as low density, outstanding heat and sound insulation, mechanical damping, low water vapor permeability and reduced absorption of humidity are unique characteristics of this class of material. Following different approaches, open-cellular, closed cellular, or integral foams can be produced. Some of the most important applications for foamed products can be found in the fields of packaging, insulation, and sound insulation [118].

To produce low densities and a homogenous foam structure, physical blowing agents are used. Furthermore, compared to chemical blowing agents, they usually enable better process stability at lower costs.

Relative foam density refers to the volume fraction of polymer in foam. Low density foams exhibit volume fractions of polymer below 0.1 [116].

2.2.2 Blowing agent

A blowing agent is defined as a substance that produces a cellular structure in a polymer matrix. Blowing agents include gases that expand when pressure is released, liquids that develop cell walls upon change to gaseous state, and chemical agents that decompose or react under the influence of heat or catalyst to form a gas.

The blowing agent is a key parameter in controlling foam density, cellular microstructure and foam morphology, thus defining end-use performance.

In closed-cell structure, the blowing agent can be retained in the cellular foam structure until it diffuses out. The rate of diffusion can be up to years, thus being interesting for insulation purpose. In contrast, the blowing agent can escape immediately after the foam formation, or can form an intermediate stage.

Physical blowing agents provide gas for expansion of polymers by change in physical state. This may involve volatilization (boiling) of a liquid, or the release of a compressed gas to atmospheric pressure after being incorporated into a polymer (at elevated temperature and pressure). Common gaseous physical blowing agents are the inert gases carbon dioxide (CO_2)

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