Physics of breadmaking

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Physics of breadmaking

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Stellingen

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1. In brooddeeg gemaakt van bloem, water, zout en gist vormen de oppervlakte-eigenschappen van het gas-deeg oppervlak niet de belangrijkste faktor voor het verkrijgen van een groot broodvolume en een fijne kruimstruktuur.
Dit proefschrift

2. Suspensies van emulgatoren als SSL en DATEM in water kunnen een zeer hoge oppervlakte-dilatatiemodulus bezitten, nadat het oppervlak bij kamertemperatuur een mechanische behandeling heeft ondergaan. Dit verklaart deels de werking van SSL en DATEM als broodverbetermiddel.
Dit proefschrift

3. Dynamische metingen aan bloemdegen met dure apparatuur zijn eerder geschikt ter bevrediging van de onderzoeker dan om direkte informatie te verkrijgen over de bakkwaliteit van tarwe.

4. Het hoger gashoudend vermogen en de fijnere kruimstruktuur van goed bakkende tarwebloem, vergeleken met die van slecht bakkende, kan grotendeels worden verklaard door de verschillen in rekversteviging, biaxiale rekspanning en uitrekbaarheid van het deeg rond de expanderende gasbellen.
Dit proefschrift, Van Vliet et al., J. Texture Studies, 23, 1992, 439-460.

5. De bewering van He en Hoseney dat de druk in de gasbellen in een deeg van slecht bakkende tarwebloem zo hoog wordt dat het koolzuur eerder naar de omgeving zal diffunderen dan naar de gasbellen, is onjuist.
He and Hoseney, Cereal Chem., 69, 1992, 1-6.

6. De aanduiding 'Deze verpakking is biologisch afbreekbaar', zegt net zo weinig als bijvoorbeeld 'Kaas gedraagt zich als een vloeistof'. De tijdschaal waarover de processen verlopen, is van belang om de juistheid van deze beweringen te kunnen beoordelen.

7. De stabilisering van CO_2-emissies door geïndustrialiseerde landen in het jaar 2000, zoals voorgeschreven in het VN-klimaatverdrag, is een utopie.
'Scanning the future, a long-term scenario study of the world economy 1990-2015', Centraal Plan Bureau, SDU, Den Haag, 1992.

8. In tegenstelling tot wat eerder verondersteld werd, blijkt hydroxymethylfurfural stabiel te zijn tijdens verhitten.
H.E. Berg, Reactions of lactose during heat treatment of milk: a quantitative study, Ph.D. thesis, 1993.

9. Bij de bepaling van de grootteverdeling van tomatencellen met de natzeefmethode, zoals uitgevoerd door Tanglertpaibul en Rao, is geen rekening gehouden met de vervormbaarheid van de cellen.
Tanglertpaibul and Rao, 1987, J. Food Sci., 52, 141-145.

10. Veel bedrijven vinden het gepromoveerd zijn van een toekomstig werknemer minder belangrijk dan werkervaring. Blijkbaar beseffen zij niet wat de werkzaamheden van een AIO zoal kunnen inhouden.
'Werkervaring belangrijker dan proefschrift', Intermediair, 22 oktober 1993.

11. In de Nederlandse landbouw is het gebruikelijk dat in tijden van slechte economische resultaten de agrarische ondernemers een stuk harder gaan werken maar daarmee minder verdienen.

12. Gelukkig voor al die mensen die voor hun kraanwater op Rijnwater zijn aangewezen, kan door Hirst et al niet aangetoond worden dat de struktuur van water een "geheugen" heeft, hetgeen eerder beweerd werd.
'Het geheugen van water (slot)', De Volkskrant, 11 december 1993.
Hirst et al, Nature, 366, 9 december 1993. Davenas et al, Nature 333, 30 juni 1988.

13. Het oudste en het op één-na-oudste beroep hebben elkaar niet noodzakelijkerwijze al die tijd in stand gehouden.
"Bakker, het op één-na-oudste beroep (...)" in 'Bakker wordt nooit knoppendrukker'.
De Gelderlander, 18 juni 1993.

14. Men kan zich afvragen wat bedoeld wordt met de slogan "Brood, daar zit wat in!" als men weet dat brood ruim 75% lucht bevat en het resterende deel voor minstens 40% uit water bestaat.

Stellingen bij het proefschrift "Physics of breadmaking" door J.J. Kokelaar.
Wageningen, 15 februari 1994

voor mijn ouders

Abstract

Kokelaar, J.J. (1994). Physics of breadmaking. Ph.D. thesis, Wageningen Agricultural University, Wageningen, The Netherlands. (pp. 129, English, French and Dutch summaries).

Keywords:
Dough, gluten, wheat lipids, surfactants, emulsifiers, SSL, DATEM, gas bubble behaviour, surface rheology, bulk rheology, breadmaking.

Abstract:

Bread dough is a foam and the stability of the gas bubbles towards disproportionation and coalescence during the breadmaking process determines for a large part the final appearance of the baked bread with respect to crumb structure and loaf volume. Gas bubble behaviour in bread dough is determined by both surface and bulk rheological properties of dough (components). These properties were studied and their relevance to breadmaking was established.

Surface dilational moduli of different dough components were determined. It appears that wheat lipids and added surfactants as SSL and DATEM can retard disproportionation to a large extent if these components are present in the right concentration and modification. Wheat proteins will hardly retard this foam instability mechanism.

Dynamic measurements and biaxial extension tests on wheat and rye flour as well as wheat gluten doughs were performed. Both flour and gluten doughs show strain hardening at 20 and at 55 °C. Wheat cultivars with good breadmaking performance exhibit stronger strain hardening properties than poor baking ones and rye. Next to strain hardening, biaxial stress and extensibility are important parameters determining bread quality.

During mixing both the surface tension and the viscosity of the dough determine the (minimum) radii of the entrapped gas bubbles. Directly after mixing surface properties dominate primarily gas bubble behaviour by retarding disproportionation, especially if surfactants like SSL or DATEM are added. Already during first proof bulk properties, especially biaxial stress, extensibility and strain hardening, start to dominate gas bubble stability and this remains as such during almost the remainder of the breadmaking process. In the final stage of oven rise surface properties may contribute to the stability of some dough films that have become very thin.

Voorwoord

Het proefschrift is af en het is tijd geworden om iedereen die op één of andere manier bij dit onderzoek betrokken is geweest eervol te vermelden.

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Als doctoraalstudent hebben Netty van Marle, Ariette Matser, Gerard de Jong, Frank Boerboom en Marina Rombouts een bijdrage geleverd. In het kader van een afstudeeropdracht van de IAH-Larenstein heeft Annette van Koutrik aan het onderzoek meegewerkt. Allemaal bedankt voor jullie inzet.

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Gist-brocades BV in Delft heeft een financiële bijdrage aan dit onderzoek geleverd. Johan Plijter was namens dit bedrijf bij het onderzoek betrokken en de samenwerking was prima.

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Anita

Contents

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5 Relevance of surface and bulk rheological properties to breadmaking

Chapter 1

General introduction

Wheat has been used as a food since early history. Compared to other cereals it has unique properties which makes it very suitable for breadmaking (1.1). All wheat components have an effect on the final baked product but it is generally accepted that gluten proteins determine for the largest part bread quality (1.2). The breadmaking process can be divided into three main stages: mixing, fermentation and baking (1.3) and it can be seen as a combination of many chemical and physical subprocesses (1.4). In this thesis bread dough is considered as a foam. Two physical mechanisms which strongly affect the final foam are disproportionation and coalescence of gas bubbles. The aim of the study is to determine the contribution of both surface and bulk rheological properties of dough to foam stability and to establish the relevance of these properties to breadmaking (1.5).

1.1 Wheat and bread

Wheat is one of the oldest crops cultivated by man and it is the most abundant food crop worldwide. There is evidence that the wheat plant developed from a type of wild grass native to the Middle East (Orth and Schellenberger, 1988). A large number of products can be made of wheat including cakes, cookies, pasta and breakfast cereals. The most important use of wheat flour is in breadmaking.

Wheat is unique amongst other cereals in several aspects (Hoseney and Rogers, 1990). First, when it is mixed with water it can form a cohesive dough with viscoelastic properties. A second unique aspect, related to the first, is that wheat flour dough is, more than any other cereal flour dough, able to retain gas during the breadmaking process. This is essential for producing light, spongy products with a regular crumb structure. Thirdly, wheat flour dough sets in the oven during baking due to the gelatinization of the starch and changes that occur in a part of the proteins (Bloksma, 1990). Although in general all wheat flours have bread making potential, using different wheat cultivars may lead to large differences in bread quality. Important quality requirements a leavened bread has to meet are a high volume, a fine and regular crumb structure, a firm crust with the right colour and a low staling rate. Other quality characteristics comprise taste, flavour and nutritional aspects. A high loaf volume and a fine crumb structure are determined for a large part by the behaviour of the gas bubbles in dough throughout the whole breadmaking process.

1.2 Wheat flour composition

Before use the wheat granules are milled into flour, bran and germ. More detailed information about milling of wheat can be found in e.g. Bass (1988). White flour, mainly consisting of the starchy endosperm of the kernel, contains three major components viz. carbohydrates (70-80%), proteins (8-18%) and lipids (1.5-2.5%) all expressed as percentage on dry flour (MacRitchie, 1984). Non-starch polysaccharides (2-3% of the dry flour) are mainly originating from cell wall material (Meuser and Suckow, 1986).

Starch is the most abundant component of wheat flour and it consists of two populations of starch granules with different size: the large, lenticular (A-type) granules having diameters from 14-40 μm, and the small, spherical (B-type) granules with a diameter from 1-10 μm (Evers, 1971). In fact, starch is the most essential component in wheat flour for breadmaking. It is impossible to bake bread, with an acceptable crumb structure, without starch whereas the protein fraction can be replaced by gelforming materials like guar (de Ruiter, 1986).

Wheat protein is regarded as the most important factor determining bread quality with respect to crumb structure and loaf volume, especially one part of the protein fraction, the gluten proteins. Traditionally, wheat proteins have been classified into four types based on their solubility (Osborne, 1907): albumins, soluble in water; globulins, soluble in salt solutions; gliadins (prolamins), soluble in 70% (v/v) ethanol and glutenins (glutelins), soluble in dilute acid or alkali. The names of the protein fractions as given by Osborne are still in use today, although the composition of especially gliadin and glutenin is not always clear. Gliadins and glutenins, the gluten proteins, represent ca. 80% of the total proteins in flour (Wrigley and Bietz, 1988). The gliadin proteins are rather small, 30 to 75 kDa in molecular weight (Shewry et al., 1986), and single chained. When isolated, wet gliadins are very sticky (Hoseney and Rogers, 1990). The glutenin molecules are much larger and consist of subunits with a molecular weight of 30-145 kDa (Bietz and Wall, 1972; Bietz et al., 1975). The molecules are mainly polymerized by head-to-tail disulphide bonds without cross-links in between the different polymer chains (Ewart, 1979) or with only a few (Graveland et al., 1985). Polymers with a molecular weight of a few hundred thousands to 20 million have been reported (Huebner and Wall, 1980).

Although minor in weight percentage, wheat lipids have a great effect on baking performance. Especially the polar lipids are benificial while the non-polar fraction is detrimental (MacRitchie, 1983).

Non-starch polysaccharides also form a minor part of wheat flour. Since this fraction consist for the larger part of arabinoxylans the term pentosans is used often (Lineback and Rasper, 1988). To a certain extent this component also contributes to the baking performance of a flour (Meuser and Suckow, 1986). It has a high water binding capacity and 23% of the water in dough is said to be associated by the non-starch polysaccharides (Jelaca and Hlynka, 1971; Kim and d'Appalonia, 1977). The mechanism of how they affect the breadmaking process is not yet clear (Gruppen, 1992).

Gluten

Gliadin and glutenin are the so-called gluten proteins. Gluten (Latin for glue) can be obtained by rinsing a dough with water until most of the albumins, globulins and the starch are removed. The remaining gluten ball consists for the larger part of gliadins and glutenins (75-85% of dry weight). The remaining part of the gluten consists mainly of carbohydrates (10-15%) and lipids (5-10%) (Wrigley and Bietz, 1988). In bread dough the gluten proteins form a network through the whole dough and this network is able to retain water, starch granules and the entrapped and expanding gas bubbles.

Up to now several models for gluten structure in dough have been proposed in order to explain its viscoelasticity. One of these models assumes a continuous network of proteins connected through disulphide bridges formed during dough development (Bietz and Huebner, 1980). Thiol-disulphide interchange reactions could explain the viscous flow of dough (Bloksma, 1975) while the permanent crosslinks are said to be responsible for the elastic deformation. Ewart (1979) has proposed the linear glutenin model where glutenin molecules are interconnected head to tail to form a large molecule. According to Amend and Belitz (1989 and 1990), the protein strands in gluten, formed by wetting the flour, are extended and torn apart into films which form layers or sheets during mixing. Hydrogen bonding is also considered to be important in gluten proteins. For instance, solvatation of gluten in D_2O instead of H_2O increases the gluten strength due to a higher strength of the deuterium bonds compared to hydrogen bonds (Tkachuk and Hlynka, 1968; Inda and Rha, 1982, 1991). Due to the low charge of the gluten proteins hydrophobic interactions are present as well.

As is said before, gluten is known as the main varying factor between cultivars in determining bread quality. Both quantity and quality of the proteins play a role. Therefore a lot of research has been done to elucidate the mechanism behind it (e.g. Tkachuk and Bushuk, 1991; Janssen, 1992). However, up to now, the way in which all the gluten components interact to give bread dough its unique structure is still largely unknown.

1.3 Breadmaking

Orth and Schellenberger (1988) have reviewed the history of the use of wheat as a food crop. Written references to breadmaking date back to about 2600 B.C.. The ancient Egyptians perfected the art of breadmaking. Baking was also a serious craft during the classical period of Greek and Roman domination of Western civilization. New and different baked products were developed after the Industrial Revolution. Over the years bread shapes have not changed very much, but the larger available variety of ingredients like e.g. fats, eggs, spices as well as the increased use of mixtures with other flours such as barley, rye, rice and soy have allowed the introduction of a great diversity in baked products.

The basic formulation for breadmaking has not changed very much throughout the centuries. Bread is still mainly composed of flour, water, yeast and salt. New is that often oxidants and/or emulsifiers are added. In general, the breadmaking process can be divided into three main stages:

- Mixing and kneading of the ingredients into dough. In this thesis the term mixing will be used.
- Fermentation period also called proof which can be divided into first proof, pan proof and final (or tin) proof. The proof periods are interrupted by several punching and moulding operations.
- Baking, starting with the oven rise, also called oven proof or oven spring.

The most significant aim of the mixing step is the formation of the gluten network and the occlusion of air bubbles (Bloksma, 1990). The resistance of the dough against deformation during mixing increases to a maximum first and starts to decrease upon further mixing later. If the dough is mixed too long overmixing can occur. The fact that overmixing does not occur if dough is mixed under nitrogen (Baker and Mize, 1937) implies that it is the result of an oxidation process, although its explanation is not completely clear.

During the fermentation period the yeast produces carbon dioxide which diffuses into the gas bubbles and so causing them to expand. In this step the dough pieces may undergo several punching, rounding and moulding steps.

These last operations cause the removal of a part of the carbon dioxide and the subdivision of gas cells. Next, the dough is placed into bread pans (tins) and after a final proof period the loaves are transferred into the oven for the last step of the process: baking. During this process the gas cells expand further due to an increase in yeast activity, the formation of water vapour and thermal expansion of the gas (Bloksma, 1986).

The duration of the complete breadmaking process depends very much on the process chosen. Large differences occur between practices in different countries and also between bakeries in one country. The process may vary from about 3 hours in a standard Dutch process to less than 90 minutes in the Chorleywood Breadmaking Process (Bell et al., 1977).

Flour improvers such as ascorbic acid or potassium bromate are usually added in most countries. Due to the oxidative action, probably involving protein sulphhydryl and disulphide groups, cross-linking of the protein chains occurs. This could be the explanation for the observed decrease in extensibility of the dough and an increase of dough resistance to extension (Fitchett and Frazier, 1986; Mailhot and Patton, 1988). Often lipid-like components are added such as shortenings (a mixture of fats) and emulsifiers which are examples of bread improvers. Doughs containing fats or emulsifiers continue to expand longer in the oven than doughs without these additives (Tamstorf et al., 1986) thus resulting in a higher bread volume. Emulsifiers such as diacetyl tartaric acid esters of monoglycerides (DATEM) and sodium stearoyl-2-lactylate (SSL) are also called dough strengtheners because fermenting doughs containing such an additive have a higher shock resistance (Krog, 1990) which can be essential for instance during transport into the oven.

1.4 Physics of breadmaking

Breadmaking is both a chemical and a physical process: chemical because of the formation of cross-links between protein chains by S-S S-H interchange, the action of oxidants, the reactions between different components in the dough and the transformation of sugars into carbon dioxide and ethanol by the yeast. The development of flavours and the browning of the crust are also results of chemical reactions. However, above all, breadmaking is a physical process consisting of different subprocesses which will be discussed in short.

At the start of breadmaking the flour particles are wetted. The water together with mechanical treatment cause the (gluten) proteins to change from a hard glassy material in a rubbery and deformable one. Water vapour sorption behaviour of wheat gluten has been studied by e.g. De Jong et al. (1993). Later on, a transport of CO_2, ethanol and water vapour from the dough into the gas cells occurs if their saturation concentration in the dough is exceeded. Gas transport between the bubbles occurs during disproportionation. During the breadmaking process, transport of surface active components like proteins and lipids to and from the gas-dough interface will occur as well.

Examples of some other subprocesses are the subdivision of gas bubbles during mixing due to shear forces in the dough, the expansion of the gas bubbles due to overpressure in them resulting in the extension of both the dough mass and the surface layer around the bubble. The possible rupture of (gelatinized) dough membranes is also an aspect worth considering and depends on the mechanical properties of the dough at large deformations.

During baking heat is transported from the outside of the dough towards the inside mainly by convection: the presence of the gas bubbles facilitates the transport of heat because water evaporates at the warmer side of the gas bubble and condensates again at the colder side of it (Sluimer, 1986).

Bread dough consists of a continuous network of proteins containing water, starch granules, yeast cells, gas bubbles and other components. Because of the presence of gas bubbles in a continuous "liquid" dough mass, dough is a foam. During breadmaking the gas bubbles present in the dough are disturbed continuously. First strongly during mixing and kneading and later due to continuous expansion in the fermentation stage. The bubbles are broken up further during moulding operations and expand again during final proof and oven rise. Different deformations and deformation rates play a part during these processes.

The behaviour of the gas bubbles in dough determines mainly the final appearance of the bread crumb and the bread volume. Many small gas bubbles should be entrapped and enough of them should be held in the dough despite of all the intermediate moulding and rounding steps. During fermentation and oven rise the gas bubbles should stay apart from each other and no severe coalescence should occur before the dough sets due to starch gelatinization in order to prevent either the formation of a coarse crumb structure and the loss of gass leading to a low bread volume. Both the surface layer and the dough around the gas cell may exert a certain resistance against this expansion. The magnitude of it is important with respect to bubble growth rate and bubble stability.

1.5 Aim and outline of this thesis

When this study started the aim was to estimate the contribution of the properties of the gas-dough interface to the gas bubble stability in bread dough.

Especially, the role of the gluten was to be studied since this was known as a compositional factor determining bread quality. Additionally, the surface properties of certain surfactants often added to the other dough ingredients were to be studied since it was believed that these components would improve bread quality by their behaviour in the gas-dough interface. It was clear that the contribution of the surface properties could not be judged in the right way without knowing more about the bulk rheological properties of dough under breadmaking conditions. Therefore, this aspect was studied as well.

Flours of 4 wheat cultivars with pronounced differences in baking performance were used to relate the results found to baking quality. The results of the baking test as well as the effect of the added surfactant SSL (often used as a bread improver in daily practice in bakeries) are shown in figure 1.1.

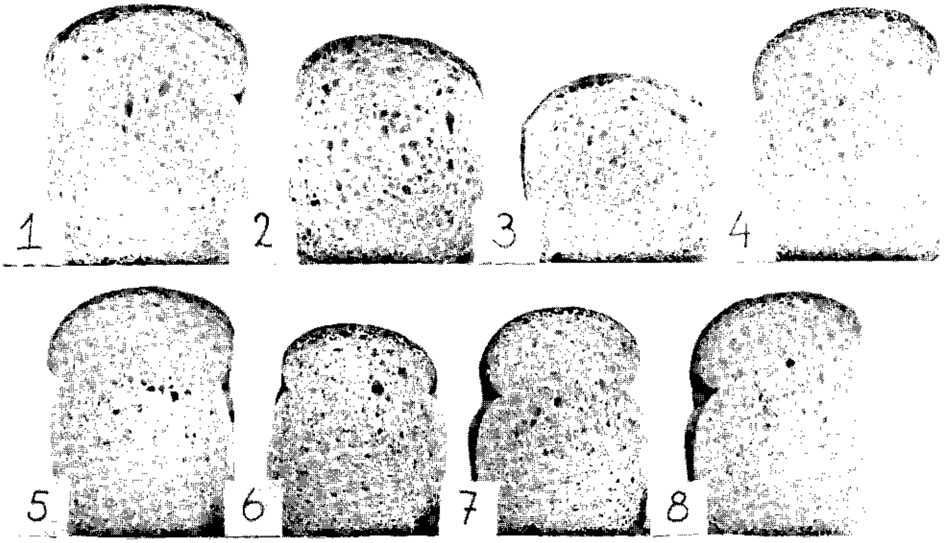

***Figure 1.1** Bread baked from 4 different wheat flours used in this study without (upper row) and with added SSL (0.25% on flour basis) (lower row). Explanation of numbers: 1+5: Spring, 2+6: Taurus, 3+7: Arminda and 4+8: Vedette wheat flour*

In chapter 2 general foam making and stability principles are discussed, followed by an overview of gas bubble behaviour in bread dough. This gas bubble behaviour is determined by both the surface and the bulk rheological properties of the dough. Surface properties of dough components as gluten, wheat lipids and the surfactants SSL and DATEM are presented in chapter 3. In this chapter, DSC and X-ray measurements of two emulsifiers are also discussed. These measurements were performed to get more information about the structure of the added surfactants in the presence of water. In chapter 4 bulk rheological properties of flour and gluten doughs of 4 wheat cultivars with different baking performance as well as those of rye flour dough are presented. Next to the results of fundamental tests those of more empirical ones are given. The contribution of both types of rheological properties to the stability of gas bubbles during breadmaking are discussed in chapter 5. In this last chapter the main conclusions of this thesis are also given.

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Chapter 2

Gas bubble behaviour in bread dough

Bread dough can be considered as a foam. The stability of the gas bubbles in this foam is affected by different instability mechanisms (2.1). The behaviour of the gas bubbles, or cells, in dough during mixing, fermentation and baking determines the final appearance of the baked bread. This behaviour is largely determined by the surface and bulk rheological as well as the fracture properties of the dough (2.2). An attempt is made to formulate the physical requirements a dough has to meet for good breadmaking performance (2.3).

2.1 Foam stability in general

Bread dough can be considered as a foam; during mixing of the dough ingredients, small air bubbles are entrapped and held by the dough matrix. During the fermentation stage and the oven rise air bubbles grow out and the foam, containing a low volume fraction spherical gas cells, is transformed to a foam with probably even a polyhedric structure. Only in the last stage of the oven rise the dough-foam structure becomes a bread-sponge structure. Before going into detail about the gas bubble behaviour in bread dough, general foam stability principles will be discussed as far as they are relevant for dough.

2.1.1 Foam making

A foam can be prepared by beating air into a given amount of liquid. Moreover, during the mixing process the relatively large air bubbles entrapped are broken up into smaller ones. The bubbles are elongated under the influence of the stress σ exerted by the moving mass. This elongation is counteracted by the Laplace pressure inside the bubble ΔP, which is given by:

$$\Delta P = \frac{2\gamma}{r} \tag{2.1}$$

in which γ is the surface tension and r is the bubble radius. This implies that the local stress σ applied has to be larger than the Laplace pressure before smaller bubbles are formed. For shear flow this can be expressed as:

$$\sigma = \frac{dv_x}{dy}\eta^* \geq \frac{2\gamma}{r} \tag{2.2}$$

in which dv_x/dy is the shear rate and η^* is the apparent shear viscosity. In reality the flow pattern during mixing will be a combination of rotational, shear and elongational flow. So, assuming that mixing time is long enough, the final size of the bubbles will be determined by the following factors: the local shear rate of the "liquid" caused by the moving mixing rod, the (apparent) viscosity and the surface tension of the liquid. The surface tension in expansion is the most relevant parameter. The bubbles will be broken up until an equilibrium between the shear stress and the Laplace pressure is reached, assuming that no substantial coalescence between bubbles occur afterwards. If elongational flow is considered in disrupting the bubbles the elongational viscosity of the liquid must be taken. The effect of this on bubble size is discussed in section 2.2.

2.1.2 Foam stability

The three most important instability mechanisms which play a part in determining the stability of gas bubbles in a foam are creaming, disproportionation and coalescence (Prins, 1988).

Creaming

Gas bubbles may cream as a result of buoyancy. The surrounding liquid exerts a viscous resistance on a moving bubble. If the viscosity of the liquid is high, the bubbles will only rise slowly through the fluid. In the case of bread dough the viscosity is so high that creaming does not play a part on the time scale of the breadmaking process (Bloksma, 1990a).

Disproportionation

The growth of larger bubbles at the expense of smaller ones is called disproportionation. The driving force of this process is the difference in Laplace pressure inside the bubbles, which causes that the gas concentration around a smaller bubble is higher than around a larger one. As a result a gas concentration gradient in the liquid between the bubbles occurs, causing gas diffusion from a small bubble to a larger one. This process is self-accelerating because the smaller the gas bubbles are, the higher the Laplace pressure in them will be. The rate at which a small isolated bubble near a much larger bubble diminishes and eventually disappears can be derived from the de Vries equation (de Vries, 1958):

$$r_t^2 = r_0^2 - \frac{4RTDS\gamma}{P_0 h} t \qquad (2.3)$$

where r_t is the bubble radius at time t and r_0 is the bubble radius at time $t = 0$. R is the gas constant, T the temperature, D the diffusion coefficient and P_0 the atmospheric pressure. The solubility of the diffusing gas S as well as the thickness of the film h between the bubble and the environment are important variables. During disproportionation in a bread dough equation 2.3 will not give the exact rate but it illustrates the important variables.

In this equation it has been assumed that the surface tension of the shrinking bubble surface has a constant value. However, in most food foams surface active materials like proteins and lipids are present. Because adsorption and desorption of surface active material after a change in surface area takes some time, a change in surface tension at expansion or compression of the surface will normally occur (Prins, 1988). A way to express this behaviour of the surface is by the next equation:

$$\Delta\gamma = \eta_s^d \frac{d \ln A}{dt} \qquad (2.4)$$

where η_s^d is the surface dilational viscosity and A is the surface area. η_s^d is a useful parameter to characterize the surface far from equilibrium while it is deformed at a certain rate. Ronteltap (1989) has extended the theory of de Vries by incorporating the surface dilational viscosity in it.

When during compression of a surface the surface tension becomes lower, the Laplace pressure inside the bubble will become lower as well. This leads to a slowing down of the disproportionation process because the difference in Laplace pressure (eq. 2.1) between the bubbles becomes smaller. Lucassen (1981) derived that the process can even be stopped if the surface dilational modulus E is larger than half the surface tension over the time scale considered.

$$E > \frac{\gamma}{2} \qquad (2.5)$$

where:

$$E = \frac{d\gamma}{d\ \ln A} \tag{2.6}$$

The surface dilational modulus E is a measure of the resistance of a surface against deformation. In other words, it is a measure of the 'stiffness' of the surface. The theory of Lucassen assumes that if the decrease (or increase) of surface tension outweighs the decrease (or increase) in bubble radius the driving force for disproportionation will vanish. The process will only stop completely if the surface behaviour is ideal elastic indicating that over the relevant time scale the surface dilational modulus is independent from the time scale. For viscoelastic surfaces, as mostly present around gas cells in foods, the surface dilational modulus contains an elastic and a viscous component (Lucassen and van den Tempel, 1972). The ratio between the viscous and the elastic component is called the loss tangent ($\tan\theta$). If the surface behaves ideal elastic then the loss tangent is equal to zero because the viscous component is zero. Both components depend on time scale, so E and $\tan\theta$ do as well. It is therefore important that E as defined by equation (2.6) should be taken at relevant time scales if we want to apply the results on situations in practice.

The viscoelasticity of a surface can be determined by means of a dynamic measurement in which an applied sinusoidal change in surface area causes a sinusoidal change in surface tension (see chapter 3).

For foams consisting of gas dispersed in a (nearly) Newtonian liquid, like beer foam, surface (rheological) properties play the most important role in foam stability problems. For a viscoelastic product, like bread dough, the mechanical (rheological and fracture) properties of the bulk must be taken into account as well. The relevant deformation type of the dough mass around a gas cell is biaxial extension in case of an expanding bubble (Luyten, 1988; Akkerman et al., 1990). This deformation gives rise to a biaxial stress σ_B. The building up of this stress may be important in determining bubble stability, certainly if the material around the expanding gas bubble exhibits so-called strain hardening (Kokelaar et al., 1993). Bread dough exhibits this behaviour which was shown by Janssen (1992). A material is strain hardening if the resistance of it against deformation (or strain) is higher for a relatively more extended test piece than for a relatively less extended one. So, σ_B must be known as a function of the biaxial strain ϵ_B and due to the viscoelasticity of dough also as a function of the strain rate $\dot{\epsilon}_B$ because the expansion rate is not constant throughout the breadmaking process (Bloksma, 1990a). The ratio of the biaxial stress and strain rate is called the (apparent) biaxial extensional viscosity η_{BE}.

$$\eta_{BE} = \frac{\sigma_B}{\dot{\epsilon}_B} \tag{2.7}$$

Coalescence

Coalescence in a foam is the merging of two gas bubbles caused by the rupture of the film between them. The rupture of a dilute liquid film can be induced by several mechanisms like a disturbance of the film causing local thin spots and the presence of hydrophobic or spreading particles (Prins, 1988). In case of a rising bread dough the films between the gas bubbles are continuously expanding and this must be taken into account when film stability mechanisms are discussed.

When a thin film is locally expanded, not enough surface active material may be present to restore the amount originally adsorbed. The depletion of surface active material causes an increase of the surface tension at further expansion of the film. It causes a thin film to have elastic properties due to the large surface area/volume ratio, the so called Gibbs film elasticity. The higher surface tension makes a further expansion of the thin film more difficult than that of a film which is not expanded. The Gibbs film elasticity E_f can be calculated using equation 2.8 (Lucassen, 1981).

$$E_f = -\frac{2\, d\gamma/d(\ln \Gamma)}{1+(1/2)h\ dc_b/d\Gamma} \tag{2.8}$$

where Γ is the adsorption of the surfactant, c_b the concentration of the surfactant in the bulk and h the film thickness. From 2.8 it is clear that film elasticity is higher for thinner films than for thicker films and it provides thin liquid films containing a surfactant with a stability mechanism. This was experimentally demonstrated by Prins et al. (1967). E_f depends on the concentration of surfactant in the film. If the concentration in the liquid is high enough E_f is equal to two times the surface dilational modulus E since a film has two surfaces. After stretching of a film to an extent where the surfactant concentration at the surface is lower than at the bulk-air interface in equilibrium, E_f is higher than 2E. During further stretching the concentration of surfactant at the interface can become so low that E_f decreases on further extension and eventually becomes almost 0 (Lucassen, 1981). If extension continues rupture occurs because the resistance against extension is then lower at the more extended spot than in the surrounding. Moreover, Prins (1976) has shown that a thin film which is being stretched always breaks as soon as γ exceeds a critical value γ_{cr}, which depends on the system.

In a liquid film a local thin spot can form, for example because of a sudden disturbance. If the Gibbs mechanism acts, this thin local spot has a higher surface tension than its surroundings resulting in a surface tension gradient. This causes a flow of liquid towards the thin spot which is called the Gibbs-Marangoni effect (Lucassen, 1981). This mechanism also works when a liquid film is stretched (Walstra, 1989).

The presence of a hydrophobic particle in a hydrophilic aqueous film contacting both surfaces causes the film surfaces to be forced into a convex shape. In this part of the film the Laplace pressure is higher and the liquid in the film starts to flow away from the particle leading to rupture of the film (Prins, 1988).

The presence of a particle containing spreadable material, for instance an emulsion droplet, can lead to film rupture if this particle reaches the surface. The spreading of material over the surface causes liquid to flow along with it and extensive spreading so may lead to film rupture if the penetration depth of the spreading motion is of the same order as film thickness (Prins, 1988).

In considering the stability of a dough film, bulk properties can play an essential role especially when the films are still relatively thick.

The resistance of a dough film to extension is built up of both surface and bulk forces.

* The surface component consists of the equilibrium surface tension of the film γ, which is the Gibbs free energy required to enlarge the surface, and an extra resistance due to the increase in surface tension $\Delta\gamma$. $\Delta\gamma$ depends on the surface dilational modulus E $(= d\gamma/d\ln A)$. Assuming linear behaviour, $\Delta\gamma = (\Delta A/A)E$. For non-linear behaviour (often at large deformations) E will depend on ΔA which is expressed in eq. 2.9 as $E(\Delta A)$.

* The bulk force is the biaxial tensile stress σ_B built up during biaxial extension of a film with thickness h.

So the contribution of both the surface and the bulk component is equal if:

$$2(\gamma + E(\Delta A)) = h\sigma_B \qquad (2.9)$$

In this way an estimate can be made of the film thickness h at which during thinning the surface properties become important compared to the rheological ones when the values of the relevant parameters are known. For thin films the Gibbs film elasticity E_f becomes the relevant parameter instead of 2E. However, for estimating h, E can be useful.

2.2 Gas bubble behaviour in bread dough

The incorporation and the behaviour of the gas bubbles in bread dough will be discussed successively for the three main stages in the breadmaking process, mixing, fermentation and baking.

Mixing

The mixing of the dough ingredients serves three, for breadmaking essential, purposes (Bloksma, 1990a). The first is to mix all ingredients: water, flour, salt and other additives, into a dough mass which is homogeneous on a macroscopic scale. The second important effect of mixing is the formation of a continuous protein network, often called gluten development. The specific mechanical properties of this mass facilitates that entrapped gas bubbles are held within the dough especially during the proofing stage.

The incorporation of air in the dough and the breaking up of large entrapped bubbles into smaller ones is a vital step in the breadmaking process. If the mixing time is too short, too few air bubbles are enclosed that can grow due to CO_2 production. The crumb structure and the loaf volume are for a large part determined by the occlusion of many small air cells during mixing which should be held separate from each other in the dough throughout the whole breadmaking process. After the ingredients have formed a continuous phase, gas cells are held in the dough and are broken up during further mixing. The air bubbles entrapped act as nuclei in which the CO_2 produced by the yeast cells will diffuse (Baker and Mize, 1941).

The breaking up of the air bubbles can occur by shear or elongational flow. A rough estimate of the resulting minimum gas cell radius can be made using equation (2.2). The shear rate of the dough during mixing is 10 to 50 s^{-1} and the apparent viscosity at these rates is 470 to 300 Pa.s (Bloksma, 1990a). It is not possible to measure the surface tension of dough itself but the equilibrium surface tension of a dough suspension is approximately 40 $mN.m^{-1}$ (Eliasson and Lundh, 1989; Evers et al., 1990; Sasaki et al., 1991). It would be more realistic to use the value of the surface tension in expansion which will be somewhat higher, but for an estimate of the bubble radius this difference is not so important. The minimum radius calculated using these values is 5 to 40 μm.

If we consider elongational flow in disrupting the bubbles we have to know the elongational viscosity of the dough at relevant strain rates. Dough is a non-Newtonian material which implies that the ratio of the elongational viscosity and the shear viscosity (Trouton ratio) exceeds 3. In the case of dough the ratio is of the order of 100 to 1000 (Bloksma, 1990a). Assuming the same values for the elongational strain rates as for the shear strain rates during mixing the minimum bubble radius obtained at elongational disruption would be 100 to 1000 times smaller than in shear flow giving about 0.005 to 0.4 μm. Such very small gas bubbles can not be detected using different microscopic techniques (Moss, 1972; Carlson and Bohlin, 1978) or image analysis (Campbell et al., 1991).

According to Campbell et al. (1991) the bubble size distribution directly after mixing is neither normal nor log-normal. The bubbles they observed had a radius of 20 to 200 μm. The smaller ones could have escaped from observation; the order of the radii reported is the same as calculated by applying equation (2.2).

An added surfactant like SSL (Sodium Stearoyl-2-Lactylate) lowers the interfacial tension between oil and water considerably (Krog, 1981) and will probably also lower the surface tension of the gas dough interface. This may lead to the occlusion of more and smaller air bubbles. The total volume of gas entrapped during mixing is said to be the same as in a dough without added emulsifiers (Junge and Hoseney, 1981).

Fermentation

After mixing, approximately 10% of the dough volume consists of occluded air (Bloksma, 1981, 1990b). The number of the gas bubbles is estimated to be between 10^{11} and 10^{14} m^{-3} (van Vliet et al., 1992). They reported that in a final bread the number of visible gas cells has diminished by a factor of 10^2 to 10^4. This implies that most gas cells have disappeared due to disproportionation or coalescence or have become so small that they are invisible to the naked eye.

The yeast cells in the dough already start to produce carbon dioxide (and ethanol) during mixing. They consume the oxygen dissolved in the dough and the O_2 in the bubbles will diffuse into the dough mass and will probably be consumed immediately as well. Mainly nitrogen and maybe a small amount of carbon dioxide produced will be present in the bubbles at the start of the proof period. This indicates that the gas composition in the bubbles is different from that in the dough. At first, some gas bubbles may grow against the Laplace pressure because more carbondioxide will diffuse into the gas cell than nitrogen into the dough phase. When the gas composition inside the bubbles becomes roughly in equilibrium with the local composition of the dissolved gas in the dough mass, the Laplace pressure difference between gas bubbles of different radii determines primarily the local differences in concentration of the different gasses. Then disproportionation becomes the dominant process leading to shrinking of the smaller bubbles.

Yeast cells need a short period to obtain maximum gas production but after a certain time they have produced so much CO_2 that the saturation concentration around certain bubbles is reached. According to Bloksma (1990a) there is a transition from a slow growth to a faster growth of the bubbles after about 1700 s (28 min) from the start of the fermentation period. Around the larger bubbles the equilibrium solubility of CO_2 is smaller due to a lower Laplace pressure than around smaller bubbles. Therefore larger bubbles will grow at a lower CO_2 concentration than smaller ones. This leads to an unequal growth of the bubbles and to a broader bubble size distribution.

There will be a critical radius below which a bubble will not grow at all during the fermentation period because the saturation concentration around these bubbles is not reached. If we assume a solubility of CO_2 of 4.3×10^{-2} kmoles/m^3 dough at one atmosphere ($=10^5$ Pa) (Bloksma, 1990a) then the solubility of the gas around a gas bubble is 4.3×10^{-7} kmoles/(m^3.Pa) x Laplace pressure ($2\gamma/r$). γ is 40 mN/m and the CO_2 production rate is taken as 2.5×10^{-5} kmoles/(m^3.s). Then the time t it takes before the saturation concentration around a bubble with a radius r is reached, is given by:

$$t = \frac{4.3\text{x}10^{-7}\ 2\gamma}{2.5\text{x}10^{-5}\ r} = \frac{1.38\text{x}10^{-3}}{r} \tag{2.10}$$

For a bubble filled with CO_2 and a radius of 10 μm it will take about 2 minutes before more carbon dioxide will diffuse into the bubble than out of it. For a bubble with a radius of 1 μm it will take 10 times longer before the saturation concentration will be reached assuming that no shrinking occurs during that time. Moreover, the gas produced will diffuse through the dough mass towards regions in the dough where the concentration is lower, i.e. around larger gas bubbles. This indicates that the smallest bubbles probably will not grow at all.

The bubbles which do not grow will probably not disappear. On the one side because of the presence of N_2 inside the bubbles which is rather insoluble in water (about 50 times less soluble than CO_2) and on the other side because E becomes higher than $\gamma/2$ (see section 2.1.2). Very small bubbles with a diameter of a few microns are observed in the dough membranes between two larger bubbles by for instance De Bruijne et al. (1990).

The relative volume of gas in a liquid can be defined as

$$\frac{V_l+V_g}{V_l} \tag{2.11}$$

where V_l is the volume of the liquid and V_g the volume of the gas. At the end of the fermentation period the relative volume is 4 to 5 and at the end of the oven rise 5 to 7 (Bloksma, 1990b). In a foam with a narrow gas bubble size distribution the bubbles would start to deform each other at a relative volume of about 3.3. This is not necessarily the case in bread dough. If the bubble size distribution in dough is broad the small bubbles will be accomodated in between larger ones. Besides, the smaller ones still can have a sperical form when the larger ones already start to deform each other. Probably, this will be more important in a poor quality bread loaf. In such a bread often the crumb structure shows the remnants of gas bubbles with all kind of different radii.

Van Vliet and others (1992) have calculated that during fermentation the surface area is enlarged by a factor of 5.4 in approximately 2 hours. In the fermentation stage the biaxial extensional strain rate is between 1.1×10^{-3} and 8.6×10^{-5} s^{-1}.

Baking

During baking temperature rises and the relative volume of the gas bubbles increases to between 5 and 7 due to several factors: increased production of carbon dioxide until the yeast cells are inactivated at about 50°C, evaporation of water, CO_2 and ethanol into the gas cells and thermal expansion of the gasses (Bloksma, 1990a). Initially, the gas bubbles expand faster at the outside of the dough than in the middle of the loaf because temperature increases faster at the outside. In several minutes the starch granules in the dough will start to swell and gelatinize, giving the membrane a more solid character. The expansion of the solid dough membrane will continue as a result of a further expansion of the gas phase until rupture occurs. It is questionable whether this happens before or after gluten protein cross-linking occurs (above 87°C (Attenburrow et al., 1990)) because the temperature increase is very fast. Probably, the changes in the proteins as a result of heating are not very essential for the solidification of the dough since it has already been shown that it is possible to make bread without gluten or other proteins (de Ruiter, 1986).

During baking the biaxial extension strain of the dough around the gas cell is said to be about 8×10^{-4} s^{-1} (van Vliet et al., 1992) but expansion of gas bubbles at the outside of the dough is faster since high temperatures are reached sooner at the outside of the dough than in the centre of it.

2.3 Physical requirements for good breadmaking performance

The main factors determining good breadmaking performance are: quality of the raw materials, the right recipe, good equipment like mixers for proper dough handling and a good oven and perhaps the most important: a qualified baker. From this point of view breadmaking seems quite simple. However, very subtle differences between the wheat cultivars used or for instance a slight change in the added amount of water can already induce large differences in the final bread quality.

This thesis handles about physics of breadmaking and in this section we will try to formulate qualitatively the physical requirements for obtaining a good quality bread. In chapter 5 we will give a more semi-quantitative discussion. Good quality is defined here as a loaf of bread with a high bread volume and a fine crumb structure, although there are other aspects (see section 1.1). Considering bread dough as a foam made from a viscoelastic material several conditions for good baking performance should be fulfilled during the breadmaking process. The requirements will be discussed for the different stages in the breadmaking process: mixing, fermentation and the oven stage which encompass a further rise and the transition of a foam into a sponge structure. The requirements will be divided in surface and bulk rheological ones. A summary of these requirements is given in tables 2.1 and 2.2 while a more extensive discussion per stage is given below.

***Table 2.1** Surface rheological properties required for good baking performance*

stage	surface tension		surface dil. viscosity η_s^d surface dilational modulus E or Gibbs elasticity E_f
	in expansion	in compression	
mixing	low	low	η_s^d: low
fermentation	high	low	E: high
baking	low/high*	irrelevant	E_f: high

* see text

Table 2.2 Bulk rheological properties required for good baking performance

stage	apparent viscosity	resistance to deformation	extensibility	strain hardening
mixing	above minimum	low	irrelevant	high
fermentation	above minimum	optimal	high	high
baking	above minimum	optimal	high	high

Mixing

During mixing breaking up of the gas cells will occur until an equilibrium between the shear and elongational forces applied by the dough mixer on the one hand and the Laplace pressure on the other is established. With equation 2.2 an estimation of the minimal bubble radius can be made. Regarding the surface properties, a low surface tension in expansion of the dough-air surface favours the production of small bubbles. If the surface tension in expansion is low than it will also be low in compression. The surface of a gas bubble should not exert much resistance to expansion so the surface dilational viscosity should be low.

Regarding the bulk properties, the apparent viscosity of the dough must be above a minimum value to prevent severe creaming. The viscosity is almost always high enough in breadmaking (Bloksma, 1990a). To entrap air bubbles easily, the resistance to deformation of the dough should be rather low. The strain to rupture is not a relevant requirement in this stage. The same can be said for strain hardening, although at a later stage of mixing strain hardening may already help in retarding disproportionation. The size distribution of the bubbles that grow out during fermentation should be narrow to get a uniform enlargement of the air bubbles during the rise period.

Fermentation

In the beginning of the fermentation stage disproportionation of the gas bubbles in the dough will be important and at the end of fermentation stage coalescence may occur.

Directly after mixing air bubbles with a diameter of 10 to 100 μm are present in the dough. Assuming a surface tension of the gas-dough interface of 40 mN/m, the Laplace pressure inside the bubbles is 1.6×10^4 to 1.6×10^3

N/m^2. This difference in Laplace pressure may lead to growth of the larger bubbles at the expense of the smaller ones. Disproportionation can be stopped or slowed down if the surface tension of the shrinking gas bubble decreases and stays low enough in compression. This will be the case if the surface dilational modulus is so high that it exceeds half the surface tension as was already mentioned in section 2.1.2. The surface dilational modulus should stay high enough during the time that shrinking of bubbles can take place. Theoretically this should be until the dough-foam structure becomes a sponge structure. For most breadmaking procedures used in The Netherlands this is approximately 2.5 hours. A high surface dilational modulus also indicates that the surface tension of a surface that is subjected to a small expansion is high.

There is an additional reason why disproportionation will stop. The deformation of the dough mass around the expanding bubble becomes so high that the increase in the stress in the dough due to strain hardening exceeds the stress due to the supersaturation of CO_2. This stress is somewhat higher than the Laplace pressure. The strain hardening mechanism contributes to a regular crumb structure: if the stress around an expanding bubble becomes too high the carbon dioxide will diffuse towards a smaller less expanded bubble which is near. Considering a dough layer around gas cells with initially the same thickness which are extended to a different extent, the more extended ones build up a higher resistance to further deformation. This higher resistance of the more extended layer implies that the less extended layer can be extended easier during further rise of the dough. This leads to a more regular foam structure because the relatively less expanded bubbles will grow easier than the relatively more expanded ones. Moreover, strain hardening is an important factor for preventing coalescence of gas cells due to rupture of the dough membrane in between.

The dough film between growing bubbles should have an optimal resistance against extension. If the resistance or stress is too high then only limited or no expansion of the dough will occur. This will lead to a low bread volume. If the resistance to extension is too low, the gas bubbles will expand very fast leading to early rupture and the formation of large holes in the bread. So the resistance may have an optimum value. Excessive gas loss will occur if the strain at which the films rupture is small.

Baking

During ovenrise bubble expansion is fast and the dough membranes become thin. Membranes must stay stable until the dough mass has become solid due to gelatinization of the starch.

For thin films in which surface properties may become important the surface tension should stay low in expansion to prevent spreading of surface active material. If no spreading material is present a high surface tension is favourable for stabilizing the film. The surface tension should not increase too much upon extension of the film because then the critical surface tension could be exceeded leading to rupture of the film. For very thin films the Gibbs elasticity should be high.

The strain hardening behaviour must also exist at higher temperatures and the resistance to biaxial extension must be optimal. Moreover, the fracture strain of the dough membranes must be large enough.

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Chapter 3

Surface rheological properties of dough components

Surface rheological properties of dough components may be important in determining final bread quality since these properties may contribute to the stability of gas bubbles in dough. In this chapter the principles of surface rheological measurements are presented as well as a short review of relevant literature (3.1). Various dough components were tested with different instruments applying either small deformations close to equilibrium to the surface, large deformations approaching a situation comparable to a continuous expanding bubble or both. The effect of NaCl, ethanol and of a higher temperature (45-50°C) was studied (3.2). In this study no differences in surface rheological properties of wheat cultivars with different baking performance could be found (3.3). Therefore it is concluded that surface rheological properties are not the main factor in determining bread quality. However, from the results of the sinusoidal oscillation tests (3.3.1) it is clear that certain dough components are effective in retarding disproportionation especially wheat lipids and added surfactants in the right concentration. It is shown that a suspension of the surfactants SSL and DATEM in water can exhibit very high surface dilational moduli after having undergone a mechanical treatment only. From the results of the continuous expansion tests (3.3.2) it appears that a surface containing all dough components shows a low resistance to expansion especially at more elevated temperatures. Values of surface tension during expansion are discussed with respect to the stability of thin dough films. The conclusions of this chapter are given in (3.4).

3.1 Introduction

As is mentioned in Chapter 2 surface properties of dough components may be important in relation to breadmaking since these properties will contribute to the final quality of the baked bread loaf.

During mixing of the dough air bubbles must be entrapped and for obtaining a fine crumb structure it is favourable that these air bubbles are broken up into very small ones. In this respect a low surface tension especially during expansion of the surface is required (see section 2.3).

In order to keep enough bubbles in the dough during the later stages of the breadmaking process disproportionation should proceed only to a certain extent and result in a minimum number of relatively large gas cells with a small size distribution. Coalescence of the bubbles should be prevented because severe coalescence can cause a low final bread volume and/or an irregular crumb, even with large holes in it. To prevent or slow down disproportionation it was shown that a high dilational modulus of the surface and a low surface tension during compression are favourable. To minimize coalescence the surface tension in expansion should be low if spreadable material is present. However, the building up of a surface tension gradient is favourable for film stabilization (see section 2.1.2).

During the baking stage in the oven especially coalescence must be prevented until the dough-foam structure becomes a bread-sponge structure and surface tension during expansion at higher temperatures may be of importance for dough film stability in the same way as for preventing coalescence during fermentation.

3.1.1 Surface rheology

Surface or interfacial rheology is that part of science which studies the change in forces acting in a surface as a result of an applied deformation of that surface over a certain time scale. Deformation can be dilational, bending and/or in shear. We will confine ourselves to dilational deformation and as a measure of the forces acting in the surface, surface tension differences will be taken. For a comprehensive review on surface rheology see van den Tempel (1977). The parameters which are useful for this study, such as the surface tension γ, the surface dilational viscosity η_s^d, the surface dilational modulus E and the Gibbs film elasticity E_f, have already been introduced in section 2.1.

3.1.2 Surface rheological measurements

Close to equilibrium

An example of a surface rheological measurement which is used to study the properties of a surface close to equilibrium is a sinusoidal oscillation test, often called dynamic measurements. This kind of test is useful as a tool to characterize the surface. The different parameters determined and their dependence on the frequency of surface deformation gives a characterization of the nature of the surface. By comparing the results with those of surfaces with a known composition one can get information whether a surface 'behaves' like a model surface containing e.g. soap, lipid or protein molecules.

To determine the surface dilational modulus a small sinusoidal dilational deformation is applied to the surface and the resulting sinusoidal change in surface tension is measured. For viscoelastic surfaces the surface dilational modulus is a complex parameter and consists of a real and an imaginary component (Lucassen and Van den Tempel, 1972):

$$|E| = \sqrt{E_d^2+(i\eta_d\ \omega)^2} \qquad (3.1)$$

where the real part is E_d, the elastic part, comparable to the storage modulus in bulk rheology (see section 4.1.2), and $i\eta_d.\omega$ is the imaginary part. The product $\eta_d.\omega$ is the viscous part of the modulus and comparable to the so called loss modulus. η_d should not be mixed up with η_s^d which is a parameter characterizing the properties of the surface during steady state expansion or compression far from equilibrium. The ratio between the viscous and the elastic part is equal to the *tangent of the loss angle (phase difference) between the applied sinusoidal* variation of the surface area and the resulting sinusoidal variation of the surface tension. If the surface behaves purely elastic the loss tangent is equal to zero.

$$\tan\theta = \frac{\eta_d\ \omega}{E_d} \qquad (3.2)$$

The viscoelasticity of a surface as a function of the time scale can be determined by measuring E as a function of the frequency of surface deformation. To allow an unambiguous interpretation of the results, measurements must be performed within the linear region so that experiments can be compared to each other. In this region the moduli do not depend on the magnitude of the applied surface area deformation.

Far from equilibrium

To characterize a surface far form equilibrium expansion or compression tests at constant deformation rate were done. In this study both type of tests were performed because the relevant types of deformation of the gas bubble surfaces in bread dough are expansion (during dough mixing, fermentation and oven rise) and compression (during mixing and disproportionation of the gas bubbles). These deformations are usually large in contrast to the small deformations applied in the oscillation tests.

Large deformations experiments are described by e.g. Ronteltap (1989) who studied beer surfaces using various methods like a falling film apparatus and an overflowing cylinder apparatus. The latter apparatus has been studied extensively by Bergink-Martens (1993) who also tested various surfactant solutions in it.

Ronteltap (1989) performed surface expansion experiments of beer surfaces in a Langmuir trough equipped with one barrier for single expansion or with an endless belt with six barriers to approach a situation of continuous steady state expansion. Compression measurements were done using the same apparatus. From the surface tension and the relative rate of expansion or compression, the surface dilational viscosity can be calculated using equation 2.4. Results from earlier experiments have shown that the value of η_s^d depends strongly on the value of dlnA/dt. For practical systems like beer and milk the dependence of η_s^d on dlnA/dt can be described by a power law function (Prins, 1990):

$$\log \eta_s^d = m \log \frac{\mathrm{dln}A}{dt} + n \qquad (3.3)$$

The absolute value of the surface dilational viscosity depends strongly on the value of n. The value of m characterizes the shear thinning behaviour of the surface. For a large number of practical systems such as coffee, beer, milk and cream it is found that the value of m is close to -1 but always somewhat higher (-0.95 for example). This implies strong shear thinning behaviour (Prins, 1990).

3.1.3 Surface rheological properties of dough components: literature

Several workers have mentioned a possible importance of surface properties of dough components in relation to gas bubble stability in dough (Carlson and Bohlin, 1978; Carlson, 1981; Bloksma, 1981; Lundh et al., 1988; Gan et al., 1990; Eliasson and Silverio, 1991; Eliasson et al., 1991; Sahi, 1993). Against this background the foaming behaviour of wheat protein solutions was studied by Mita et al. (1977, 1978) and of the aqueous phase of dough by MacRitchie (1976). Different techniques have been used to examine the surface properties of dough components but up to now mostly surface pressure-surface area (so-called π-A curves) have been determined. π is the difference between the surface tension of the used pure solvent (usually water) and the surface tension of the surfactant solution.

Often in this respect gluten proteins were studied because of their widely recognized role in determining bread quality. Sometimes the technique used was chosen because of the possibility to study the properties of the insoluble gluten proteins in a monolayer under different conditions (Tschoegl and Alexander, 1960a+b; Tao et al., 1989) or to study the interactions between gluten proteins and lipids (Hamer et al., 1991; Paternotte et al., 1993). In this section a review will be given of the relevant surface properties of dough components like proteins, lipids and surfactants.

Flour

Wheat flour particles, spread on a water surface, lower the surface tension due to the spreading of surface active material. According to Eliasson et al. (1991) the spread material consists of protein. The minimum equilibrium surface tension in compression is about 42 mN/m at 6.2×10^{-3} m^2/mg (Lundh et al., 1988). Evers et al. (1990) measured a surface tension of 50 to 55 mN/m at 5.6×10^{-3} m^2/mg without compression of the surface. It is very likely that lipids spread as well.

A 10% aqueous extract of flour has a surface tension of about 42 mN/m (Evers et al., 1990; Castle and Sahi, 1991). Sahi (1993) found that the surface tension of an extract of dough (dough liquor) of a poor baking flour was lower (35 mN/m) than the surface tension of a good baking flour (48.9 mN/m). This was caused for a large part by the higher amount of lipids in the dough liquor of the poor baking flour. According to Lindahl (1987) the equilibrium surface tension of the water soluble fraction of wheat flour at a concentration of 2 mg/ml was ca. 45 mN/m.

Gluten

Most of the experiments for determining the surface rheological properties of wheat proteins have been performed on whole gluten or on the two gluten fractions: gliadin and glutenin. Already in 1960 Tschoegl and Alexander (1960 a+b) studied the properties of whole gluten (dispersed in 0.1 M HCl in 2-chloroethanol) spread at the air-water surface. Surface tension after compression of the surface was lowered to about 40 mN/m. Eliasson and Silverio (1991) also worked with gluten, but they spread particles directly on the water surface. They concluded that the relatively small gliadin molecules spread faster over the surface than the much larger glutenin molecules. The equilibrium surface pressure of gliadins on a water surface is 25 mN/m ($\gamma=47$ mN/m). In compression a surface with gliadins reaches a surface tension of about 32 mN/m (depending on the amount of compression/expansion cycles). Gliadins can be pressed out of the surface more easily than glutenins. The latter proteins may give a surface tension of lower than 30 mN/m (Lundh et al., 1988). These researchers concluded that during successive compression/expansion actions *further disulphide cross-linking of molecules could occur*, leading to a higher stability of the protein films. According to Tao et al. (1989) non-covalent aggregation forces may also lead to more compact glutenin molecules.

Surface moduli of gluten were also determined by Tschoegl and Alexander (1960b). They found values of 2 dyn/cm (= 2 mN/m) for a gluten film which is very low compared to values found for other proteins which vary between 10 and 80 mN/m (Benjamins et al., 1975, Graham and Phillips, 1980). This difference can be due to the different measuring technique used; Tschoegl and Alexander determined the shear modulus, the others determined a dilational modulus, the latter usually being higher for protein films (Benjamins and van Voorst Vader, 1992).

Wheat lipids

It has been well established that wheat lipids have a large effect on breadmaking performance although they are only a minor constituent of wheat flour. According to MacRitchie and Gras (1973) and MacRitchie (1977, 1981) bread dough is a foam and lipids may modify the foam stability and thus the final loaf volume and texture. They divided the lipids into three classes with respect to their foam stabilizing properties: the very non-polar compounds like the triglycerides, the lipids with intermediate polarity including free fatty acids, monoglycerides and monogalactosyl diglycerides (MGDG) and the polar galactolipids and phospholipids. The first group, which has little surface activity, has little influence on bread volume. The second group of intermediate polarity is said to decrease substantially loaf volume while the third group would be beneficial for loaf volume (DeStefanis and Ponte, 1976; Chung et al., 1978; MacRitchie, 1983).

Surface properties of a polar wheat lipid digalactosyl diglyceride (DGDG) were determined by Carlson (1981). DGDG can form a lamellar phase with water and multilamellar films can be present at for instance the air-water interphase. Carlson studied the monolayer characteristics of DGDG and found that the surface tension decreased to about 30 mN/m just before the collapse point. Hamer and co-workers (1991) made π-A curves of different wheat lipids. They observed that the surface tension of a monolayer of the most polar lipid used in the experiment (DGDG) at the collapse point was lower (27 mN/m) than the minimum surface tension of 'intermediate' polar lipids like MGDG (29 mN/m) and monoglycerides (35 mN/m). Surface tension of triglycerides did not change very much during compression, which is to be expected because they do not spread over the surface.

Added surfactants

Non-flour lipid additives are commonly used in breadmaking. There are two main groups of these additives: the saturated fats or shortenings and the surfactants or emulsifiers (MacRitchie, 1983). Shortenings are used especially in short-time breadmaking processes. In this chapter only the effect of surfactants will be discussed. Krog (1990) gives a review of food emulsifiers and their physico-chemical properties. Special attention has been paid to X-ray diffraction patterns of different lyotropic mesophases of emulsifiers. These are liquid-crystalline phases of an emulsifier and water. These systems exhibit certain properties alike liquids and other properties alike crystalline bodies. Schuster and Adams (1984) reviewed the emulsifiers used in bread and other baked products. Both DATEM (diacetyl tartaric acid esters of monoglycerides) of C16/C18 monoglycerides and SSL (sodium stearoyl-2-lactylate) are stable in an α-crystal form. The x spacing as indicated in figure 3.1 is a characteristic short spacing of 4.1 Å for the so-called α modification. The molecules in figure 3.1(a) are ranged according to the so-called dubble-chain length (DCL) packing. Another possibility is the single-chain length packing (SCL) where the hydrocarbon chains of two adjacent layers penetrate each other (Krog, 1990). When emulsifiers are heated in the presence of water to temperatures above the Kraft-point (temperature above which the hydrocarbon chains transform from the solid into the liquid state) and cooled down, the α-gel phase can be formed.

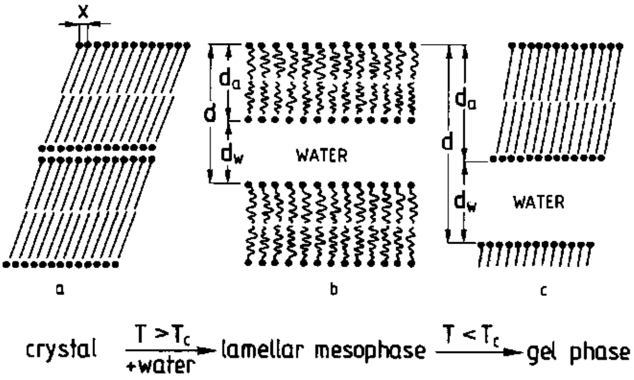

Figure 3.1 Structure models of an emulsifier (a) in the crystalline state, (b) formation of a lamellar mesophase above T_c (Kraft point) with water and (c) formation of a gel phase below T_c. d, d_a, d_w can be measured with X-ray diffraction, x is the specific α spacing (after Krog, 1990).

In general surfactants improve loaf volume and texture in bread and prolong shelf life. According to Krog (1981) surfactants that are most effective in bread like SSL, ethoxylated monoglycerides (EMG) and DATEM are able to form lamellar mesophases or gel structures in water. It has been shown that for polar lipids the lamellar liquid-crystalline phase is the most effective form in which this component can be added to bread dough in order to improve loaf volume (Eliasson and Tjerneld, 1990). According to Schuster and Adams (1984) and references therein, surfactants in a dough can function as dough conditioner in two ways: 1) by interaction with gluten proteins and so reinforcing the gluten network and 2) by the formation of ordered structures with water and thereby supporting the native flour lipids in their foam-stabilizing function.

Surface properties of a food emulsifier were determined by Westerbeek (1989). He studied the interfacial rheological properties of glycerol lactopalmitate (GLP) and found that this emulsifier was able to form an ordered structure (α-gel phase) in the presence of water and that this lamellar structure gave the surface a high dilational modulus. This α-gel phase was also studied by small angle neutron scattering (Westerbeek, 1989; van Tricht et al, 1993). Westerbeek (1989) concluded that the presence of such 'stiff' surfaces in whippable toppings could prevent disproportionation of gas bubbles.

3.2 Materials and Methods

3.2.1 Materials

Flour

Flour of two wheat cultivars with pronounced differences in baking performance, Spring and Taurus, were chosen for this study based on the described properties in the so called 'Variety list of agriculture crops 1989', published in The Netherlands.

- Spring, a mixture of good baking American wheat cultivars
- Taurus, a British wheat with very poor bread baking performance

Gluten from Rektor, a German wheat with relative good baking performance was used to determine the effect of gluten particle size on the surface rheological properties. Additional experiments were performed on glutens of a few other cultivars, such as:

- Camp Remy, a good baking French wheat cultivar
- Arminda, a poor baking Dutch wheat cultivar

- "Zeeuwse bloem", a mixture of very poor baking Dutch wheat flours (mainly used for baking cookies).

Flour was milled with a Bühler flour milling device to an extraction rate of 75%. The composition of the Spring and Taurus flours is given in Table 3.1. Chemical analyses were not performed on the other flours.

***Table 3.1** Composition of the flours in weight percentage of total flour*

Flour	moisture	protein	lipids	starch	ash
Spring	15.57	13.81	0.93	64.4	0.45
Taurus	15.31	10.22	1.03	66.7	0.36

The total sum of the analysed components is not 100%. The difference consists partly of non-starch polysaccharides and cellulose.

"Dough" suspensions

To make a flour suspension that imitates a dough as closely as possible, flour was mixed with water and salt in a Farinograph up to 500 Brabender Units. The dough was freeze dried and ground in a Retsch mill. 0.5% (w/w) of dough powder was carefully suspended in demineralized water with or without 4% NaCl. This flour concentration was chosen because it proved to be relatively easy to suspend this amount of flour in water while the suspension did not became too viscous. Increasing the dough concentration to 2% did not have an effect on either the surface tension or the surface dilational properties. The concentration of NaCl is approximately the concentration of NaCl in the water phase of bread dough.

In order to study whether the diluted dough suspensions of the different flours still exhibited different properties, foaming experiments have been performed. However, it proved to be very difficult to make a foam of the suspensions probably because of the presence of small gluten lumps and starch granules. No further attempt has been made to study the foaming behaviour of the suspensions more thoroughly.

Gluten

Glutens of Spring and Taurus flour were prepared by a small scale Batter process (Weegels et al., 1988). 5 kg flour and 3.5 l water were mixed into a dough. Mixing time for the poor baking flour was somewhat shorter than for the good baking one (5 minutes instead of 8 minutes). After a rest period the dough was diluted with another 5 l water into a kind of a batter under continuous mixing.

This batter was pumped into a large container where it was diluted again with 4 l water. The gluten, which was by then present in the form of coagulated protein lumps, was separated from the rest of the slurry by leading it over a stack of four vibrating sieves with different pore sizes. In case of the good baking flour Spring most of the coagulated gluten was held on the second sieve while the biggest lump of gluten of the poor baking flour Taurus was already held by the first sieve. The fraction containing the highest yield was used for the experiments. The glutens were freeze dried and ground with a Retsch grinder equipped with a 200 micrometer sieve. The composition of the glutens is given in table 3.2.

***Table 3.2** Composition of the glutens in weight percentage of total gluten*

Gluten	moisture	protein	glutenin/ gliadin ratio	lipids	starch
Spring	2.07	82.6	0.83	2.52	6.1
Taurus	2.24	73.5	0.70	1.86	11.1

The difference between the analysed weight percentage and 100% consists partly of non-starch polysaccharides. The rest is unknown.

Glutens of Rektor, Camp Remy, Arminda and Zeeuwse bloem flour were made by washing out a dough, optimally mixed in a Farinograph, under streaming tap water. The gluten ball obtained was freeze-dried and ground.

Wheat lipids

Wheat lipids were extracted from Spring flour by shaking 1 kg of flour with 2.5 l water-saturated 1-butanol for 1 hour. This solvent was used because it is said to extract the total nonstarch lipid fraction (Morrison et al., 1975). The solvent was evaporated using a Rotavapor-R rotating film evaporator (Buchi) at 90°C. This "total lipid" fraction was weighed and dissolved in petroleum-ether 40-60. The lipid solution was stored under N_2 gas in the refrigerator.

Surfactants

Sodium Stearoyl-2-Lactylate (SSL) and Diacetyl Tartaric acid Esters of Monoglycerides (DATEM) were obtained from Quest International in Zwijndrecht, The Netherlands. Suspensions were made at a concentration of 0.1%. In bread dough 0.25% on flour weight basis is added, which is roughly 0.5% on water basis. The surfactants are said to form complexes with proteins or starch (Schuster and Adams, 1984). This implies that not all the added surfactant will be available for the gas-dough interface. We assumed 0.1% 'free' surfactant in the dough water phase as reasonable.

Solvents

Petroleum-ether 40-60 and 1-butanol were from Merck. Water-saturated-1-butanol was made by shaking the butanol with demineralized water.

3.2.2 Methods

Sinusoidal oscillation tests

Ring trough

The surface rheological parameters E, E_d and η_d were measured as a function of the radial frequency ω in a special Langmuir trough with a cylindrical barrier called 'ring trough'.

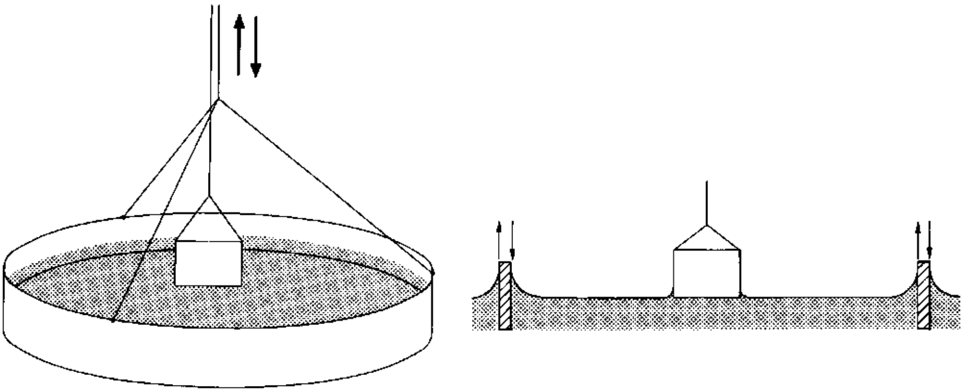

***Figure 3.2** Schematic representation of the ring trough with Wilhelmy plate, left: side view, right: cross section (from Kokelaar et al., 1991).*

The enclosed surface is expanded and compressed by moving a roughened glass cylinder up and down in a sinusoidal way. The surface tension, which will change as a result of the changing surface area, is continuously measured by a glass Wilhelmy plate. More details about this method are given by Kokelaar et al. (1991). The apparatus is shown schematically in figure 3.2.

Sinusoidal oscillation tests in the ring trough were performed at room temperature (ca. 23°C) unless mentioned otherwise with:

- suspensions of freeze dried dough in water (also at 45°C)
- freeze dried gluten powder sprinkled on the water surface
- spread and/or dissolved components from gluten powder spread outside the ring of the ring trough and diffused towards the clean surface inside the ring
- wheat lipids dissolved in petroleum-ether spread on the water surface
- suspensions of either SSL or DATEM in water (also at 50°C)
- combinations of wheat lipids and SSL at the surface

The results presented are mean values of measurements on at least two suspensions/solutions.

It appeared that the differences in measured surface dilational moduli between different dough suspensions of the same wheat flour (duplicates) were sometimes 25-50%. The reproducibility of the results for sieved gluten was better (10-20%). Differences between results for both lipids and surfactants were approximately 10%.

Langmuir trough

Sinusoidal oscillation tests as well as compression/expansion tests were also performed in a Langmuir trough from TNO in Zeist. Maximum surface area of the rectangular surface was 750 cm^2. The surface was compressed or expanded by means of a teflon barrier. The frequency of surface area deformation and the speed of the barrier movement were set by a computer. Surface tension was measured with a platinum Wilhelmy plate.

The measurements with the Langmuir trough were performed at room temperature on:

- wheat lipids dissolved in petroleum-ether spread on the water surface
- digalactosyl diglyceride (DGDG), a polar wheat lipid fraction obtained from TNO-Zeist, dissolved in petroleum-ether
- a suspension of SSL in water

Measurements were performed in duplicate. Differences in the measured parameters between duplicates were ca. 10%.

Expansion/compression tests

Langmuir trough

Expansion and compression tests were performed in a Langmuir trough. The trough was either equipped with a single barrier to perform a single compression of the surface or equipped with a caterpillar belt with six barriers moving around. The last type of deformation was used in order to approach steady-state expansion of the surface. Both setups are shown in figure 3.3.

Measurements were performed on:

- flour suspensions (also at 45°C)
- gluten powder (only single compression)
- SSL and DATEM suspensions (also at 50°C)

All measurements were done at least in duplicate. Differences in results were less than 10%.

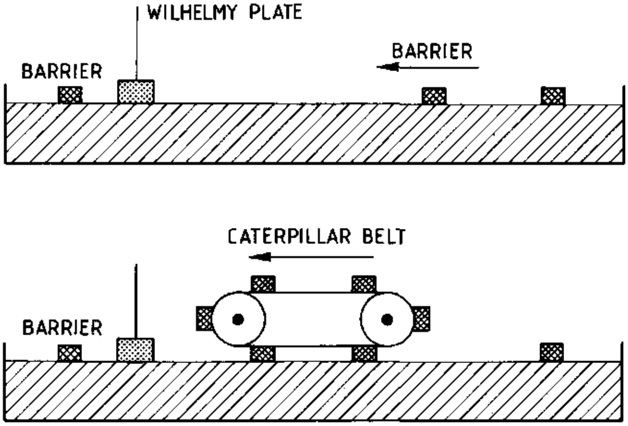

***Figure 3.3** The Langmuir trough equipped with a single barrier and a caterpillar belt (from Ronteltap, 1989).*

Overflowing cylinder

The overflowing cylinder as described by Bergink-Martens et al. (1990) was used to create a continuous expansion of the surface at the top of the cylinder (see figure 3.4). The setup of the cylinder is such that compression of the surface is effectuated in the collecting vessel. In this way an attempt was made to imitate the expansion and compression as occuring during dough mixing. However, the deformation rate at the surface in the overflowing cylinder apparatus is about 10 s^{-1} while during dough mixing the deformation rate is ca. 0.1 s^{-1}.

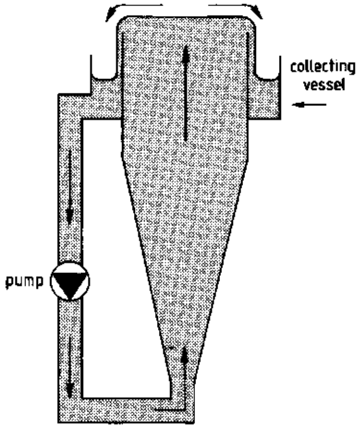

Figure 3.4 Schematic representation of the overflowing cylinder apparatus (from Bergink-Martens et al., 1993).

DSC and X-ray measurements

These kind of measurements were done to get some information about the crystalline structure of the powder and the suspensions of the surfactants SSL and DATEM.

DSC

Differential Scanning Calorimetry measurements were performed with a DSC-2 from Perkin-Elmer. The rate of heating and cooling down of the samples was 10 K/min. Measurements were performed with powder and suspensions in water.

X-ray

X-ray diffraction measurements of short and long spacings were performed at AKZO (Arnhem, the Netherlands) with three different cameras using CuK-α radiation. A Kiessig camera (Ni filter); a Statton camera (graphite monochromator) and a Siemens D 5000 reflection diffractometer (equipped with a possibility to heat the samples, Ni filter) were used.

Both surfactant powders as well as suspensions (0.5, 10 or 25 % w/w) were studied. Measurements were done at 30 and 60°C and after cooling down to 20°C.

3.3 Results and discussion

This section presents the surface rheological properties of dough suspensions and separate components like gluten, gliadins, lipids and added surfactants. At first the results of the sinusoidal oscillation tests (dynamic measurements) will be discussed (3.3.1) followed by the results of the continuous expansion and compression tests (3.3.2) and the single compression tests (3.3.3). In 3.3.4 the results of DSC and X-ray test of the added surfactants SSL and DATEM are presented.

Wheat cultivars

There was no clear difference between the surface rheological parameters determined of dough suspension or gluten from the good baking Spring and the poor baking Taurus wheat cultivar. Results obtained from additional experiments on Rektor, Camp Remy, Arminda and Zeeuwse bloem gluten were in agreement with this observation. Differences were always equal to or smaller than the differences between duplicates. Therefore, mostly the results are shown for only one cultivar.

In fact, this is one of the most important results of this study. It may indicate several things. The first is that, although surface rheological properties may play a role in determining bubble stability in bread dough, it is not the main factor in determining baking quality. Another possibility is that the used model systems are not suitable to imitate a dough system. Bread dough is much more viscous and has undergone a mixing step which may give the surfaces of the entrapped gas bubbles a special composition and/or conformation.

3.3.1 Sinusoidal oscillation tests

Flour suspensions

The surface dilational modulus and the loss tangent of a Spring dough suspension as a function of the radial frequency is plotted in figure 3.5. From figure 3.5 can be seen that the surface modulus varies between 30 and 120 mN/m at room temperature. The loss tangent is 0.6 at the lowest and 0.2 at the highest frequency tested. Considering the requirement of the gas bubble surface to prevent disproportionation, $E>\gamma/2$ and $\tan\theta=0$ (Lucassen, 1981) (see 2.1.2), it can be concluded that over longer time scales investigated which are more relevant for the disproportionation process in dough (see chapter 2) the modulus is higher than half the surface tension of the surface but the loss tangent is considerably higher than 0.

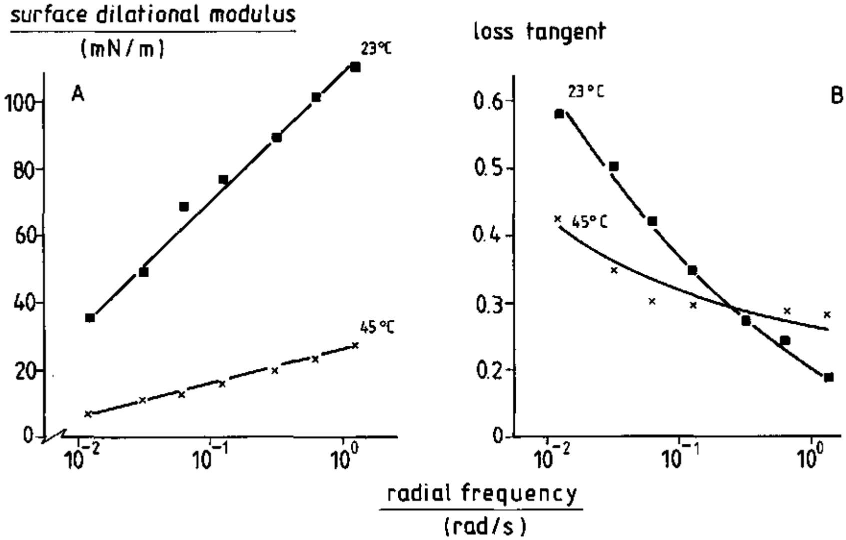

Figure 3.5 (A) Surface dilational modulus and (B) loss tangent as a function of the radial frequency of 0.5 % w/w Spring dough suspension. Surface tension in equilibrium γ_{eq}=42 mN/m at 23°C and 40 mN/m at 45°C. Temperature during measurements is indicated.

So, probably over still longer time scales E will become lower than $\gamma/2$ indicating that disproportionation will be slowed down but not stopped.

If the measured system is comparable to dough, the results show that disproportionation of gas bubbles in bread dough can not be prevented by the stiffness of the surface. However, the process may be retarded. It is questionable whether the surface has enough time to build up its surface stiffness in the short time between mixing and the start of disproportionation. On the other hand it could be possible that the modulus increases during compression of the bubble surface due to the formation of certain closely packed structures. This has not been investigated.

At 45°C the surface modulus is ca. 5 times lower at every frequency tested. The surface has also become somewhat more elastic at lower frequencies as illustrated by the curve of the loss tangent. Disproportionation is not so likely to occur at stages in the breadmaking process where temperatures in the dough are more elevated; i.e. during the oven rise, due to strain hardening of the liquid dough phase (see chapter 2). However, the value of the modulus determines at which thickness of the dough films between the gas bubbles surface properties start to be more important than bulk properties in determining film stability (see chapter 5).

Effect of NaCl

The surface rheological parameters were also determined of a 0.5% Spring dough suspension in water containing 4% NaCl. The found differences with suspensions without added NaCl were comparable to the differences between duplicate measurements.

Effect of ethanol

Due to fermentation ca. 3000 cm^3 CO_2 is formed in a bread dough for a 800 g loaf using a Dutch formula (Sluimer, 1987). 1 mol of CO_2 formed means that also 1 mol of ethanol is formed. Calculated on the water phase in bread dough this comes down to 0.6% w/w in the bulk. Two experiments were performed. In one experiment ethanol was added by means of a syringe to a suspension present in the ring trough for some time in such a way that the final concentration would be 0.6% w/w. This was done to imitate the formation of ethanol during the fermentation process although the ethanol was not added in small amounts. In the other experiment ethanol was added up to the same concentration during preparation of the dough suspension. In figure 3.6 the results are given.

It appears that the surface dilational modulus drops suddenly after ethanol addition. The surface tension was lowered from 45 mN/m to 40 mN/m and increased again to a value of 42 mN/m. Ethanol probably evaporates very soon and is not able to lower the surface tension very much and for a long time in this system. After 50 minutes the surface modulus is still increasing and it is not unlikely that the final value approaches the value before ethanol addition.

The ethanol probably disturbes the surface network due to some adsorption but soon it evaporates and it does not fundamentally change the properties of the surface for a longer time. This could also be concluded from the results of the suspension where ethanol was added before measurements started. Both the height and the increase in time of the surface modulus are, considering the differences in results between duplicate measurements, similar to those of a Spring dough suspension without ethanol. It could be possible that all the ethanol was evaporated before the measurements were started, but if ethanol has a substantial effect at this concentration on the surface components it would have been clear from the results.

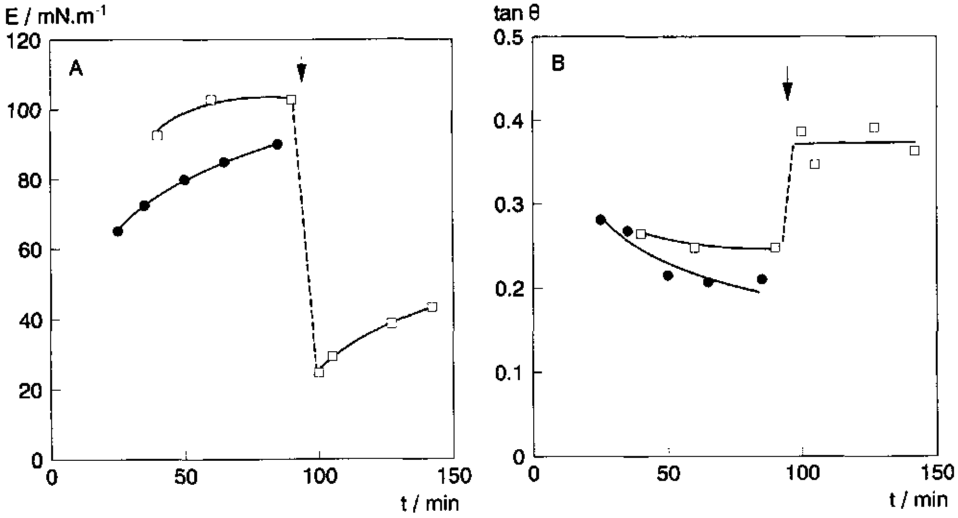

Figure 3.6 (A) Surface dilational modulus E and (B) loss tangent tanθ of a 0.5% w/w suspension of Spring dough as a function of ageing time. Ethanol added after 90 minutes (□-□) and ethanol added before measurements were started (●-●), c(ethanol) = 0.6% w/w.

The lack of effect of ethanol is not consistent with the results obtained by Dickinson and Woskett (1988) who observed a complete loss of the interfacial shear viscosity of an interface between hexane and a caseinate solution when 1 wt% ethanol was added beforehand. They also found a considerable drop in surface shear viscosity when ethanol was added after 24 hours. In their systems it was more difficult for the ethanol to evaporate through the hexane phase.

Gluten powder

Sinusoidal oscillation tests were performed also on gluten powder spread on the water surface. It appeared that reproducable results could only be obtained if a fraction of the gluten powder with a rather narrow particle size distribution was used. In figure 3.7 the effect of particle size on the surface dilational modulus is shown. Certain components from the gluten powder will spread from the gluten particles. As a result the surface tension of the water is lowered. More components spread from the larger total surface area of the small particles and it is therefore that the surface tension of the surface with the small particles is lower. This is also clear from figure 3.8 where such

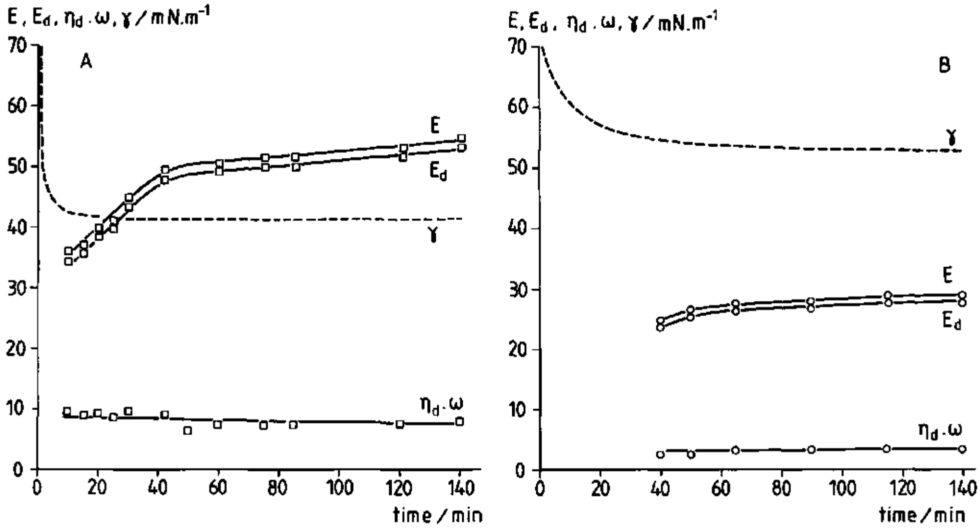

***Figure 3.7** Surface dilational modulus E, elastic E_d and viscous component $\eta_d.\omega$ and surface tension γ of a water surface containing Rektor gluten powder (A) 10 mg particles (diameter 45-70 μm) and (B) 12 mg particles (diameter of 1-1.4 mm), $\omega = 0.314$ rad/s (from Kokelaar and Prins, 1991).*

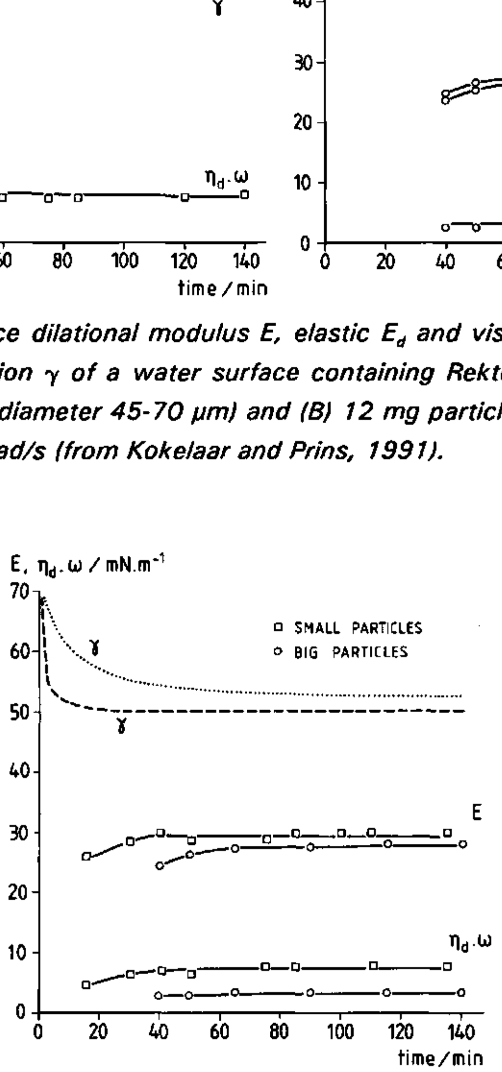

***Figure 3.8** Surface rheological parameters E, E_d and $\eta_d.\omega$ and surface tension γ as a function of time of a water surface containing Rektor gluten: 1 mg small (diameter 45-70 μm) and 12 mg big particles (diameter 1-1.4 mm), $\omega = 0.314$ rad/s (from Kokelaar and Prins, 1991).*

amounts of particles were spread on the water that the total surface area was approximately similar. The obtained surface tensions are very much alike as well as the values for the surface rheological parameters.

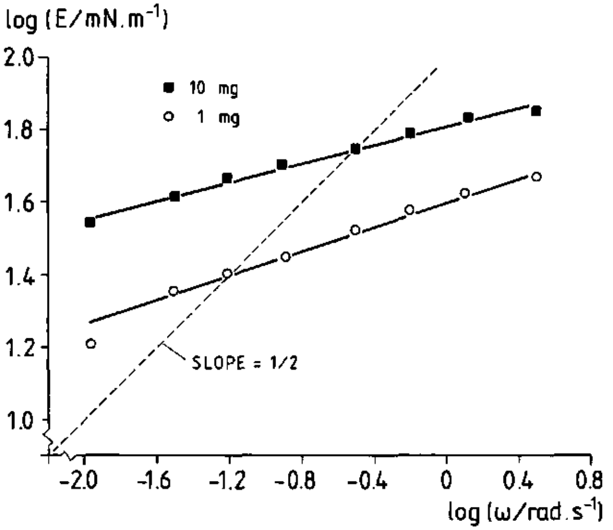

***Figure 3.9** Surface dilational modulus E as a function of the radial frequency ω of a water surface containing 1 or 10 mg Rektor gluten particles (diameter 45-70 μm) (from Kokelaar and Prins, 1991).*

In figure 3.9 the frequency dependence is shown. We applied the theory of Veer and van den Tempel (1973) for surfaces containing surface active particles on the results. This theory predicts that if the slope of log E-log ω is 1, relaxation of the surface tension during deformation of the surface occurs by exchange of material between the particles and the monolayer in between. If the slope of the curve is 0.5 then relaxation processes occur by exchange of material between the monolayer and the bulk solution under it. From the results it can be concluded that the theory of Veer and van den Tempel (1973) does not fit on this system. Probably, the components having left the gluten particles are not eager to re-associate with them again so almost no relaxation in this way occurs, neither is there much material exchanging with the bulk solution under it.

The minimal surface tension of a surface full with gluten particles is ca. 27 mN/m. This value indicates that lipid like material has spread. The surface dilational modulus of this surface is ca. 100 mN/m. Of course components like proteins will have spread as well but these alone would have lowered the surface tension to approximately 45-50 mN/m as observed e.g. for different caseins and the surface dilational modulus would have been 20-50 mN/m as found for non-associating proteins (Benjamins et al., 1975; Graham and Phillips, 1980). The surface properties of a surface containing gluten powder are probably determined by both lipids and proteins.

In figure 3.10 the surface dilational parameters of Spring and Taurus gluten, sprinkled on the water surface, are shown. It is clear that no significant differences between these two gluten types are found. For comparison, the results of a few other glutens are shown as well, amongst which was a Taurus gluten made by washing a dough under a streaming tap (Taurus 2).

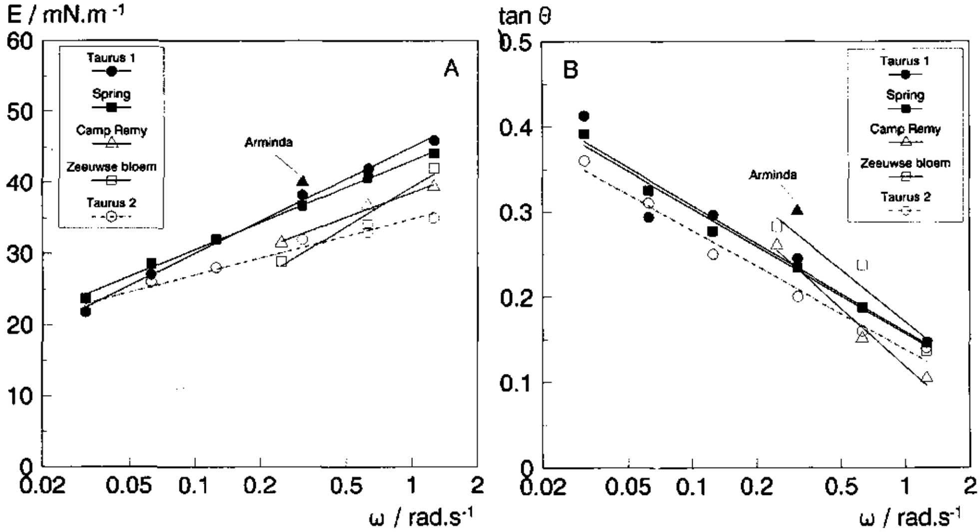

***Figure 3.10** (A) Surface dilational modulus E and (B) loss tangent tanθ as a function of the radial frequency ω of a water surface containing ca. 10 mg of gluten powder. Surface tension with Spring gluten was 43 mN/m, Taurus 1: 40.5 mN/m, Taurus 2: 40 mN/m, Camp Remy: 40.6 mN/m, Zeeuwse bloem: 36 mN/m, Arminda: 42 mN/m.*

To get information about components that have spread, the surface between the particles should be analyzed. However, it proved to be very difficult to take a sample of the surface without taking a few particles as well. Therefore, we spread particles outside the glass ring of the ring trough and we took a sample of the components which were diffused through the underlying water phase towards the clean water surface inside the ring. In this sample both proteins (mainly gliadins) and lipids (mainly non-polar) were found. Surface rheological properties of this surface were also determined. It appeared that the minimal surface tension of these water soluble components was 42 mN/m and the modulus increased to ca. 100 mN/m after about 3 hours.

Gliadins

The surface rheological properties of a solution of isolated gliadins in water (10 mg/l) were determined. The surface tension of the solution was 45 mN/m and the surface dilational modulus was 20-50 mN/m depending on the frequency (see fig. 3.11). Paternotte et al. (1993) found a modulus of 35 mN/m ($\gamma=47$ mN/m, $\omega=0.942$ rad/s) although the way in which they made the surface was different. The frequency dependence was comparable to that of flour suspensions. This indicates also that the surface rheological properties of a surface containing gluten particles, which are different from the surface properties of gliadins alone, are also determined by other spread components, most probably spread lipids.

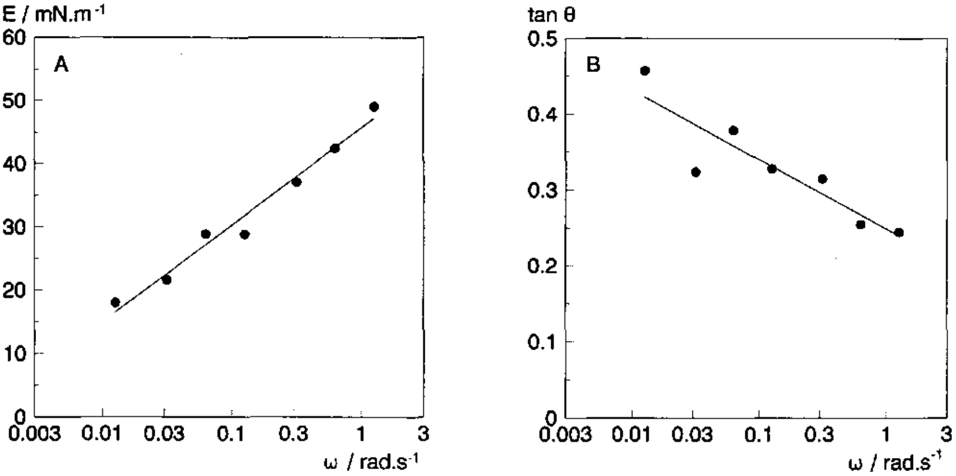

Figure 3.11 (A) Surface dilational modulus E and (B) loss tangent tanθ as a function of the radial frequency ω of a gliadin in water solution (10 mg/l), $\gamma_{eq}=45$ mN/m.

It appears that flour suspensions, gluten powder on water and a gliadin solution all have a surface dilational modulus between 20 and 100 mN/m depending on the frequency. At lower frequencies all these surfaces have a rather low modulus which contains a considerable viscous component. This would indicate that the requirements according to Lucassen to stop disproportionation are not fulfilled at a surface containing dough or gluten components.

The surface modulus is however higher than $\gamma/2$ at frequencies above 10^{-2} rad/s which may lead to a slowing down of the process.

Wheat lipids

The surface tension and the surface dilational modulus of a water surface containing spread lipids was determined as a function of the concentration. A known amount of lipids was first dissolved in petroleum-ether and a certain amount of solvent drops was carefully brought in contact with the water surface. The drops spread and the petroleum-ether evaporated very quickly. In a control experiment it was made sure that the petroleum-ether did not effect the surface tension of water after evaporation. However, it can not be excluded that the solvent may have an effect on the surface properties of the lipids. The results of the measurements are given in figure 3.12.

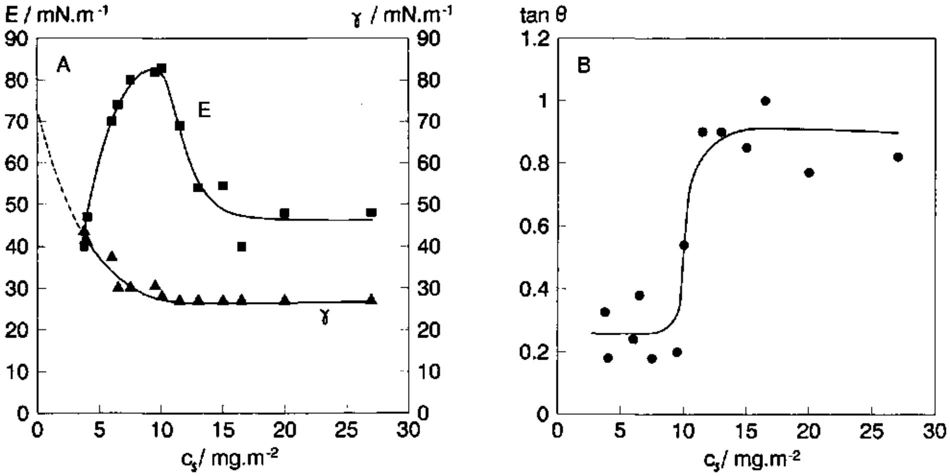

***Figure 3.12** (A) Surface tension γ, surface dilational modulus E and (B) loss tangent tanθ as a function of concentration of Spring 'total' lipids at the surface c_s, $\omega = 0.314$ rad.s^{-1}.*

The surface dilational modulus is higher at higher lipid concentrations at the surface as long as the surface tension has not yet reached its minimum value. At higher lipid concentrations at the surface the surface dilational modulus can be as high as 60-90 mN/m, but then the frequency dependence is also relatively high (see fig. 3.13). At the lowest concentrations the modulus is not very frequency dependent as is clear from the low slope of the E-ω or the tanθ-ω curves of the three lowest concentrations tested. This suggests that at these low concentrations no exchange of material with the surface layer itself or with the bulk solution beneath it takes place, probably because there is not enough material available.

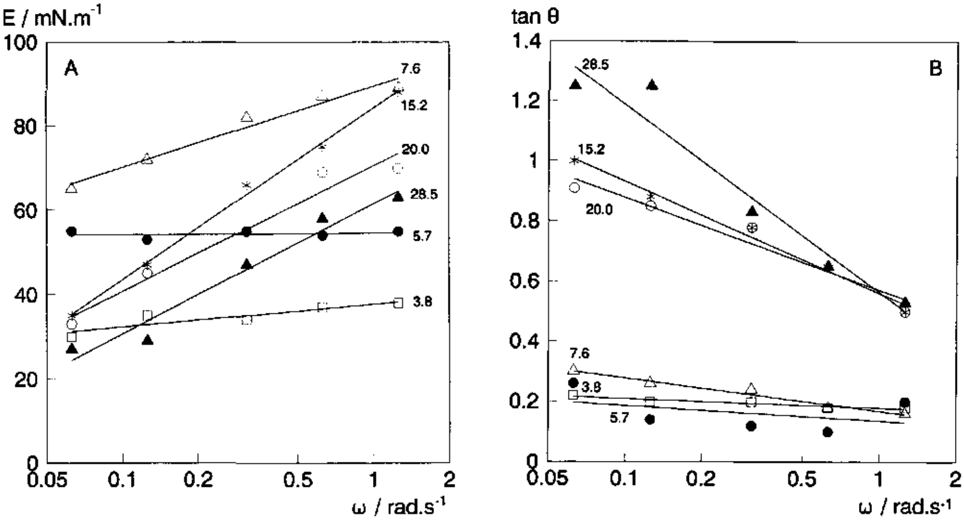

***Figure 3.13** (A) Surface dilational modulus E and (B) loss tangent tanθ as a function of the radial frequency ω of Spring 'total' lipids, lipid concentration at the surface is indicated in mg/m^2.*

The above results would be of great practical use assuming that the surface of the gas bubbles in dough would be composed of lipids. Unfortunately up to now there is no agreement about the exact composition of these surfaces. It is probably a mixture of lipids and proteins. In that light the work of Paternotte et al. (1993) where surface rheological measurements are performed on surfaces containing protein-lipid mixtures is very promising. We can of course make a simple calculation of the surface concentration if we assume that all the lipids present in flour are present in the surface. For that purpose we assume that 1 kg of flour, containing 20 g lipids, results in about 1.21x10^{-3} m^3 dough after mixing with a surface area of the gas bubbles of ca. 6 m^2. This surface area expands with a factor of approximately 8 (van Vliet et al., 1992) to ca. 48 m^2. The maximal lipid concentration at the surface may then be estimated as 420 mg/m^2. This is much higher than the concentration used in the experiments. However, it is highly probable that part of the lipids in bread dough will associate with e.g. proteins and starch and maybe a part is present as emulsion droplets. So practical values for the lipid concentration at the gas bubble surface will be much lower.

Surfactants

Surfactants like SSL and DATEM are added to the other dough components in the form of a powder. To investigate their surface rheological properties in relation to bubble stability in dough we should therefore perform measurements at conditions as during dough making, fermentation and at elevated-temperatures. The fact that SSL exhibits a very high modulus at 30°C or lower after the solution has been heated (see fig. 3.14) should in this respect be considered as an interesting point but it can not explain the improving effect of SSL on breadmaking. Moreover, DATEM does not show a high surface modulus after heating but also has known bread improving properties.

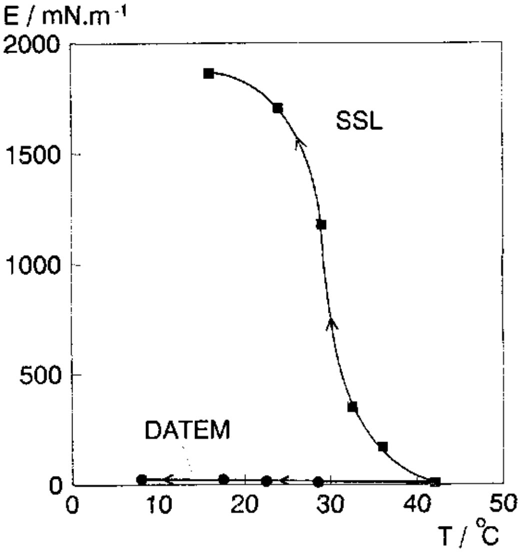

Figure 3.14 Surface dilational modulus E as a function of temperature of a 0.1% w/w SSL and of a 0.1% w/w DATEM suspension during cooling down after heating to 60°C. ω=0.0628 rad/s.

In order to imitate the deformations that occur during dough mixing, involving expansion and compression of the dough and of the gas bubble surfaces, an SSL and a DATEM suspension were pumped through the overflowing cylinder apparatus. The surface at the top of the cylinder was continuously expanded while it was more or less compressed again in the collecting vessel. After pumping the suspension through the cylinder for about one hour it was carefully poured into the ring trough and the dynamic surface moduli were determined. In figure 3.15 the results are given.

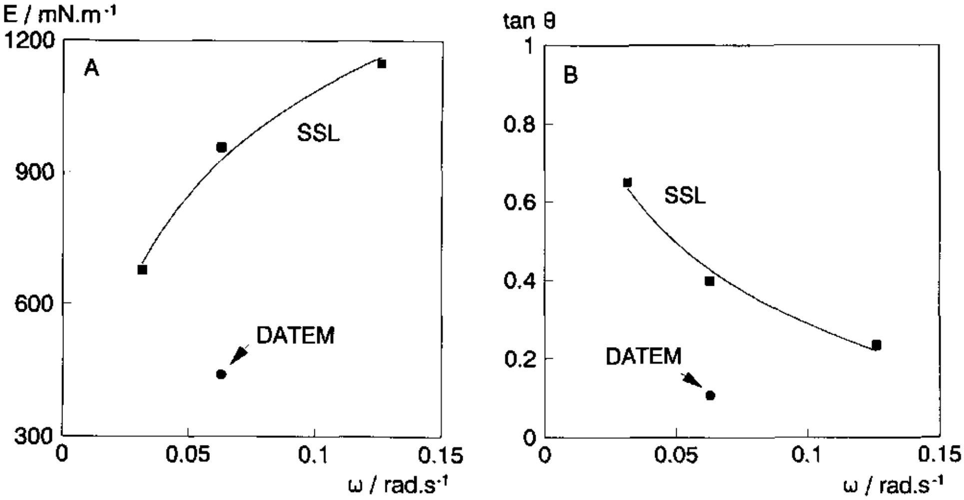

***Figure 3.15** (A) Surface dilational modulus E and (B) loss tangent tanθ as a function of the frequency ω of a 0.1% w/w SSL resp. DATEM suspension after it was treated in the overflowing cylinder at room temperature. γ_{eq}(SSL)=27 mN/m, γ_{eq}(DATEM)=37 mN/m.*

It is clear that at room temperature, without heating the suspension beforehand, both an SSL and a DATEM suspension in the concentration tested may have very high values of the surface dilational modulus after a mechanical treatment. The surface fulfils the requirement of Lucassen (1981) that $E > \gamma/2$ over the frequency range tested. E is even far higher than $\gamma/2$. The surface also has viscous properties since tanθ is clearly higher than zero. The decrease in E at lower frequencies is fast and at longer timescales the surface might even not be stiff enough to prevent disproportionation. If due to a small compression the surface tension stays low then the driving force for disproportionation at the fermentation stage is also gone. Due to the compression itself, the modulus can become higher as a result of a closer packing or the formation of more ordered structures. The results of such experiments are presented in section 3.3.3.

In another experiment where preheated SSL suspension was brought under a water surface the surface modulus varied from 270 to 330 mN/m at frequencies from 0.0125 to 0.628 rad/s respectively. Probably the final concentration of surfactant at the surface was lower than in case of the 0.1% suspension, although the surface tension was the same (27 mN/m). In chapter 5 it will be discussed whether the findings are relevant under breadmaking conditions.

Combination experiments

A few experiments were performed in order to investigate the interaction or competition between lipids and the surfactant SSL. These components have the same surface tension of 27 mN/m and therefore it seems natural to assume that if one component has settled in the surface the surface tension difference between lipids and SSL is practically zero and therefore the other component will not spread. During mixing of the dough however the surfaces are continuously expanded and components will probably all be exposed to the surface. To imitate this an experiment was done in which the Langmuir trough contained a surface with a spread polar wheat lipid fraction DGDG. The dilational modulus of this surface was determined after it had been expanded from 150 to 600 cm^2 and again after compression to the original surface area. This experiment was performed to see if expansion and compression cycles could induce a higher surface dilational modulus. The results of it are given in Table 3.3. After expansion there was probably not enough material left per unit area to form some kind of a network in the surface so the resulting E was very low.

In another experiment a preheated suspension of SSL was brought under a surface of spread DGDG by means of a syringe. The surface dilational modulus was determined before and after expansion and again after compression.

Table 3.3 *Surface tension and dilational modulus (ω=0.942 rad/s) of a surface containing polar wheat lipid and/or SSL after expansion and compression*

Surface area	150 cm^2		600 cm^2		150 cm^2	
γ or E (mN/m)	γ	E	γ	E	γ	E
DGDG	30	55	52	3	32	55
SSL susp. (heated) under DGDG	26.5	100	33	100	26	1000
SSL unheated*	22	1200	30	100	22	1200

* after 4 expansion/compression cycles

From the results shown it is clear that preheated SSL can displace lipids from the surface. In a third experiment an SSL suspension made at room temperature was subjected to 4 expansion/compression cycles. From the data in Table 3.3 it is clear that this treatment also results in a high E and that after strong expansion of the surface the high modulus of SSL disappears but returns again after compression.

3.3.2 Continuous expansion tests

Flour suspensions

Flour suspensions were subjected to continuous expansion at various rates. The results of these experiments are summarized in figure 3.16. The effect of temperature on these properties was investigated by carrying out the experiments at room temperature and at ca. 45°C.

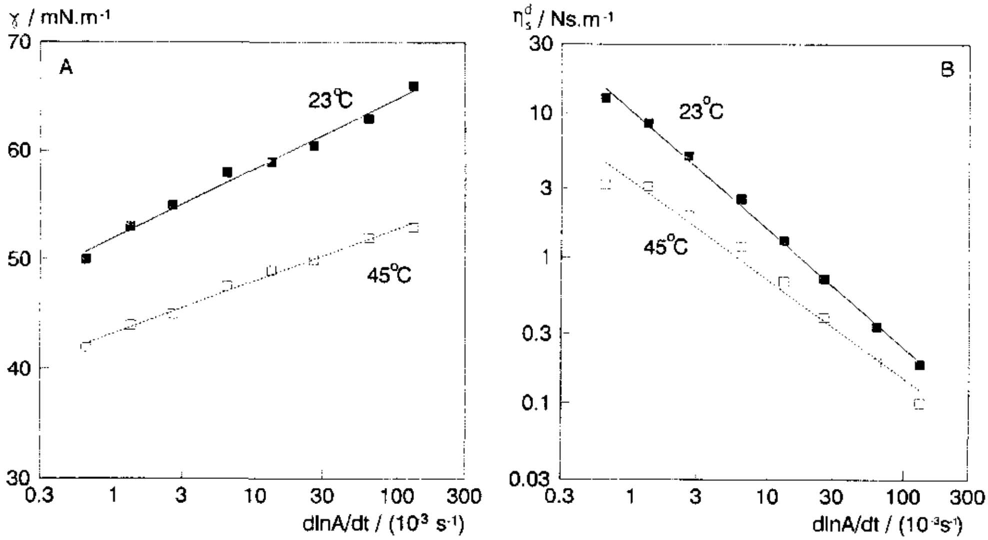

Figure 3.16 (A) Surface tension γ and (B) surface dilational viscosity η_s^d as a function of the relative expansion rate dlnA/dt of a 0.5% w/w Spring dough suspension. $\gamma_{eq}(23°C) = 42$ mN/m, $\gamma_{eq}(45°C) = 40$ mN/m. Temperature during measurements is indicated.

The data in figure 3.16A show that the surface tension of a dough suspension increases proportional to the logarithm of the expansion rate over the considered range. Also at the lowest expansion rates studied a surface tension gradient is built up. If these results are plotted as the surface dilational viscosity against relative deformation rate, the curves obtained can be described fairly well by a power law equation like eq. (3.3). The values for the power law constants n and m are given in Table 3.4.

Table 3.4 *Power law constants of a 0.5% w/w Spring dough suspension*

Temperature	23°C		45°C	
Constants	n	m	n	m
expansion	-1.55	-0.9	-1.62	-0.7

At a temperature of ca. 45°C the surface viscosity is approximately 2.5 times lower than at 23°C. This indicates that at higher temperatures the resistance of a dough suspension surface to expansion is lower than at room temperatures. If the chosen system is comparable to bread dough this would imply that the resistance to expansion due to surface "stiffness" is lower during oven rise than during proofing conditions (at the same expansion rate).

Surfactants

At different expansion rates the steady state surface tensions of SSL and DATEM suspensions were measured in order to get an idea of the surface tension during expansion at proofing and baking conditions. The results are given in figure 3.17.

SSL in the concentration tested at 50°C is able to keep the surface tension low (27 mN/m) during expansion up to expansion rates of 0.03 s^{-1}. Such a low surface tension may be favourable to prevent other surface active materials like lipids from spreading. On the other hand film stability due to the presence of a surface tension gradient will be absent or at a minimum in the presence of SSL at higher temperatures. From fig. 3.17B the shear thinning behaviour of the SSL suspension at 23°C and of the DATEM suspension at 23 and 50°C is clear. The power-law constants are given in table 3.5.

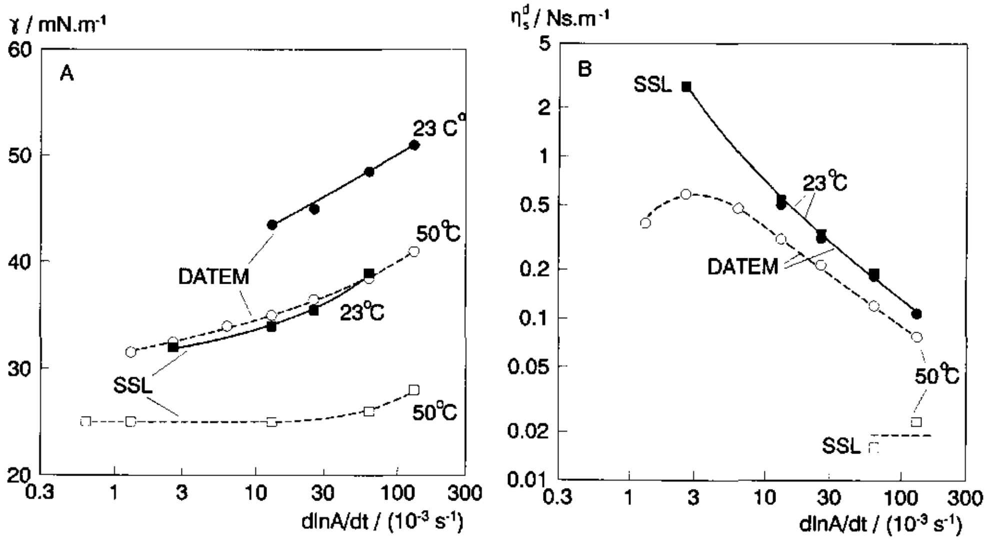

Figure 3.17 (A) Surface tension γ and (B) surface dilational viscosity η_d^s as a function of the relative expansion rate of an SSL and a DATEM suspension (both 0.1% w/w). Temperature during measurements is indicated. γ_{eq}(SSL) = 27 mN/m, γ_{eq}(DATEM) = 37 mN/m.

Table 3.5 *Power-law constants for 0.1% SSL and DATEM suspensions*

Temperature	23°C		50°C	
Constants	n	m	n	m
SSL	-1.75	- 0.70	-	-
DATEM	-1.75	- 0.70	-2.3	- 0.6

None of the suspensions of SSL and DATEM show a behaviour similar to many practical systems like beer and milk. The consequences for the behaviour of the surfaces of the gas bubbles during expansion is that the surface tension during expansion is rather low, also at room temperatures. The temperature under dough mixing conditions will be close to room temperature so due to the presence of surfactants surface tension of dough during expansion is low. This implies that the Laplace pressure which has to be exceeded for breaking up the gas bubbles is lower than in the absence of surfactants. This indicates that the entrapped air bubbles in the mixing stage can be broken up more easily into smaller bubbles than without surfactants present. Smaller gas bubbles after an identical mixing procedure due to the presence of surfactants have been observed by e.g. Junge and Hoseney (1981).

3.3.3 Single compression tests

Flour suspensions and gluten powder

Single compression tests of the surface were performed to study the decrease in surface tension during compression of the surface at a low rate. The surface area was compressed to 23% of its original value. For dough suspensions the surface tension was lowered to ca. 30 mN/m. For gluten powder sprinkled on the surface this was ca. 20-30 mN/m dependent on the initial amount of spread powder. This is illustrated by figure 3.18. The results presented are single measurements.

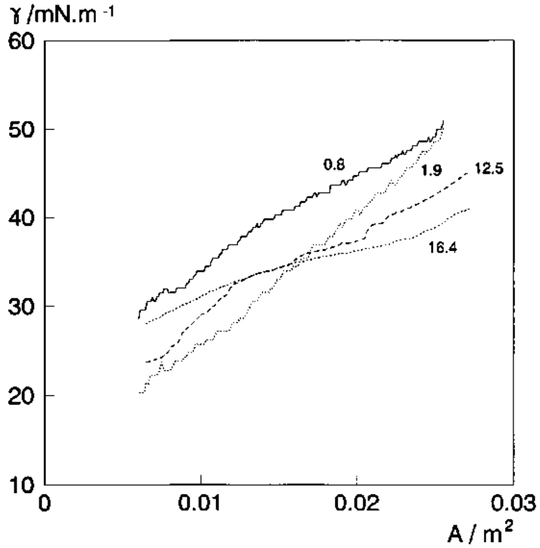

***Figure 3.18** Surface tension γ during compression of a surface containing different initial amounts of Spring gluten powder with particle radii between 45 and 70 μm. Amount of gluten powder on the surface is indicated. Initial relative compression rate 2.70×10^{-2} s^{-1} for surfaces with 0.8, 1.9 and 16.4 mg gluten and 1.35×10^{-2} s^{-1} for the surface with 12.5 mg gluten.*

At small amounts of powder, material from the powder particles will spread due to the difference in surface pressure. The composition of the spread material will then probably be different from that of a surface with a larger amount of particles. Therefore, during compression the change in surface tension may also be different.

Surfactants

To investigate further whether the surface of an aqueous SSL or a DATEM suspension has the required properties to slow down disproportionation during compression at low rates, the surface tension of these suspensions was measured during single compression of the surface. The results of the dynamic measurements showed that an SSL and a DATEM surface have considerable viscous components. The surface should keep its high surface dilational modulus also during a constant compression. If the surface tension decreases fast and stays low during compression then this is an indication that the surface keeps its high dilational modulus.

The suspensions tested had undergone different treatments: 1) no treatment at all but suspending the surfactant in water at room temperature, 2) heating the surfactant suspension to 60°C and cooling down to room temperature, 3) pumping the suspension through the overflowing cylinder without increasing the temperature which will be marked as 'mechanical treatment'.

If a suspension of both surfactants investigated was not preheated or mechanically treated the surface tension decreased only slightly during a small compression of the surface. On the other hand when an SSL suspension was preheated or pumped through the overflowing cylinder, the surface tension decreased already enormously at a similar compression. Obviously this is due to the high surface dilational modulus which is formed after both kinds of treatment. In agreement with the sinusoidal oscillation tests, the surface tension of a DATEM suspension which was preheated did not decrease very much at a small compression. When the suspension had been mechanically treated in the overflowing cylinder, the surface tension immediately dropped on compression to values of about 7 mN/m, comparable to the SSL suspensions. It must be noted that the initial relative compression rate during the measurements was 2.70×10^{-2} s^{-1} except for the mechanically treated SSL suspension where it was 1.35×10^{-3} s^{-1}. Relative deformation rates during disproportionation may be different. However, these values of the surface tension in compression will certainly be low enough to retard disproportionation to a large extent considering the high E at the similar time scales.

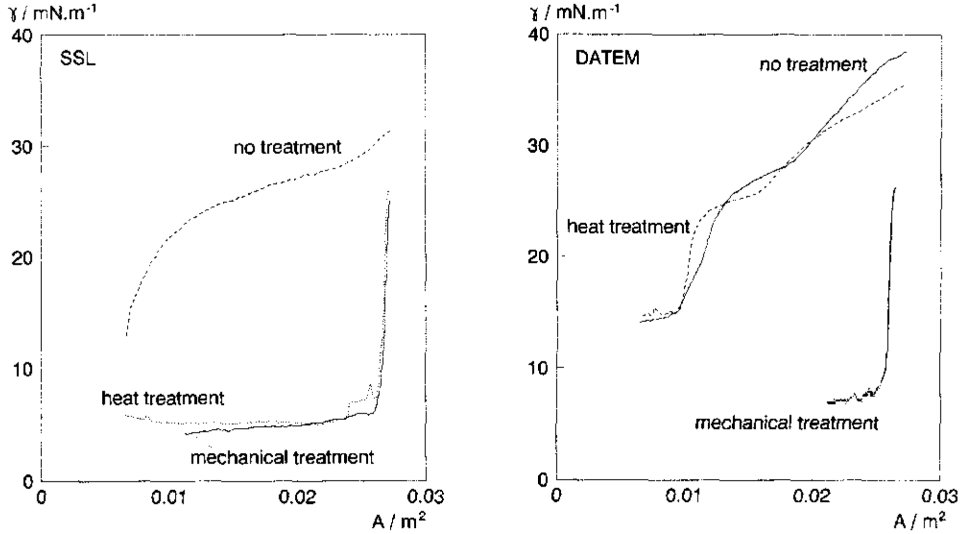

Figure 3.19 Surface tension γ during compression of the surface of different SSL and DATEM suspensions (0.1% w/w). Pre-treatment of the suspension is indicated. Initial relative compression rate was 2.70×10^{-2} s^{-1}, except for the mechanically treated SSL suspension where it was 1.35×10^{-3} s^{-1}. Temperature during measurements ca. 23°C.

3.3.4 DSC and X-Ray tests

DSC

When SSL and DATEM powder were heated, a phase transition could be observed around 317 K resp. 314 K. These can be regarded as the melting 'points' of the powders. From the rather broad melting traject it can be concluded that both powders have a heterogeneous composition. In figure 3.20 the results for the surfactant suspensions are shown.

When a 5% SSL suspension was heated, cooled down and heated again, the following heat effects were observed. During the first heating, a melting peak was seen at 317 K. During cooling down a broad exotherm peak was observed between 313 and 304 K. This peak probably indicates the formation of a certain structure, e.g. an α-gel structure. Another possibility is that recrystallization has occured. During reheating only a small amount of energy is absorbed at 319 K probably due to melting of an α-gel-like phase or of recrystallized SSL. Two peaks were observed during the first heating at 317 and 322 K when such an experiment was performed with DATEM. Both peaks are within the melting region as observed for the pure powder by DSC.

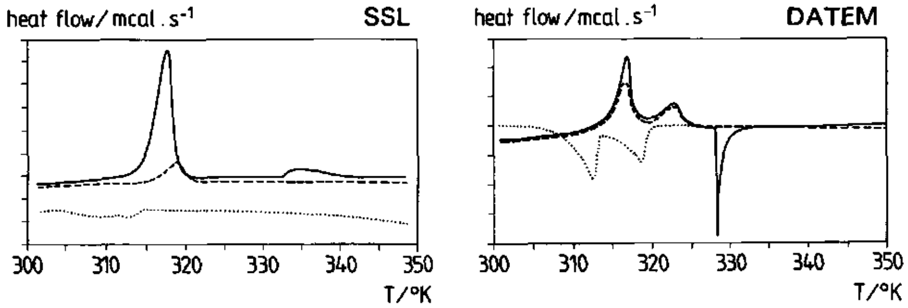

***Figure 3.20** Heat flow during heating (———), cooling down (…………) and reheating (– – – –) a 5% w/w SSL suspension and a 5% w/w DATEM suspension as determined by DSC.*

The appearance of two peaks probably points at a demixing of the suspension. The exotherm peak at 328 K is noteworthy and could imply the formation of a fluid crystalline structure. During cooling down of the DATEM suspension no endotherm transition is observed at 328 K. Apparently, if a liquid crystalline state is formed at 328 K, this is stable during cooling. Two exotherm peaks with roughly the same energy effect as the two peaks observed during heating were found at further cooling. This can indicate a recrystallization of the material. At reheating, the two melting peaks with roughly the same ΔH as before, were observed again but no exotherm transition was seen.

From these experiments it can be concluded that in an aqueous SSL suspension the crystallized structure in the powder disappears and does hardly reform again during and after cooling. Probably an α-gel phase is formed. For a DATEM suspension however the crystalline structure of the powder disappears during heating and is formed again during cooling. Apparently no kind of gel structure was formed. This may explain that no high surface dilational modulus was found after heating and cooling down of a DATEM suspension.

X-ray

From the results of X-ray diffraction measurements on both SSL and DATEM powder it appears that both powders are present in the α-crystalline modification. This can be concluded from the strong reflections at 4.14 Å. DATEM powder gives a rather weak reflection at 4.66 Å which is said to come from a β-modification (Krog, 1990). Reflections at 39.1 Å repeating at higher orders indicate a layer-like arrangement of molecules. This spacing is in fair agreement with a SCL (single-chain length) packing which is reported as 38 Å (Krog, 1990). SSL also exhibits long-range ordening (spacing of 40.2 Å) although the reflections could not be interpreted as a layer-like arrangement.

All 25% w/w suspensions of SSL and DATEM gave a spacing of 4.13 Å at 30 and 60°C and after cooling down to 20°C. In the diffraction pattern of the DATEM suspension a very weak 4.6 Å reflection of the β-modification was observed at 30°C while in the SSL suspension a very weak reflection at 4.33 Å was observed at this temperature. Both these reflections were absent at 60°C and did not return after cooling down. For both suspensions a small-angle reflection was observed at 48 Å at 30°C although this was much stronger in the SSL than in the DATEM suspension. After heating and cooling down this reflection was much weaker.

The interpretation of these results in relation to the dynamic surface properties is difficult because in contrast to the surface rheological experiments no clear differences in the SSL and DATEM suspensions after heating and cooling down were found. However, in the X-ray experiments the concentration of the surfactants in water was much higher (25%) than for the surface rheological ones (0.1%). This may be the reason for the discrepancy. At a concentration of 0.1% no reflections could be observed in the X-ray experiments.

3.4 Conclusions

From the results of the experiments several conclusions can be drawn on the effect of surface (rheological) properties of flour dough components, including added surfactants, on the gas bubble stability in dough.

The first very important finding was that no significant differences were observed between the surface properties of good baking wheat cultivars and poor baking ones. This can imply several things:

- Differences in baking performance between a good and a poor breadmaking wheat cultivar are not due to surface properties.
- Although surface properties can have an effect on the gas bubble behaviour in bread dough this is not the main factor determining bread quality. However, both theoretical considerations and the observed effect of SSL and DATEM leads to the conclusion that although surface properties are probably not the most important factor they still play a role in determining bread quality.
- The experiments as described in this chapter are not the right ones to study the surface properties of flour and gluten. We worked with diluted systems,

which is a requirement for performing surface rheological measurement. However, in this way we may have created a totally different surface composition than present at a gas-dough interface.
- It may also be possible that during mixing in the first stage of the breadmaking process gas bubble surfaces with a very special composition or containing components with a special conformation are formed, which are not at all present in a freeze dried dough suspension.

The results of the sinusoidal oscillation tests (dynamic measurements) show that the surface dilational modulus of dough suspensions, gluten powder, gliadins and wheat total lipids is lower or equal to approximately 100 mN/m for all systems and they all have partly viscous properties. Dough suspensions and gliadin solutions have a surface tension of 40-45 mN/m while a surface full with gluten powder or with spread lipids has a surface tension of 27 mN/m (section 3.2.1).

If the tested systems can be regarded as dough than these properties as measured close to equilibrium show that disproportionation of gas bubbles, involving the growth of the larger bubbles at the expense of the smaller ones, can not be prevented due to the "stiffness" of the shrinking bubble surface because of the viscous properties. The surface tension does decrease during compression of the surface (section 3.3.3) but rather gradually. Disproportionation will therefore be slowed down only, but it will not be stopped. Wheat lipids at low concentrations give the surface rather elastic properties over all the frequencies tested. This is beneficial in retarding disproportionation.

The surface dilational properties close to equilibrium of a surfactant suspension show for the tested surfactants SSL and DATEM surface dilational moduli of 500 to 1000 mN/m after a mechanical treatment (expansion + compression). Such high moduli could be obtained even if the surfactant suspension was not preheated beforehand. During compression the surface tension of these mechanically treated suspensions drops dramatically at very small deformations and stays low at further compression. Such added surfactants are certainly favourable in providing the gas bubble surface with a high stiffness. It is dependent on the surfactant concentration at the surface whether the stiffness will be high enough at longer time scales to stop disproportionation, but this process will be at least strongly retarded over the time scales relevant for breadmaking.

With respect to the stability of dough films in the fermentation stage and the oven rise the surface tension of steady-state expanding surfaces of dough and surfactant suspensions was measured. Dough suspensions behave like other practical systems as beer and milk (Prins, 1990). It must however be said that the concentration of the dough suspension, 0.5% w/w of dough solids, is much lower than the concentration of solids in real dough. It could be well possible that the shear thinning behaviour is different for a more concentrated system.

The tested SSL and DATEM suspensions had a less shear thinning behaviour than practical systems as beer and milk or dough suspensions, especially at a temperature of 50°C. The resistance of a surface containing SSL or DATEM, as expressed in the value of n, is also much lower than for the practical systems mentioned. Due to their low surface tension even during expansion of the surface the addition of SSL ($\gamma_{eq}=27$ mN/m) and to a lesser extent of DATEM ($\gamma_{eq}=37$ mN/m) causes that entrapped air bubbles may be broken up more easily into smaller ones in the mixing stage. A low surface tension during expansion is favourable to prevent the spreading of other surface active components in the film. The most favourable situation would be that no rupture of the film occurs before the starch gelatinization has taken place.

In chapter 5 a more comprehensive discussion of the stability of gas bubbles in dough will be given.

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Chapter 4

Bulk rheological properties of flour and gluten doughs

It is known that bulk rheological and fracture properties of dough play a role in determining bread quality and therefore these properties were studied as well. The first part of this chapter comprises an introduction in the bulk rheological techniques used in this study (sinusoidal oscillation and biaxial extension tests) and a literature review on bulk rheological properties of flour and gluten doughs, in which special attention is paid to strain hardening properties of dough (4.1). Used materials and methods are given (4.2). The results of the different experiments are presented in the following sections: first the properties at small and large deformations of flour and gluten doughs of one special cultivar and the effect of some variables (4.3.1), followed by a discussion on the similarities and differences between a flour and a gluten dough (4.3.2). Next, the bulk rheological properties of 4 wheat cultivars with different breadmaking performances and rye are compared. For the different wheat flours also extensograms, alveograms and the results of a baking test are presented (4.3.3). Flour and gluten doughs of wheats with differences in baking performance show different strain hardening behaviour in biaxial extension at 20°C and also at 55°C. Additional data on the stress level during extension and extensibility of the doughs are necessary to explain the differences in baking performance between the 4 wheat flours tested (4.4).

4.1 Introduction

As is widely recognised, bulk rheological properties of bread dough are important in determining bread quality. Among other cereal flours, wheat flour has almost unique viscoelastic properties which are necessary to produce the spongy structure of a baked bread loaf. In a study on breadmaking physics, the rheological properties of the dough are of major importance and cannot be left out of consideration. In order to obtain information about the structure of both flour and gluten doughs and about the forces existing between the different parts of the (protein)network, it is useful to perform tests applying small deformations on the material. The information on stresses in the dough under conditions which are approaching those in a fermenting bread dough can be obtained by performing biaxial extension tests. The relevant deformation type of the dough around an expanding gas bubble is biaxial extension as is the case in e.g. a ripening cheese with holes in it (Luyten, 1988; Akkerman et al., 1990). These two types of tests were performed in this study.

4.1.1 Bulk rheology

Rheology is the science dealing with the relation between the deformation (strain) of a material, the stress applied and the timescale. In this section some basic principles of rheology will be given. For a more comprehensive discussion see e.g. Ferry (1980) or Barnes et al. (1989). Special attention to dough rheology has been given by e.g. Bloksma and Bushuk (1988) and Menjivar (1990) (see also section 4.1.3).

Regarding their mechanical properties, materials can be divided into three groups viz. elastic, viscous and viscoelastic materials. These groups differ in their ability to store the energy supplied to the material when a stress is applied. Ideal elastic (Hookean) materials deform immediately to a certain strain when a stress σ is applied. The material can store all the strain energy supplied. This energy is totally released after the stress is taken away and the material regains its original shape. The ratio between stress and the relative deformation (strain) is called the modulus. Depending on the way in which the material is deformed it is called the shear modulus or the tensile (or Young) modulus, G and E respectively. For linear elastic materials holds:

$$\sigma = G\,\gamma \tag{4.1}$$

where

$$\sigma = \frac{F}{A} \tag{4.2}$$

In these equations F is the force, A is the surface area on which the force is applied and γ is the shear strain. In ideal viscous materials all the energy supplied is dissipated immediately as heat due to the resulting flow of the material. The material starts to flow at a certain deformation rate independently of the deformation. It will not regain its original shape after the applied stress is taken away. The ratio between the applied stress and the relative strain rate $\dot{\gamma}$ is called the viscosity η.

$$\sigma = \eta\,\dot{\gamma} \tag{4.3}$$

For viscoelastic materials the relation between stress and strain depends on the time scale of the experiment. Its reaction on an applied stress or strain consists partly of an elastic contribution and partly of a viscous one. Such a material contains both bonds that can store the strain energy and bonds that will break due to the heat movement and reform stress-free during deformation.

Normally at relative short time scales the material behaves more elastic while at longer time scales the viscous behaviour becomes more important. The viscoelasticity of a material has several consequences for its rheological properties:

1. The stress required to keep a material at a certain strain level decreases with increasing time scales.
2. The value of the modulus will be lower if it is determined over longer time scales.
3. Part of the strain is permanent.

Both hydrated gluten and flour doughs behave viscoelastic. Since a range of deformation rates are applied to the dough during the breadmaking process the time scale dependence of its rheological behaviour should be well known. Only then valid conclusions about the rheological properties of the material during breadmaking can be drawn.

4.1.2 Bulk rheological measurements

There are various ways of applying a stress or a strain to a material (Whorlow, 1992). The effect of different experimental set-ups on the determined rheological (fracture) properties of food materials was evaluated by Luyten et al. (1992).

In the study described in this thesis two types of tests were used as mentioned in the introduction. Sinusoidal oscillation tests and lubricated uniaxial compression tests. The last type of test can be regarded as a biaxial extension test (Chatraei et al., 1981). Both types of tests will be discussed below.

Sinusoidal oscillation tests

In a sinusoidal oscillation test, also called dynamic test, a sinusoidally varying stress or strain is applied to the material and the resulting sinusoidally varying strain resp. stress is measured (Ferry, 1980). For a viscoelastic material the stress will be out of phase with the strain by a phase angle δ due to the viscous properties of the material. The total modulus, usually denoted as G^*, contains an elastic and a viscous part; the storage modulus G' and the viscous or loss modulus G'' respectively. G' and G'' are given by:

$$G' = \frac{\sigma_0}{\gamma_0}\cos\delta \tag{4.4}$$

$$G'' = \frac{\sigma_0}{\gamma_0}\sin\delta \tag{4.5}$$

where σ_0 and γ_0 are the maximum stress and strain respectively. The ratio between the loss and the storage modulus equals the tangent of the phase or loss angle δ between strain and stress:

$$\tan\delta = \frac{G''}{G'} \tag{4.6}$$

The viscoelasticity of a material over a range of time scales can be studied by determining G' and G" as a function of the radial frequency. The results can only be compared unambiguously with others if they are obtained from experiments in the so called linear region. This is the region where the values of the moduli are independent from the magnitude of the strain.

biaxial extension tests

In a biaxial extension test a cylindrical test piece is compressed between two parallel plates due to a lowering of the upper plate which moves at a constant speed v (Chatraei et al., 1981). The diameter of the plates R is identical to the initial test piece diameter (see figure 4.1) and care is taken to minimize friction between the tested material and the plates. The force F_t is recorded continuously as a function of time. The resistance to the biaxial deformation, characterized by the apparent biaxial extensional viscosity η_{BE}, can be calculated as shown below.

The relative deformation of the test piece at a certain point can be described by the Hencky strain ϵ_h (Peleg, 1977) which will be simply called ϵ:

$$\epsilon = \ln(\frac{h_t}{h_0}) \tag{4.7}$$

where h_0 is the original height of the test piece and h_t the height at time t (see Fig. 4.1). During compression with a test speed of v the relative rate of deformation $\dot{\epsilon}$ increases because the height of the test piece decreases:

$$\dot{\epsilon} = \frac{d\epsilon}{dt} = \frac{dh}{h_t\,dt} = \frac{v}{h_t} \tag{4.8}$$

The biaxial extensional strain rate $\dot{\epsilon}_B$ is defined as:

$$\dot{\epsilon}_B = -\frac{\dot{\epsilon}}{2} \tag{4.9}$$

Since the radius of the part of the deformed material on which the force F acts is constant, the normal stress difference σ_{rr}-σ_{zz} (see Figure 4.1) can be written as:

$$\sigma_{zz} - \sigma_{rr} = \frac{F_t}{\pi R^2} \tag{4.10}$$

The apparent biaxial extensional viscosity η^*_{BE} which is given by the ratio between the stress and the biaxial extensional strain rate can then be given as:

$$\eta^*_{BE} = \frac{\sigma_{rr} - \sigma_{zz}}{\dot{\epsilon}_B} \tag{4.11}$$

Combination of equations 4.7 to 4.10 gives

$$\eta^*_{BE} = \frac{2F_t\,h_t}{\pi R^2\,v} \tag{4.12}$$

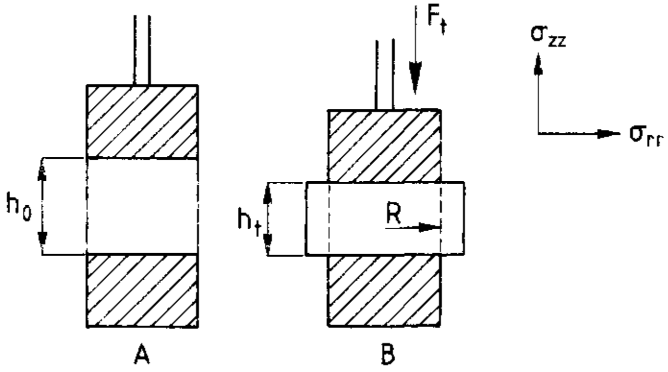

Figure 4.1 Schematic view of the geometry for lubricated uniaxial compression tests. A: situation at the beginning of the experiment; B: situation during compression. F_t *is the force at time t,* h_t *the height of the test piece at time t, R the radius of the compression plate,* σ_{zz} *and* σ_{rr} *are the normal and radial stresses respectively (from Janssen, 1992).*

4.1.3 Bulk rheological properties of flour and gluten doughs

This section presents a (non-comprehensive) review of the current knowledge of bulk rheological properties of both flour and gluten doughs. Special attention is given to one type of behaviour exhibited by gluten and flour doughs during extension: strain hardening. Strain hardening tends to be an important factor in the gas retention abilities of wheat flour doughs (van Vliet et al., 1992).

Flour doughs

The viscoelastic properties of flour doughs have been studied by many researchers. For a review of results obtained by dynamic rheological experiments see for instance Faubion et al. (1985). The linear region of flour-water dough is very small, values reported are for instance $\epsilon < 2 \times 10^{-3}$ (Hibberd and Wallace, 1966) or even $\epsilon < 2 \times 10^{-4}$ (Smith et al., 1970). It was found that the storage modulus G′ decreases with increasing water content of the dough while the loss tangent does not change very much (Dreese et al., 1988c). This indicates that water acts as a diluting agent rather than as a plasticizing agent. Navickis et al. (1982) studied dynamic moduli for different wheat varieties and found that at higher protein/water ratios G′ and G" were higher.

Bloksma and Nieman (1975) reported the effect of temperature on some rheological properties of wheat flour dough in shear. In the temperature range from 25-40°C, the apparent viscosity decreased with increasing temperature. The viscosity increased at temperatures above 40-45°C. This was explained by swelling or gelatinization of the starch granules. The shear modulus also increased at temperatures between 45 and 60°C but far less obvious than did the apparent viscosity. The increase was most clear above 55°C.

Bloksma and Bushuk (1988) gave a review of the rheological properties of dough and the various methods to measure these properties. The more empirical methods as the Brabender farinograph and the extensograph, the mixograph and the Chopin alveograph were also described. These methods are still of great importance for getting an impression of bread making quality of a wheat flour however, it is rather difficult to translate the results obtained in fundamental rheological parameters. The deformation and the deformation rate in these instruments are often very large and elastic and viscous contributions to the mechanical behaviour are difficult to separate.

Addition of a small percentage of NaCl makes the dough stiffer but also more extensible (as measured in the extensograph and the alveograph) and less sticky. However, measurements in the Farinograph show a decrease in dough resistance if salt is added. This decrease in resistance was explained as a result of the decrease in stickiness (Bloksma and Bushuk, 1988).

If emulsifiers without shortenings are added to the dough in amounts up to 0.5% on flour basis, the changes in the rheological properties are minor (Bloksma and Bushuk, 1988).

Gluten doughs

Wheat flour dough has quite unique mechanical (viscoelastic) properties due to which it is able to retain entrapped gas bubbles long enough to get a spongy product: bread. Schofield and Scott Blair already showed in 1937 that gluten is the main factor in providing dough with its unique properties and this is still accepted by most researchers in the field.

Dynamic measurements of gluten doughs have been performed by e.g. LeGrys et al. (1981), Dreese et al. (1988a+b+c), Dreese and Hoseney (1990), Attenburrow et al. (1990) and Janssen (1992). They all observed that the storage modulus G′ and the loss modulus G" increase with increasing frequencies as does the loss tangent. This implies that the resistance to deformation is higher and that the viscous properties of the material are more important at higher deformation rates.

All researchers mentioned found a decrease in G′ with increasing water content of the gluten-water dough while the loss angle stayed relatively constant as was found for flour-water doughs.

At increasing temperature G′ decreased slightly until a temperature of approximately 55 to 60°C above which G′ increased again due to swelling and gelatinization of the residual starch in the gluten samples (LeGrys et al., 1981; Dreese et al., 1988b, Attenburrow et al., 1990).

Eliasson (1990) gave a review of the effects of different additives on the dynamic properties of gluten. The effect of added starch to gluten dough, an increase of G′ and G", is said to be the result of a concentration effect of the gluten due to the fact that less water is available for the protein. Starch acts more or less like a filler material (Smith et al., 1970; Cumming and Tung, 1977). If their is an interaction between the starch granules and the protein, this already on itself will lead to an increase in G′ because G′ of the starch granules is higher than G′ of the protein matrix (van Vliet, 1988). Szczesniak et al. (1983) found a dip in the curves of G′ and G" plotted as a function of the frequency at higher starch/protein ratio. However, this effect was found at frequencies above 5 rad/s which are not comparable to strain rates during bread making conditions. The applied strains might even have been outside the linear region.

Cumming and Tung (1977) added lipids to the gluten-water dough and found that both G′ and G" decreased whereas the loss tangent did not change. It was suggested that the protein-protein interaction was somewhat hindered by the lipids but not changed fundamentally.

Uniaxial extensional measurements with gluten have been performed by e.g. Rinde et al. (1970) and Inda and Rha (1982). It was observed that the stress required to deform the gluten increased with increasing strain. An effect which is called strain-hardening. Kieffer et al. (1983) studied the influence of salts on the extensional properties of gluten and found that low concentrations of NaCl (< 3.6% on dry gluten) weakens the gluten while higher concentrations have a strengthening effect. In a later paper these researchers reported the effect of the gliadin/glutenin ratio on the mechanical properties of wheat gluten in load-extension tests. They found that at increasing prolamin (= gliadin) content the resistance to extension decreased and the extensibility increased (Kim et al., 1988).

Strain hardening

During the fermentation of dough existing gas bubbles are expanding due to carbon dioxide production by the yeast. During baking the temperature rises and evaporation of water, CO_2 and ethanol all contribute significantly to the expansion. This growth of the gas bubbles determines, with other factors, the resulting rise of the dough. The relevant deformation around an expanding gas bubble is biaxial extension (Luyten, 1988). So the most relevant mechanical properties of dough during fermentation and oven spring are those in biaxial extension. Therefore for studying breadmaking potential of doughs, experiments in which this type of deformation is applied seems to be appropriate. Such experiments have been done by e.g. Frazier et al. (1985), Bagley and Christianson (1986), Cullen-Refai et al. (1988), Bagley et al. (1988) and Janssen (1992).

The latter has studied the way in which the mechanical properties of gluten relates to breadmaking performance. An important result was that gluten and flour doughs showed strain hardening behaviour in biaxial extension which means that a relatively more extended gluten or dough film has a higher resistance to deformation than a relatively thicker, less extended, film. Gluten and flour doughs made from a wheat variety with a good breadmaking performance showed a higher resistance to compression and more strain hardening than gluten made from a poor baking wheat. The differences between the studied glutens were primarily accounted for by the difference in the gliadin/glutenin ratio and secondarily by the properties of these separate fractions (Janssen, 1992).

Van Vliet et al. (1992) developed a theory in which strain hardening behaviour of dough is related to breadmaking performance. It is based on the idea that for good breadmaking performance the dough film between two growing gas cells has to be stable against coalescence. This theory has been extended (van Vliet and Kokelaar, 1993) and can be divided in two parts.

1. The first part contains the requirements a bread dough has to meet in order to get a uniform growth of the gas bubbles in the dough during the first part of the fermentation. In this situation a growing gas bubble is surrounded by a relatively thick dough mass. The distance between the peripheries of the gas cells is assumed to be larger than or comparable to their size. It can be shown that *disproportionation will stop due to extra biaxial tensile stress around the* larger gas bubble if the radii of the gas bubbles do not differ too much. Then strain hardening will contribute to the formation of a relatively small bubble size distribution at the onset of the growth due to CO_2 production.

First, we consider two bubbles with initially the same radius. At a certain moment one bubble grows somewhat faster due to for instance a higher local carbon dioxide concentration. This faster growth will be retarded in comparison with the growth rate of a smaller bubble if strain hardening occurs so if $(d\ln\sigma/d\epsilon_B) > 0$. The requirement is somewhat more complicated due to the viscoelastic properties of the dough and the fact that for a similar growth rate in m^3/s *the biaxial strain rate around the larger bubble is smaller. Taking this into* account the criterium to stop unequal growth reads as:

$$\frac{d\ln\sigma}{d\epsilon_B} - 3\frac{d\ln\sigma}{d\dot{\epsilon}_B} = y - 3z > 0 \qquad (4.13)$$

where y is the slope of the ln σ-ϵ_B curve and a measure of the strain hardening behaviour and where z is the slope of the ln σ-ln $\dot{\epsilon}_B$ curve and a measure for the strain rate thinning behaviour.

Secondly, in the case of gas bubbles with a small initial difference in radius the requirements for strain hardening are somewhat different in order to get a uniform growth. The Laplace pressure inside the bubbles is different causing a larger solubility of CO_2 around smaller bubbles than around the larger ones. This causes more gas to diffuse into the larger bubble which will therefore start to *grow sooner. The effect of strain hardening of the dough around the* gas bubbles on the relative growth of these gas bubbles will be discussed further in van Vliet and Kokelaar (1993) but in short the requirements come down to $y-3z > 1$ in the first stage of fermentation and to $y-3z > ½$ at the end of tin proof. The exact numerical values depend to some extent on the actual biaxial stress level σ_B around the gas bubbles.

2. The second part contains the requirements for extending the dough film between two expanding gas bubbles as described by van Vliet et al. (1992). This film has to be stable against rupture during extension. A thinner relatively more extended part of a biaxially extended dough film has a larger resistance to further thinning than an in proportion thicker less extended part if the ratio of the relative increase in stress to the accompanying increase in the strain is larger than 2. So:

$$y + z\,\frac{\mathrm{d}\ln\dot{\epsilon}_B}{\mathrm{d}\epsilon_B} > 2 \qquad (4.14)$$

This equation holds for a single film with a local thin spot in it or for films surrounding gas bubbles with the same radii.

It is shown that under fermentation conditions roughly holds

$$y - 3z > 2 \qquad (4.15)$$

and at the end of the oven proof

$$y + 2z > 2 \qquad (4.16)$$

If these requirements are not satisfied then rupture of some dough films during fermentation will occur if the films are thin enough and this may lead to a coarser bread crumb and a lower bread volume eventually.

Bulk rheological requirements for good baking performance

The bulk rheological requirements of the dough which are probably required for good breadmaking properties have already been summarized in table 2.2 and further discussed in section 2.3. These were:

1. A minimum viscosity of the dough.
2. Optimal resistance to deformation.
3. Extensibility or strain up to rupture that is high enough.
4. Strain hardening in biaxial extension above a minimum.

4.2 Materials and Methods

4.2.1 Materials

Flour

Flour of 4 wheat cultivars with pronounced differences in baking behaviour were used.

1. Spring, a mixture of good baking American wheat cultivars
2. Vedette, a relatively good baking Dutch wheat
3. Taurus, a British wheat with very poor bread making performance
4. Arminda, a poor baking Dutch wheat

These wheat cultivars were chosen based on their breadmaking performance as described in the so-called *'Variety list of agricultural crops 1989'*. (See also figure 1.1).

Rye flour was also used because it is known that bread baked from rye flour without further additives does not meet the quality requirements with respect to bread volume and crumb structure.

Wheat granules were milled with a Bühler milling device to an extraction grade of 75%. The composition of the different flours is given in table 4.1. The rest consist mainly of non-starch polysaccharides like e.g. pentosans.

***Table 4.1** Composition of the flours (weight percentage of total flour)*

Flour	moisture	protein	lipids	starch	ash
Spring	15.57	13.81	0.93	64.4	0.45
Vedette	15.48	9.66	0.33*	65.3	0.51
Taurus	15.31	10.22	1.03	66.7	0.36
Arminda	14.69	9.64	0.38*	66.1	0.51

* percentage probably too low

Gluten

Glutens were prepared from the flours by a small scale Batter process as described in section 3.2.1 (Weegels et al., 1988). In case of the good baking flours (Spring and Vedette) most of the coagulated glutens were held on the second sieve while the glutens of the poor baking flours (Arminda and Taurus) were already held by the first sieve. The fraction containing the highest yield was used for experiments. The composition of the glutens is given in table 4.2.

***Table 4.2** Composition of the glutens (weight percentage of total gluten)*

Gluten	moisture	protein	glutenin/ gliadin ratio	lipids	starch
Spring	2.07	82.6	0.83	2.52	6.1
Vedette	1.87	80.1	0.91	3.10	3.9
Taurus	2.24	73.5	0.70	1.86	11.1
Arminda	2.57	77.4	0.94	2.77	9.3

Emulsifiers and NaCl

Sodium Stearoyl-2-Lactylate (SSL) and Diacetyl Tartaric Acid esters of Monoglycerides (DATEM) were obtained from Quest, Zwijndrecht. NaCl was of analytical grade. The water used was demineralized.

4.2.2 Methods

Preparation of the flour and gluten doughs

Water content of the flour-water doughs was adjusted by means of the Brabender Farinograph up to a dough resistance of 500 Brabender Units (BU). We chose to do the experiments with flour doughs with a water content as is used in practice in the bakeries. For the rheological experiments doughs were mixed in a Mixograph until maximum resistance (so called optimal dough development). The flour-water doughs contained 2% NaCl on flour basis unless mentioned otherwise. In two experiments water content was varied in doughs without salt (section 4.3.1).

In case of the gluten doughs we chose to keep the water content constant to study the differences of the gluten as obtained from the washing procedure. Gluten doughs with a water content of 53.8% (3 g gluten + 3.5 g water) on total dough weight were mixed in the mixograph up to optimal dough development. In tabel 4.3 the water content and the optimal mixing time in the mixograph of the flour and gluten doughs are mentioned.

***Table 4.3** Water content and mixing times (Mixograph) for flour doughs and gluten doughs (water content 53.8/100 g dough)*

wheat cultivar	flour dough			gluten dough
	water content		mixing time	mixing time
	g/100 g flour	g/100 g dough	minutes	minutes
Spring	55.2	35.1	4.5	5
Vedette	52.4	33.9	4	5
Taurus	50.7	33.2	2.5	1.5
Arminda	51.2	33.4	3	2

Sinusoidal oscillation tests

The sinusoidal oscillation tests were performed with a Bohlin VOR constant shear rheometer. The Bohlin was equipped with a plate-plate geometry (radius 1.5 cm). The plates were covered with emery paper to make sure that no slip could occur. The gap between the plates was set to 3 mm.

G′ and G" were determined as a function of frequency at either 20 and 55°C and as a function of temperature at one frequency. Frequency f is given in Hz. Care was taken that the measurements were done within the linear region which was determined by means of a strain-sweep at a relative high frequency (1 Hz).

Flour doughs were put between the plates directly after mixing. The measurements started after a resting period of 20 minutes. For gluten doughs a resting period of at least 30 minutes was applied so that the stress in the doughs could relax for a large part before measurements were started. To prevent drying out of the test piece, the rim of the dough was coated with grease and wet cotton-wool was placed around the dough without making contact.

Results are mean values of two measurements on at least one but mostly two different doughs (so at least two to four measurements in total). Differences in values measured were less than 20% for flour doughs and less than 10% for gluten doughs.

Biaxial extension tests

Biaxial extension tests were performed with a Zwick material testing machine equipped with a 50 N load cell. The cylindrical doughs were compressed uniaxially between two teflon plates with the same initial diameter as the test piece (20 mm).

Doughs were prepared in the mixograph and put in a teflon cylinder for 30 minutes in case of flour doughs and for 1 hour in case of gluten doughs before compression was started. The doughs were covered with a solid teflon cover with the same radius as the dough test piece itself to prevent drying out.

Initial height of the test piece was 20 mm and they were compressed to a final height of 1 mm. The plates and the test piece were lubricated with paraffin oil in order to minimize friction and drying out of the dough during measurement. Deformation force was recorded at three different speeds of the moving upper plate (5, 12 or 120 mm/min). Initial temperature of the dough was 20°C or approximately 55°C. The latter temperature was obtained by placing the teflon cylindrical forms plus cover containing the test piece in a stove set at 60°C during the resting period. Cooling down of the test pieces during compression was slowed down by placing the bottom plate and the test piece within a small thermostated glass container.

Results are mean values of two measurements on at least two different doughs (at least four measurements in total). Differences between measurements were between 10% and 20%.

Extensograms

Flour doughs containing 2% NaCl (on flour basis) and having a water content corresponding to a resistance of 500 BU were prepared in a Farinograph. A 150 g dough was rounded into a ball, shaped into a cylinder and clamped horizontally in a cradle in the Brabender Extensograph. After a resting period of 45 minutes the dough was stretched by a hook which was put over the middle of the cylinder and moved downwards until rupture occured. The stretching force was recorded as a function of time.

Results are mean values of duplo measurements on two different doughs (four measurements in total).

Alveograms

Doughs were prepared in the Chopin Alveograph mixer with a composition according to standard procedures (I.C.C.-standard no. 121). A circular sheet of dough clamped at its circumference was inflated by air and formed into a dough bubble until rupture of the bubble. The pressure inside the bubble was recorded as a function of time.

Results are mean values of measurements on four different samples from one dough.

Baking tests

The recipe used in the baking test was: 600 g flour, 2% NaCl and 2% yeast (on flour weight basis). Water was added up to 500 BU in the Farinograph. Doughs were mixed in an Artoflex mixer. Three 800 g loaves were made out of one dough. Tin proofing continued until 600 ml CO_2 was formed. The loaves were baked for 30 minutes at 240°C. Loaf volumes were measured by seed displacement. The reported values are means of three loaves. The quality of the crumb structure was assessed by the baker of TNO.

4.3 Results and Discussion

4.3.1 Effect of some variables

This section presents the bulk rheological properties of the good baking Spring flour and gluten doughs determined by sinusoidal oscillation and biaxial extension tests. The effect of water content of the flour dough, NaCl, emulsifiers and temperature on the rheological properties are discussed. The results found for Spring are sometimes compared with results for poor baking Taurus doughs.

4.3.1.1 Sinusoidal oscillation tests

The linear region was up to strains of 2×10^{-4} (for flour doughs). For gluten doughs the values of G′ and G" were constant for strains up to 0.1 (at 1 Hz). Higher strains were not tested.

Flour doughs

Water content

In Figure 4.2 the dynamic rheological parameters of Spring and Taurus flour doughs without added salt are given as a function of frequency and for a varying water content.

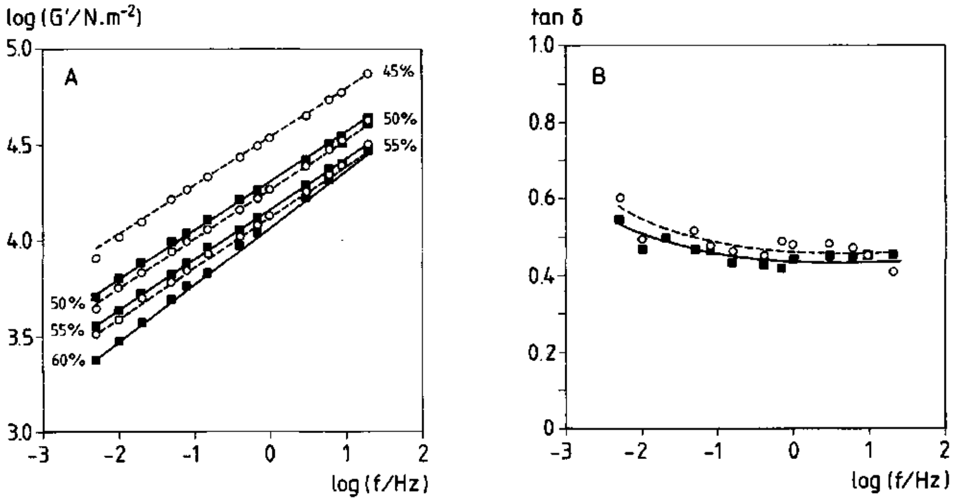

Figure 4.2 (A) Storage modulus G' and (B) loss tangent tan δ as a function of frequency f for Spring flour doughs (■-■-■) with water contents of 50, 55 and 60% resp. and Taurus flour doughs (○-○-○) with water contents of 45, 50 and 55% resp.. Water content is indicated on flour weight basis. No NaCl was added. T=20°C.

From these results it can be concluded firstly that for doughs of the same flour the storage modulus G' is lower at higher water contents and that the loss tangent does not change over the range indicated. Secondly, at the same water content G' of the good baking flour dough is somewhat higher than that of the poor baking flour dough. The first mentioned effect is in agreement with what has been observed by others. The latter effect was also reported by Smith et al. (1970) and Janssen (1992) although the differences they found were more pronounced. Their is no significant difference in tan *δ* between the good and the poor baking flour.

NaCl and emulsifiers

Both for Spring (fig. 4.3) and for Taurus (not shown) flour doughs containing NaCl (2% on flour weight basis) had a lower storage modulus G' and a somewhat lower value of the loss tangent compared to doughs without NaCl addition. The effect of NaCl may be explained by a shielding off of the charged groups of the wheat proteins by the salt leading to a weaker gluten network. Kieffer et al. (1983) found a decrease in gluten strength in uniaxial extension with increasing NaCl content for concentrations lower than 4%. The weakening of the hydrated gluten network was explained by a decreased electrostatic repulsion. They found a strengthening of the gluten network at concentrations higher than 5% which was explained by an effect of the ions on the water structure leading to an enhancement of the formation of H-H bridges and/or an increase in the formation of hydrophobic bonds.

The addition of SSL or DATEM (0.5% on flour weight basis) did not result in a significant change of G' and G" (data not shown).

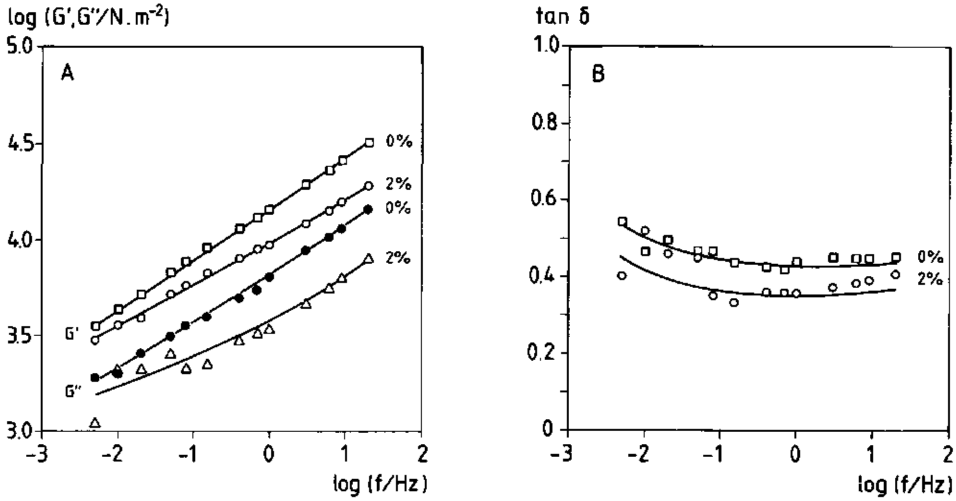

Figure 4.3 (A) Storage modulus G', loss modulus G" and (B) loss tangent tan δ as a function of frequency f for Spring flour dough. NaCl content is indicated. Water content 55% on flour weight basis. T=20°C.

Temperature

The dynamic rheological parameters of Spring flour dough at 55°C are given in figure 4.4. In figure 4.5 the change in storage and loss modulus as a function of temperature are shown.

As shown in fig. 4.5 both G' and G" decrease during heating over the temperature range from 20°C to 55°C while at more elevated temperatures (>60°C) G' and G" increase probably due to swelling and gelatinization of the starch.

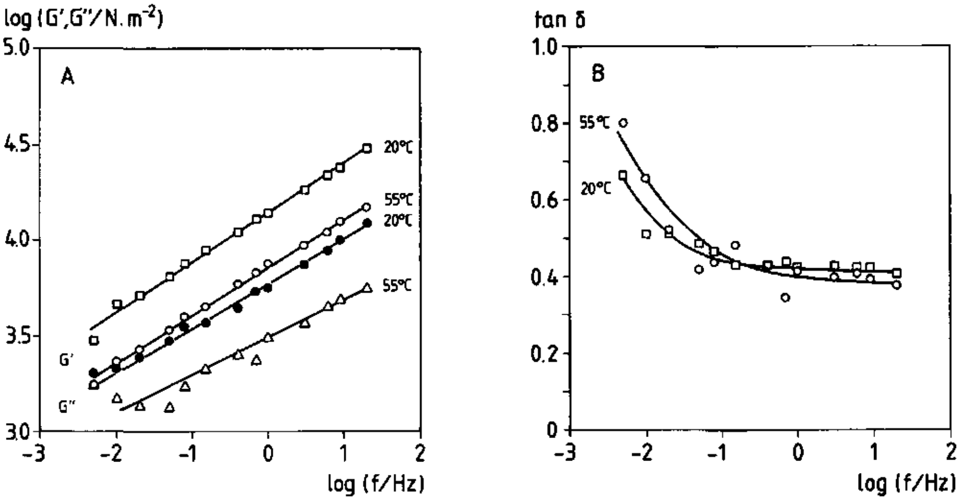

Figure 4.4 *(A) Storage modulus G', loss modulus G" and (B) loss tangent tan δ as a function of frequency f for Spring flour dough (water content 55% on flour weight basis) at 20°C and 55°C.*

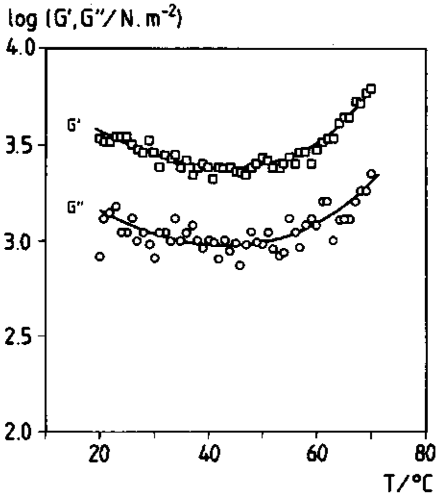

Figure 4.5 *Storage modulus G' and loss modulus G" as a function of temperature T for Spring flour dough (55% water on flour weight basis) (f=0.1 Hz).*

Gluten doughs

The data presented in figures 4.4 and 4.6 show that an increase in temperature from 20 to 55°C causes a decrease in the dynamic moduli. At higher frequencies the storage modulus G′ decreases to the same extent for both flour and gluten dough (approximately a factor of 2). At lower frequencies the change in G′ for gluten dough is much smaller while for flour dough the decrease is constant over the whole frequency range tested. For the flour dough there is no clear effect of the temperature change on the loss tangent but the Spring gluten dough tends to be more elastic at higher temperatures and low frequencies. An interesting point emerges from fig. 4.4B and 4.6B: for flour dough the usual decrease in the loss tangent with frequency is found whereas for gluten dough tan *δ* is found to increase with frequency.

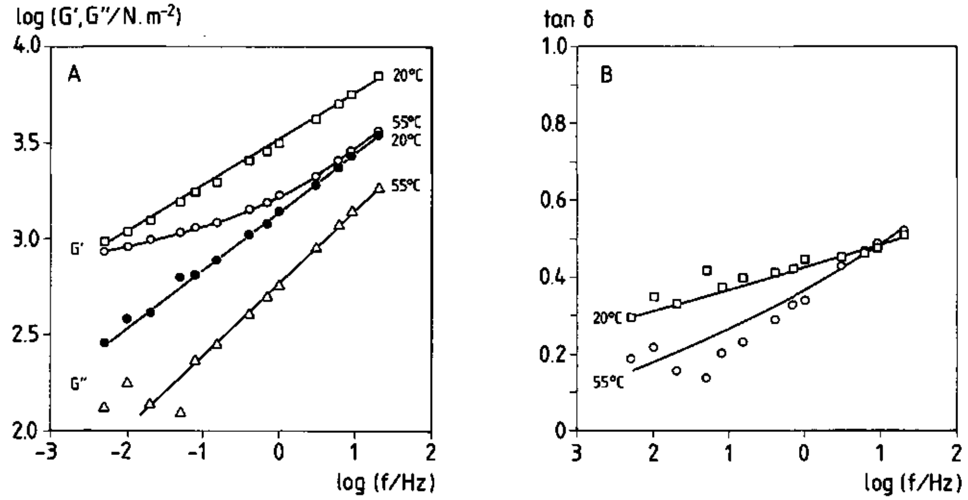

***Figure 4.6** (A) Storage modulus G′, loss modulus G" and (B) loss tangent tan δ as a function of frequency f for Spring gluten dough (water content 53.8% on dough weight basis) at 20°C and 55°C*

4.3.1.2 Biaxial extension tests

During uniaxial compression of a dough at a constant speed the height of the test piece is decreasing. This implies that the biaxial strain rate is not constant but increases during a test. For viscoelastic materials large deformation rheological properties, as the biaxial extensional viscosity, depend both on the strain and the strain rate. Therefore we have to correct for these complications if we want to compare values for the apparent biaxial extensional viscosity at different strains but at the same strain rate. In order to do this properly the following procedure should be followed to correct for the varying strain rate.

From the recorded force F as a function of the displacement of the upper plate y_t at three different speeds of the upper plate v (fig. 4.7A) stress σ (=F/A) as a function of the Hencky strain ϵ ($\ln(h_t/h_0)$ can be calculated and plotted (fig. 4.7B). For every speed the stress, or in this case the natural logarithm of the stress, can be plotted as a function of the (natural logarithm of the) biaxial deformation rate $\dot{\epsilon}_B$ at chosen values of the biaxial deformation ϵ_B, (fig. 4.7C). The biaxial viscosity η_{BE} can be calculated using equation (4.11) and plotted as a function of the biaxial deformation rate $\dot{\epsilon}_B$ at indicated biaxial deformations ϵ_B (fig. 4.7D). Moreover, the final stress-strain curve can be obtained by chosing an $\dot{\epsilon}_B$ and plotting the corresponding values for stress and strain (fig. 4.7E derived from C; data taken at $\dot{\epsilon}_B = 0.01$ s^{-1}).

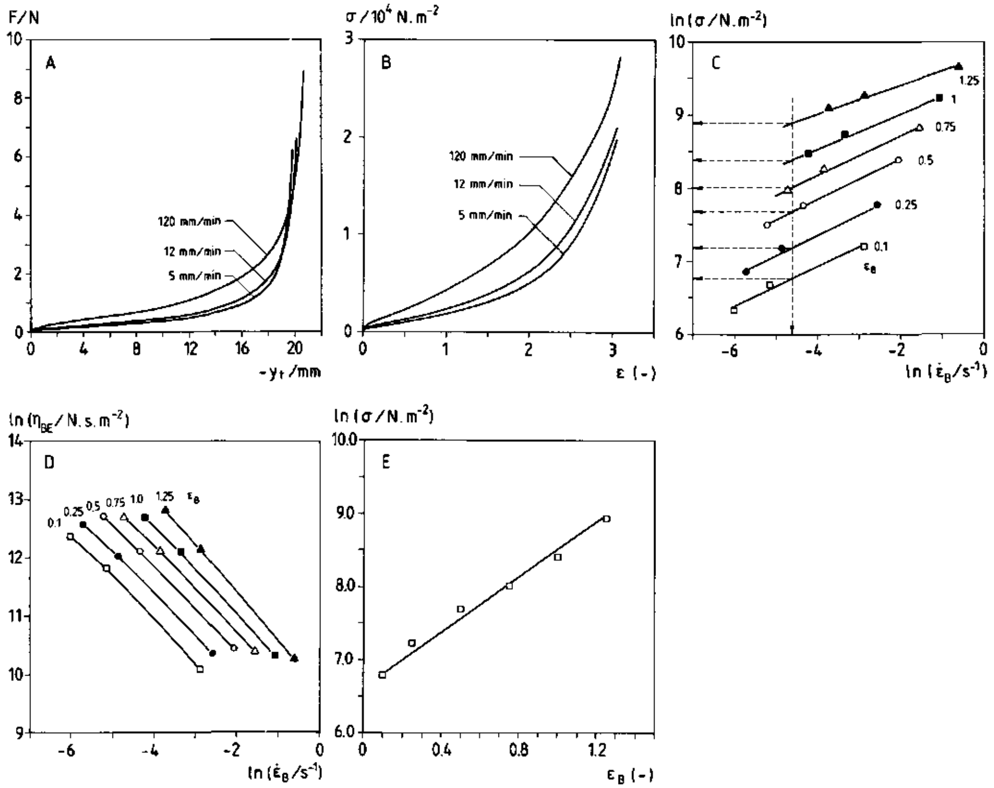

Figure 4.7 Procedure to convert the obtained force (F)-displacement (y_t) curves into biaxial extension parameters. Results of Spring flour dough (55% water on flour weight basis, no NaCl) are used. T=20°C. A and B: compression speed in mm/min is indicated, C and D: biaxial strain ϵ_B is indicated, E: $\dot{\epsilon}_B$=0.01 s^{-1}. For further explanation see text.

From fig. 4.7D it can easily be seen that dough has shear thinning properties. Fig. 4.7E shows that dough has strain hardening properties because the stress is higher at higher strains but at the same strain rate.

Flour doughs

Water content

In figure 4.8 the stress as a function of the biaxial strain is given for Spring and Taurus dough (without salt) for varying water contents. It can be concluded that doughs of one variety showed the same strain hardening behaviour for all water contents tested but that the absolute value of the stress was lower at higher water levels. Strain hardening is more pronounced for the good baking flour Spring. A similar conclusion was reached by Janssen (1992). See also section 4.3.3.

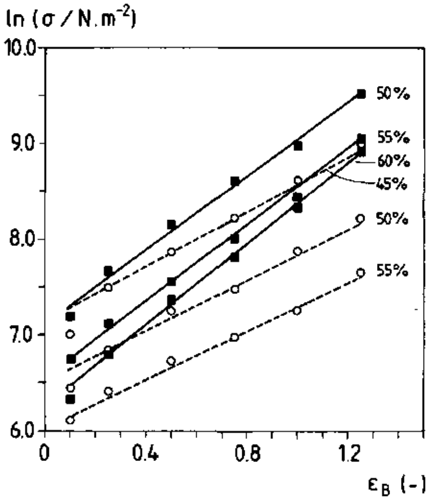

Figure 4.8 *Stress σ as a function of the biaxial strain ε_B for Spring flour doughs (■-■-■) with water contents of 50, 55 and 60% resp. and Taurus flour doughs (O-O-) with water contents of 45, 50 and 55% resp.. Water content indicated on flour weight basis. $\dot{\varepsilon}_B = 0.01\ s^{-1}$, $T = 20°C$.*

NaCl and emulsifiers

No effect of 2% NaCl or 0.5% SSL or DATEM (weight % on flour basis) on the biaxial extensional viscosity or the strain hardening behaviour of Spring and Taurus flour doughs was found. This is not in accordance with the observed effect of 2% NaCl found in the oscillation test where a lower storage modulus was found. Nor is it consistent with the results of Kieffer et al. (1983)

who found a weakening of (gluten) dough as a result of NaCl addition from 0% to 4%. Possibly the addition of 2% NaCl has a weakening effect on dough strength as observed at very small strains in the oscillation test, but during large deformations, as applied in the biaxial extension test, the weakening effect can not be notified anymore due to the strain hardening properties which may react in a different way on salt addition.

Temperature

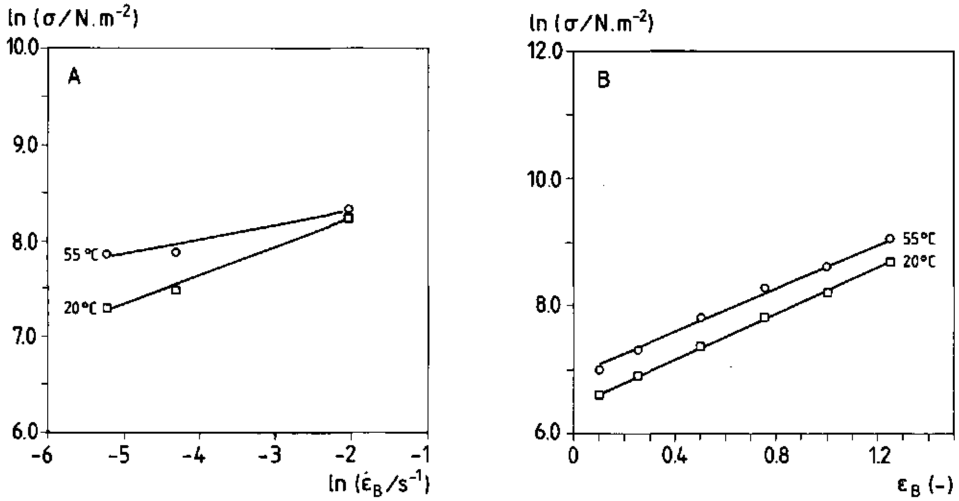

***Figure 4.9** Stress σ as a function of (A) the biaxial strain rate $\dot{\epsilon}_B$ (ϵ_B=0.5) and (B) the biaxial strain ϵ_B ($\dot{\epsilon}_B$=0.01 s^{-1}) for Spring flour dough at 20°C and 55°C.*

Figure 4.9 depicts the effect of an increase in temperature from 20°C to 55°C for Spring dough on the dependence of σ on $\dot{\epsilon}_B$ and ϵ_B. The curves in 4.9 (A) show that the slope of the curve at 20°C is higher than at 55°C indicating a weaker strain rate thinning behaviour at higher temperatures. The strain hardening behaviour (B) is hardly influenced by an increase in temperature. The stresses are even somewhat higher at 55°C. The explanation of this phenomenon is rather difficult. A possible explanation would be that a part of the starch present in the dough was already swollen and/or gelatinized. However, one would then also expect an increase in G' at these temperatures in an oscillation test. The increase in G' started only at around 60°C (see fig. 4.6). On the other hand Bloksma and Nieman (1975) found an increase in the apparent shear viscosity of flour dough at temperatures higher than 45°C. They also observed that the shear modulus started to increase significantly only at temperatures above 55°C.

Also from another point of view it is unlikely that gelatinization or swelling of a part of the starch granules is the reason for the increase in the stress. This becomes clear from a comparison with rye flour dough. For such a dough a lower σ at 55°C was observed (data not shown) while rye starch has approximately the same gelatinization temperature as wheat starch (Lorenz, 1991). A difference between wheat and rye starch is the mean diameter of the granules: approximately 20 μm for wheat and 30 μm for rye starch. However, it is not very likely that this difference is the cause for the difference in changes in σ with an increase in temperature from 20 to 55°C.

All together it is clear that the effect of an increasing temperature on the small deformation properties does not parallel exactly that on the, for bread-making much more interesting, large deformation properties.

So an explanation for the different results of both tests on the effect of a temperature increase from 20 to 55°C must be sought in the geometric scale at which the dough system was studied. In the case of large deformations as involved in biaxial extension experiments large scale structures (e.g. large inhomogenieties) are relatively much more important for the determined relation between stress and strain than in small deformation experiments. At the small scale level as in the oscillation test the flour dough can react quite differently than at a more large scale level during biaxial extension.

Gluten doughs

The effect of increasing the temperature from 20°C to 55°C on the properties during biaxial extension was also determined for gluten doughs. It appears that the absolute value of the stress in the dough during compression decreases with a factor of approximately 1.6 at a deformation of 0.5 and with a factor of nearly 2 at a deformation of 1. The strain hardening behaviour is less at 55 than at 20°C as follows from the lower slope of the curve in Figure 4.10B.

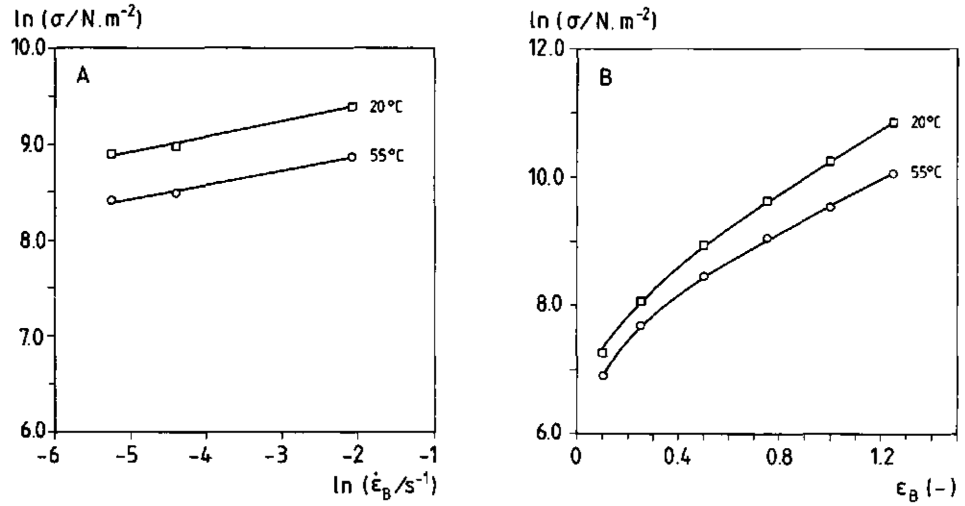

Figure 4.10 *Stress σ as a function of (A) the biaxial strain rate* $\dot{\epsilon}_B$ *(*$\epsilon_B=0.5$*) and of (B) the biaxial strain* ϵ_B *(*$\dot{\epsilon}_B=0.01$ s^{-1}*) (B) for Spring gluten dough at 20°C and 55°C.*

4.3.2 Comparison of flour and gluten doughs

Knowledge about the rheological properties of both flour and gluten doughs is important for (at least) two reasons. The first one is to investigate whether the properties of a flour dough are mainly determined by the gluten matrix or whether other factors are equally or even more important. The second reason is that at fermentation conditions the films between the expanding gas bubbles are still relatively thick and consist of all dough components. At later stages of fermentation the walls between the gas bubbles get thinner and a part of them may consist mainly of a protein matrix with starch granules which are separate from each other (Sandstedt et al., 1954). This means that during that stage film properties are dominated by the properties of the gluten protein network at least so before the swelling and gelatinization of the starch granules starts.

According to Gan et al. (1990) dough membranes consist of a protein matrix with starch gluten embedded in them but at the end of fermentation, before baking, the dough does not have enough material to cover the whole gas-dough interface and "holes" can be observed. These "holes" are no real holes but areas in the dough film just containing surface active material like lipids and/or phospholipids. However, a calculation shows that on average still a dough layer of about 100 μm is present around each gas cell. In this calculation we assumed a gas volume fraction of 0.86, a d_{32} of 500 μm and a specific surface area of 10^4 m^2/m^3. However, the dough mass will not be equally divided and the effect of a broad gas bubble size distribution was also not included. Thus for judging the breadmaking potential of a flour during fermentation and baking we should consider:

- the properties of whole flour dough at fermentation temperatures and part of baking
- the properties of gluten dough at fermentation temperatures, because some films may already locally consist of gluten during fermentation, and at elevated temperatures.

If the rheological properties of Spring flour and gluten doughs are compared the following remarks can be made:

dynamic measurements:

- The relation between the storage modulus G′ and the frequency is more or less the same for gluten and flour doughs.

- Flour dough has a more elastic behaviour at higher frequencies while gluten dough then has more viscous properties. It is very difficult to give an explanation on a molecular basis for this difference.

- At higher temperatures (55°C compared to 20°C) the storage modulus of both flour and gluten dough decreases with a factor of approximately 2 and at the higher temperature the gluten dough behaves more elastic at lower frequencies. The viscoelastic behaviour of flour dough does not change very much with temperature.

biaxial extension tests:

- The absolute value of the stress in the gluten dough is higher in biaxial extension. The protein concentration in the gluten dough is also higher (37% in gluten dough and 9% in flour dough) so a more concentrated protein network, and probably a less irregular network, will be present.

- The decrease in stress at a certain biaxial strain at 55°C compared to 20°C is larger for gluten doughs. This is not consistent with the effect of temperature on the dynamic properties of flour resp. gluten doughs.

- Gluten dough exhibits more strain hardening behaviour which is probably the effect of less disturbing components in the dough.

- The decrease in strain hardening behaviour at 55°C compared to that at 20°C is larger for gluten than for flour doughs.

From these observations it can be stated that it is very worthwhile to study both the properties of the flour as well as of the gluten doughs since there are indeed differences in the rheological behaviour. The gluten matrix in dough does not determine completely its rheological properties. Other components as starch and non-starch polysaccharides will also contribute.

4.3.3 Comparison of doughs of different cultivars

In order to relate rheological properties to baking quality of the (original) flour, experiments were done with 4 different wheat cultivars (see 4.2.1) and with rye flour. The latter was used since a very poor bread is obtained with rye flour if no other ingredients are used. Janssen (1992) already showed that rheological measurements, and more specific biaxial extension measurements, can be useful in discriminating between flours of different baking quality, but only two different wheat cultivars were used in that study and experiments were only performed at 20°C.

The wheat flour doughs tested all contained NaCl (2% on flour weight basis) and a water content corresponding to 500 BU in the Brabender Farinograph. The rye flour dough also contained NaCl and 55% water (on flour weight basis). This proved to be a water content at which the dough was easy to handle. Gluten dough water content was 117% on gluten weight basis (= 53.8% on total dough basis).

At first, the results of the oscillation tests of flour and gluten doughs will be shown, followed by those of the biaxial extension tests.

4.3.3.1 Sinusoidal oscillation tests

Flour doughs

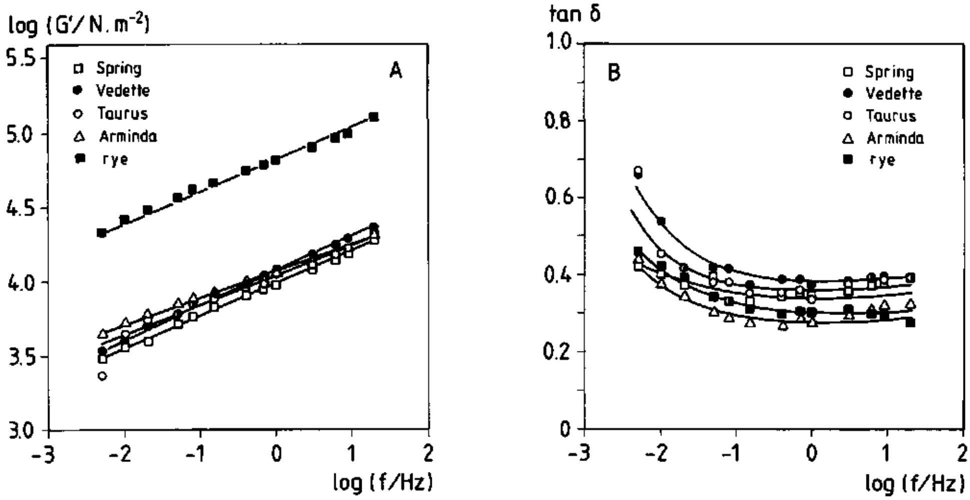

Figure 4.11 (A) Storage modulus G' and (B) loss tangent tan δ as a function of frequency f for flour doughs of 4 wheat cultivars and rye. Water content of wheat flour doughs as given in table 4.3, water content of rye flour dough 55% (on flour weight basis). T = 20°C.

All wheat flour doughs have roughly the same viscoelastic character at the chosen compositions (fig. 4.11). Rye flour dough shows about the same dependence of the moduli on the frequency, but the value of the modulus is about one order of magnitude higher.

The effect of temperature on the dynamic rheological properties for Taurus flour is comparable to its effect on Spring flour as described in section 4.3.1.1. Vedette and Arminda flour doughs were not tested at 55°C. The moduli of rye flour dough were relatively lower at 55°C, but the effect of temperature on the loss tangent was the same as for Spring flour dough.

Gluten doughs

The differences in moduli between the 4 gluten doughs are much more pronounced than between the flour doughs (see fig. 4.12). The good baking glutens have a higher storage modulus and a lower loss tangent. Janssen (1992) found the same trends in her study on two wheat cultivars. A reason that for the gluten doughs the differences between the cultivars are much more clear will be due to the fact that in these doughs the water content was constant which was not the case for the flour doughs.

The decrease of G' for Vedette, Taurus and Arminda gluten due to a temperature increase from 20°C to 55°C was approximately the same as for Spring gluten dough as reported in section 4.3.1.1.

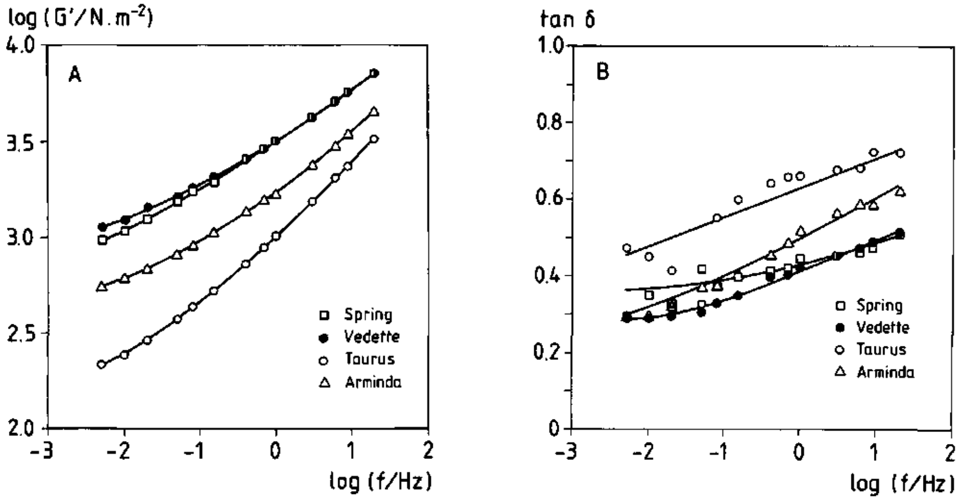

Figure 4.12 (A) Storage modulus G' and (B) loss tangent tan δ as a function of frequency f of gluten doughs of 4 wheat cultivars. Water content of wheat gluten doughs was 53.8% (on total dough weight basis). T=20°C.

4.3.3.2 Biaxial extension tests

Flour doughs

Biaxial extension tests were performed on the 4 wheat flour doughs and rye flour dough. Results show that all wheat flour doughs have approximately the same slope of the stress-strain rate curve at a biaxial strain of 0.5 (suggesting the same strain rate thinning behaviour). However, the values of the stress differ (fig. 4.13A). The very poor baking flour Arminda exhibits the highest stress level of all the tested wheat cultivars, while σ is lower for Spring, Vedette and Taurus in the order mentioned. That stress level alone is no good measure for breadmaking performance is clear from the results for the rye flour dough which in the composition used shows a much higher stress at the strain plotted. However, this could be different at higher water levels and/or different strains. The slope of the curve is lower than for the wheat flour doughs.

The resulting stress-strain curves for the doughs are presented in figure 4.13B. Although it is not immediately clear from the graph, the extent of strain hardening is different for the various doughs (see table 4.4). The two best baking wheats exhibit the strongest strain hardening (higher value of the slope) while the poor baking cultivars are less strain hardening (see Table 4.4).

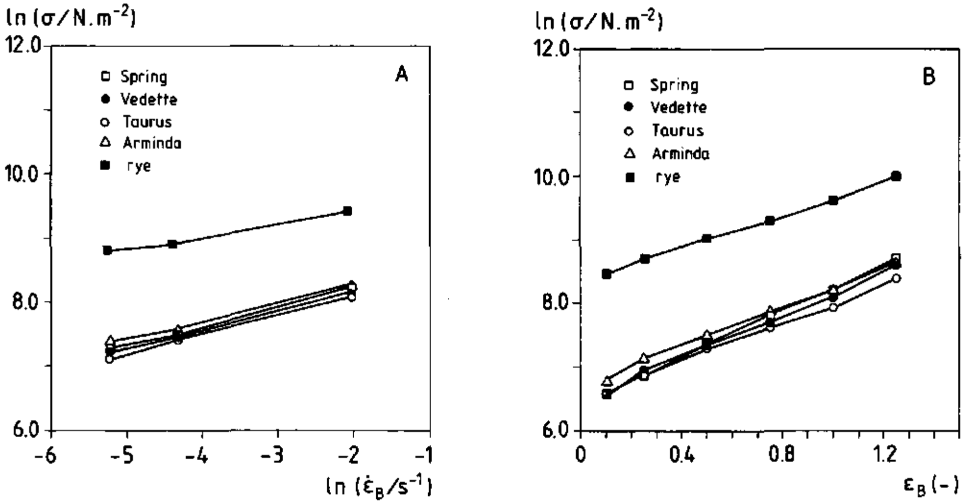

***Figure 4.13** Stress σ as a function of (A) the biaxial strain rate $\dot{\epsilon}_b$ (ϵ_B=0.5) and (B) the biaxial strain ϵ_b ($\dot{\epsilon}_B$=0.01 s^{-1}) for wheat and rye flour doughs. T=20°C.*

At a higher temperature (55°C) there is no decrease in stress required to compress wheat flour doughs to a certain strain but an increase. The biaxial extension test results are thus not consistent with the results of the oscillation tests. As is mentioned in section 4.3.1.2 the explanation for this is not clear.

Gluten doughs

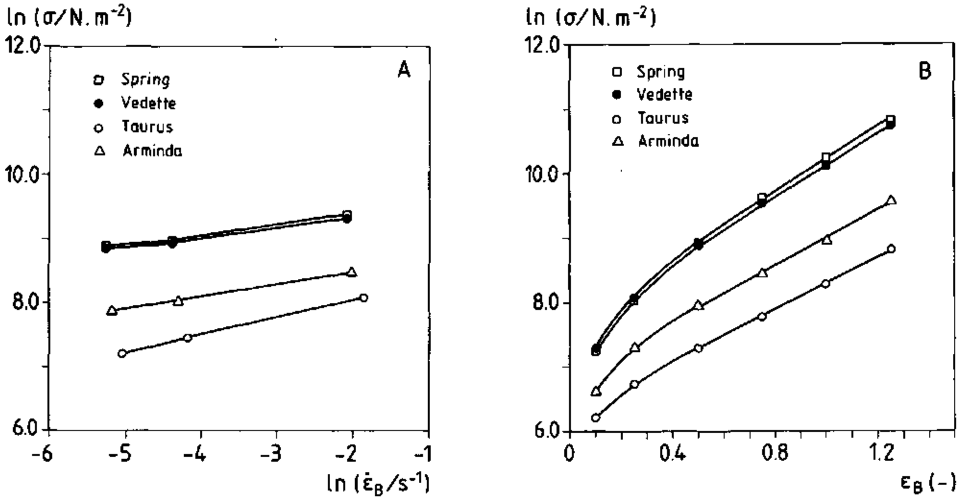

Figure 4.14 Stress σ as a function of (A) the biaxial strain rate $\dot{\epsilon}_b$ (ϵ_B=0.5) and (B) the biaxial strain ϵ_b ($\dot{\epsilon}_B$=0.01 s^{-1}) for wheat gluten doughs. T=20°C.

Results of the tests performed on the gluten doughs are presented in figure 4.14 from which it is clear that the difference in stress level during the deformation is much more pronounced for the different glutens than for the different flour doughs. Better baking cultivars show higher stress levels in the dough and more strain hardening behaviour (see table 4.5). Probably the difference in cultivar effect is partly related to the water content that is constant for the different gluten doughs but not for the flour doughs.

At 55°C the required stress for compressing Spring gluten dough is approximately 2 times lower than at 20°C while in the case of Vedette and Taurus gluten doughs there is a decrease with a factor 1.6. For Arminda gluten dough there is only a very small difference in stress level at 55°C compared to 20°C. (Values of stress chosen at $\epsilon_B = 1$ and $\dot{\epsilon}_B = 0.01$ s^{-1}.)

Comparison of strain hardening behaviour

For comparing the strain hardening behaviour in biaxial extension the slopes of the curves in Figures 4.13 and 4.14 are given in table 4.4 and 4.5 and also those at 55°C. The factor y is taken from the σ-ϵ_B curve as plotted in e.g. fig. 4.14B at biaxial strains between 0.5 and 1.2 because the strain hardening at higher strain levels is more relevant for the more advanced stages of dough rising and it is reasonable to expect that then the dough films are more liable for rupture. The columns "y-3z" and "y+2z" contain the values of the stability factors for the dough membranes as mentioned in section 4.1.3. Although the chosen temperatures 20°C and 55°C are not exactly the same as those in the dough during fermentation resp. oven proof, the values in the columns can be illustrative for both stages in the bread making process.

Table 4.4 *Strain hardening constants for flour doughs (average of four determinations)*

flour	y		z		y-3z	y+2z
	20°C	55°C	20°	55°	20°C	55°C
Spring	1.93	2.21	0.30	0.16	1.03	2.53
Vedette	2.00	1.86	0.30	0.14	1.10	2.14
Taurus	1.73	1.82	0.30	0.11	0.83	2.04
Arminda	1.77	1.61	0.28	0.13	0.93	1.87
rye	1.30	1.37	0.19	0.19	0.73	1.76

Table 4.5 *Strain hardening constants for gluten doughs (average of four determinations)*

gluten	y*		z		y-3z	y+2z
	20°C	55°C	20°C	55°C	20°C	55°C
Spring	3.02	2.62	0.16	0.15	2.54	2.93
Vedette	2.89	2.52	0.15	0.14	2.44	2.80
Taurus	2.20	2.26	0.27	0.12	1.39	2.50
Arminda	2.43	2.45	0.19	0.16	1.86	2.77

* slope at a biaxial deformation between 0.5 and 1.2

From table 4.4 it is clear that from the flour doughs tested only Spring and Vedette meet the requirement during fermentation that y-3z>1 indicating that in doughs of these two cultivars disproportionation of two bubbles with slightly different initial radii can be stopped due to strain hardening of the dough at the start of fermentation. At more elevated temperatures only Spring, Vedette and Taurus flour doughs have enough strain hardening behaviour to fulfil the criterium $y+2z>2$ but the gluten doughs all meet the requirement.

Differences in baking behaviour are well reflected in the results of the biaxial extension experiments both in the required stress to deform the gluten as in strain hardening behaviour of both flour and gluten doughs. However, the results do not explain completely all differences in baking behaviour of the wheat cultivars used. It is found that Arminda gluten exhibits a higher stress and more strain hardening behaviour than Taurus although both have almost equal (very poor) baking properties. A clear difference between their baking behaviour is that Arminda flour gives a loaf with a low bread volume and a rather fine crumb, while Taurus gives a low bread volume with an irregular coarse bread crumb (see section 4.3.3.3). The results would also predict that Spring and Vedette have roughly the same baking characteristics, but this is not the case. Spring flour gives a higher bread volume and a finer crumb structure than Vedette. This implies once again that more factors must play a role in determining baking behaviour.

Considering the stress in compression and strain hardening of the gluten doughs, the conclusion drawn by Janssen (1992) that these properties are primarily determined by the glutenin/gliadin ratio could not be confirmed by these experiments. Arminda gluten had the highest glutenin/gliadin ratio but not the highest stress level and not the most pronounced strain hardening behaviour. It appears that the properties of the separate fractions are just as important.

4.3.3.3 Baking tests, Extensograms and Alveograms

Baking tests were performed with the different flours without any additions but salt, yeast and water to get a clear impression of their baking behaviour. The results are presented in Table 4.7 (see also photographs in figure 1.1, page 7). Compared to results of baking tests in the study of Janssen (1992) where a loaf volume of 4340 ml (based on a 800 g loaf) was found for a very good beking Canadian wheat cultivar, loaf volumes found in this study were low. It is clear that the crumb structure of all the breads was very poor according to the baker of TNO. However, pronounced differences between the used flours in both loaf volume and crumb structure could be observed.

Table 4.7 *Loaf volumes and crumb structure of bread baked from different flours*

Flour	Loaf volume (ml)	Crumb structure (on a scale of 10)
Spring	3600	3.00
Vedette	3350	2.50
Taurus	3092	1.00
Arminda	2583	0.50

In order to compare biaxial extension tests with well established more empirical, dough extension testing methods, experiments were also performed with the Extensograph and the Alveograph. The results of all the tests can be compared to the results of the baking test.

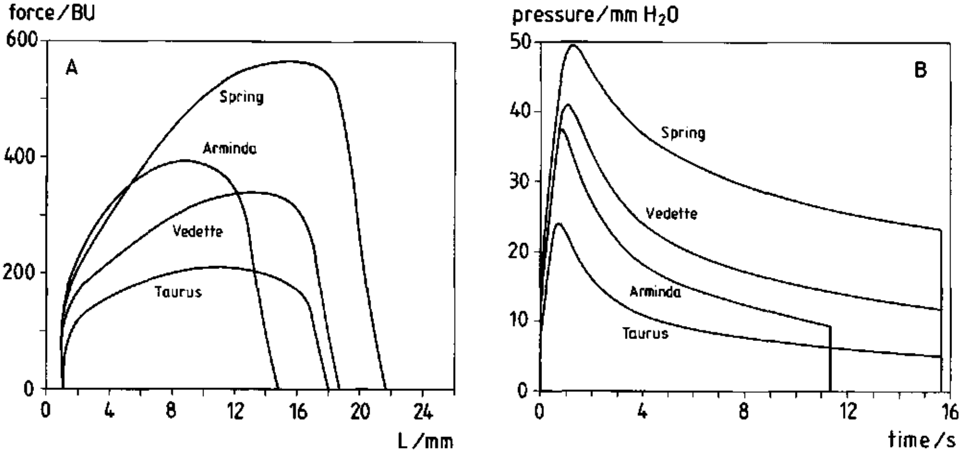

Figure 4.15 *(A) Extensograms and (B) Alveograms of 4 wheat flour doughs. BU: Brabender Units*

The extensograms and the alveograms clearly reflect the differences in baking performance: Spring flour has the best performance of the cultivars used and Vedette seems far worse especially when the results of the extensograph are considered. Arminda shows a much higher resistance to extension than Taurus but rupture occurs earlier. This could be one reason why the loaf volume of bread baked from Arminda is lower than that baked from Taurus.

It is apparent from the results presented in this chapter that performing only one test on (gluten) doughs even if this test can discriminate in general between flours which exhibit differences in baking performance, is not enough to obtain semi-quantitive conclusions on the baking performance of a flour. Only qualitative remarks can be made then and these may sometimes be wrong. A combination of different tests like lubricated uniaxial compression and an empirical extension method like they are performed in the Extensograph and the Alveograph can give the necessary information on the three bulk rheological requirements a dough should meet in order to produce a high quality bread. These requirements have already been mentioned in section 4.1.

4.4. Conclusions

Dynamic measurements in shear can show differences between different baking quality wheat glutens in such a way that good baking gluten has a higher storage modulus G′ and a lower loss tangent. Similar results were shown by e.g. He and Hoseney (1992) and Janssen (1992). Differences in the viscoelastic behaviour of the flour doughs are much smaller and depend mostly on the chosen water content of the dough. Increasing the temperature (to 55°C) leads to a clear decrease in the resistance to deformation (decrease in G′) of both flour and gluten doughs. NaCl addition (2% on flour weight basis) leads to a decrease in G′. A possible effect of emulsifiers on the dynamic rheological parameters was not clear.

However, for a study on the possible relation between the rheological properties of a wheat flour and its baking behaviour it is far more relevant to compare results of biaxial extension tests at larger deformations since this is the type of deformation around an expanding gas bubble.

Differences in biaxial extensional properties were found between cultivars with different breadmaking potential. The stress at a certain strain obtained (by using lubricated squeezing flow method) for the flour doughs does not vary much between the different flours at the water contents used during bread baking but the strain hardening behaviour is different. Alveograms, also a biaxial extension measurement, gave large differences in the pressure required to inflate the dough film although the relative differences between the flours used are more pronounced than the differences in loaf volumes as seen in baking tests.

Differences in gluten doughs as observed from the results of the squeezing flow experiments become more clear at higher temperatures. Since the membranes between the growing gas bubbles may consist locally for the larger part of gluten at the last stage of the oven proof, these properties should be considered next to those of the dough.

Gluten doughs of the good baking flours have higher resistance to biaxial deformation and the strain hardening behaviour is more pronounced. The poor baking wheat gluten Arminda exhibits a high stress but an Arminda flour dough ruptures early compared to the other cultivars both in uniaxial (Extensograph) as in biaxial extension (Alveograph). Arminda flour dough also exhibits weaker strain hardening than the good baking cultivars.

The strain hardening behaviour of the flour and gluten doughs from Spring and Vedette, the good baking cultivars, is such that it meets the requirements as mentioned in section 4.1.3. Doughs of flour and gluten from the poor baking cultivars and from rye flour do not meet the requirements. However, if the membranes consist mainly of gluten and temperature is elevated, the requirement is fulfilled by the gluten doughs of all wheat cultivars tested at 55°C.

These results combined with those of the extensibility tests in the Extensograph and the Alveograph can be of great use to explain differences in baking performance with respect to the loaf volume and crumb structure. Table 4.6 summarizes the bulk rheological requirements and the baking behaviour of the flours used.

***Table 4.6** Comparison of different wheat cultivars and rye*

Flour	strain hardening	resistance to deformation	extensibility	baking performance
Spring	+ +	+ +	+ +	good
Vedette	+	+ +	+	relatively good
Taurus	+/-	-	+	poor
Arminda	+/-	+	-	very poor
rye	-	n.d.	n.d.	extremely poor (n.d.)

Mentioned property is:

+ + present to a large extent; + present; +/- more or less present;

- hardly present; n.d. not determined

Spring and Vedette have the highest resistance to deformation, highest values for the strain hardening constant y and high extensibilities. Arminda is a poor baking wheat. The resistance to deformation is relatively high but rupture of extended dough films occurs quite soon. These properties combined with the fact that strain hardening behaviour is fairly poor suggests that thinner dough films or spots in a film expand faster than thicker parts and that rupture of the films occurs soon. A possibility could be that this low extensibility is due to the high glutenin/gliadin ratio (0.94) of the gluten. However, in the study of Janssen (1992) the tested good baking wheat cultivar had a glutenin/gliadin ratio of 1.15. The quality of the separate glutenin or gliadin fraction may be the reason for the low extensibility. In the case of Taurus, resistance to deformation is relatively low but extensibility is high. However, strain hardening behaviour is not enough to prevent thin, relatively more extended, films from getting thinner and since the resistance is low, local expansion of the membranes occurs fast leading to rupture of the film and coalescence of gas bubbles. This gives a low bread volume and a coarse crumb structure in the end.

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4.5 References

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Chapter 5

Relevance of surface and bulk rheological properties to breadmaking

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In this last chapter the main conclusions on the relevance of surface and bulk rheological properties to breadmaking are given. It appears that surface properties are primarily dominating gas bubble behaviour during the first stage of first proof and they possibly contribute to the stability of dough membranes during the last stages of oven proof before solidification of the dough. Especially wheat lipids and added surfactants in the right concentration are beneficial in retarding disproportionation to a large extent in the stage directly after mixing. Bulk properties as strain hardening and rupture strain are most important in determining gas bubbles behaviour for most of the proof period and during baking.

5.1 Introduction

In this chapter the relevance of both surface and bulk rheological properties of bread dough and its different components will be discussed in relation to the behaviour of gas bubbles in dough throughout the breadmaking process. As mentioned before, this gas bubble behaviour in bread dough is very important for the final appearance of the baked loaf. Many small gas bubbles with a narrow bubble size distribution should be entrapped in the dough during mixing. They should be held separately from each other until due to gelatinization of the starch the dough is transformed into bread. A discussion will be given during which stage of the breadmaking process (mixing, fermentation or baking) surface properties are primarily dominating bubble behaviour and during which stage bulk properties are most important.

The differences in baking performance between wheat cultivars will be discussed in relation to their different mechanical (rheological and fracture) properties.

5.2 Mixing

By means of equation 2.2 in chapter 2 an estimation can be made of the minimum bubble radius after mixing. This is determined by the local shear rate of the dough caused by the moving mixing rod, the (apparent) viscosity of the dough and the surface tension of the dough.

In this study the surface tension of a dough suspension was found to be approximately 40 mN/m which is in agreement with values found by others for comparable systems (see section 2.2). The surface tension of a water surface containing wheat lipids or the added surfactant SSL is approximately 27 mN/m. In a dough system this will probably be somewhat higher since other components will be present at the gas-dough interface as well and an equilibrium situation is probably not obtained. However, lipids and added surfactants will lower the minimal and probably also the mean gas bubble radius of the air bubbles formed during mixing. This will lead to more and smaller bubbles in the dough compared to a dough without these components.

No shear viscosity measurements on dough were performed but there is no reason to believe that apparent viscosities would differ very much from those found by Bloksma (1990a). An order of magnitude calculation (section 2.2) showed that bubble radii of the entrapped and subdivided air bubbles are approximately 5 to 50 μm if the air bubbles are disrupted in shear flow.

Considering the gas bubbles, the amount, the mean radius but also the bubble size distribution of the gas cells is important, because in later stages of the process bubbles should grow out uniformly in order to obtain a regular crumb. Therefore mixing time should be long enough to break up all entrapped air bubbles into gas bubbles with approximately the same bubble radius. In case of the Dutch breadmaking process the resulting bread volume is higher with increasing mixing times although for very long mixing times dough handling becomes more difficult because of the stickiness of the dough (overmixing).

During mixing it may also be possible that newly formed gas bubbles coalesce again after collision but this is not known as a problem in daily practice in bakeries (Sluimer, 1993).

5.3 Fermentation

In this study we assume arbitrarily that fermentation starts as soon as the mixing step ends. In fact fermentation reactions already start during mixing because then the yeast cells are already active in transforming sugars into carbon dioxide and alcohol. The oxygen in the air bubbles originally present in the dough will soon be consumed by the yeast and carbon dioxide will diffuse into the cells.

During the fermentation stage the instability mechanisms which are important in breadmaking, disproportionation and coalescence, may affect gas bubble behaviour in dough. Disproportionation will be important directly after mixing while coalescence starts to play a significant role when gas bubbles are approaching each other to such an extent that thin dough films are formed.

Disproportionation

Directly after mixing gas bubbles with radii varying from 5 to 50 μm are present in the dough (Bloksma, 1990a). With a surface tension of 40 mN/m the Laplace pressure inside these bubbles is 1.6×10^4 and 1.6×10^3 N/m^2 respectively. This difference in Laplace pressure will cause diffusion of CO_2, and to a much lesser extent of N_2, from the small bubbles to the larger ones leading to disproportionation. The shrinking of the small bubbles can be retarded or even stopped if the properties of the gas bubble surface are such that during further shrinking the driving force for disproportionation vanishes. As mentioned in section 2.1.2 this is the case if the surface dilational modulus E exceeds half the surface tension: $E>\gamma/2$ and if the surface behaviour is elastic over the time scale that disproportionation can take place (Lucassen, 1981).

Using equation 2.3 from chapter 2 we can estimate the time it takes for a bubble, filled with CO_2, with radius r_0 to shrink to a bubble with radius r_t when we take the following values for the parameters: T is 303 K, D is 1×10^{-9} m^2/s, S is 4.3×10^{-5} moles/m^3, γ is 40 mN/m, P_0 is 10^5 N/m^2 and the thickness h of the dough layer between the bubbles is 200 μm. Then we get for the gas bubble radius r_t of a small bubble against a much larger one:

$$r_t^2 = r_0^2-8.5\times10^{-13}t \tag{5.1}$$

In the absence of retarding effects due to the stiffness of the surface this would imply that a bubble with a radius of 5 μm disappears in 30 seconds while this takes 2 minutes for a bubble with a radius of 10 μm. This indicates that disproportionation is a very fast process and relative deformation rates of the surface are rather high, in the order of 10^{-1} to 10^{-2} s^{-1}. However, as was already mentioned above if the surface dilational modulus is high enough the process can be retarded.

The different components in dough will be compared regarding their ability to provide the surface with the required properties to give a substantial slowing down of disproportionation. Therefore, in figure 5.1 surface dilational moduli E of different dough components are replotted as a function of the logarithm of the radial frequency. Results of experiments on Spring dough suspension, Spring gluten, Spring wheat lipids (low concentration at the surface = 7.6 mg/m^2, high concentration = 15.2 mg/m^2) are replotted. Results are also shown for SSL after heat treatment (low concentration in suspension about 0.004% w/w) and after mechanical treatment (high concentration: 0.1% w/w).

Indicated is the frequency at which $E=\gamma/2$. Using these frequency values rough estimates can be made of the shrinking rate of a bubble during disproportionation. The following data for $E=\gamma/2$ are taken: for gliadins 22.5 mN/m, for dough and gluten 20 mN/m, for lipids and SSL 14 mN/m.

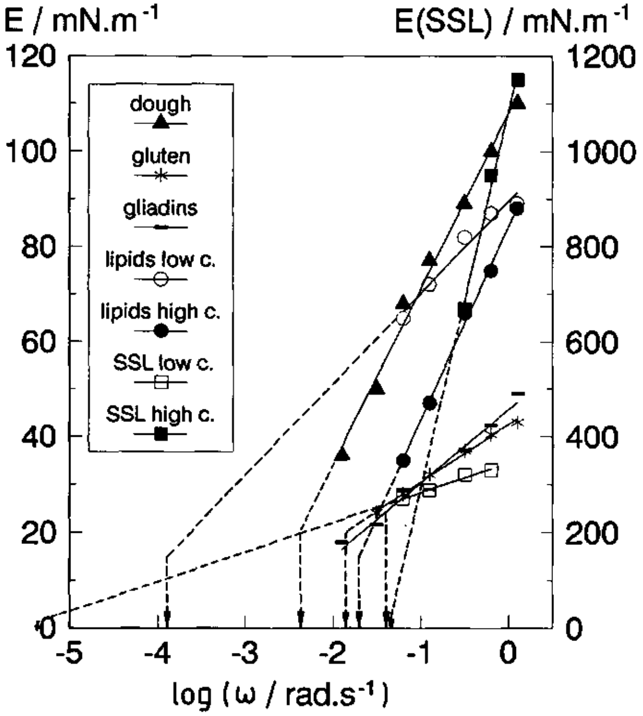

Figure 5.1 Surface dilational modulus E of different dough components as a function of frequency. For each component the frequency at which $E=\gamma/2$ is indicated. Results for SSL are plotted on the right y-axis. For further explanation see text.

The radial frequency at which $E=\gamma/2$ can be taken as a rough estimate of the resulting biaxial strain rate $\dot{\epsilon}_B$ during shrinking of a surface with the component considered because then the requirement according to Lucassen (1981) does not hold anymore. $\dot{\epsilon}_B$ can be written according to van Vliet et al. (1992) as:

$$\dot{\epsilon}_B = \frac{\ln(r_t/r_0)}{dt} = \frac{d\ln r}{dt} \tag{5.2}$$

and the local strain ϵ_B as:

$$\epsilon_B = \ln\frac{r_t}{r_0} \tag{5.3}$$

Equations 5.2 and 5.3 imply that as a first order approximation ϵ_B is 1 after $(1/\omega)$ s and thus $R_t/R_0 = 1/e$ after this time. In table 5.1 values for this time are given as well as the consequences for retarding disproportionation of gas bubbles in bread dough.

***Table 5.1** Estimation of the time in which small gas bubbles shrink to r_o /e during disproportionation for different gas bubble surface compositions*

component at the surface	log ω ($E=\gamma/2$)	time ($r_t=r_0/e$) $=1/\omega$ in s	retarding disproportionation
total dough	-2.32	209 (3.5 min)	to some extent
gluten	-1.79	62 (1 min)	hardly
gliadins	-1.34	22 (0.3 min)	hardly
lipids: low conc.	-3.81	6460 (2 hours)	very much
lipids: high conc	-1.65	45 (0.75 min)	hardly
SSL: low conc.	-5.34	$2\text{x}10^5$ (60 hours)	very much
SSL: high conc.	-1.31	20 (0.3 min)	hardly

From table 5.1 it is clear that wheat lipids and the added surfactant SSL in the right concentrations can retard disproportionation to a large extent. We have not investigated the frequency dependence of the surface dilational modulus of DATEM but it is likely that this surfactant will exhibit similar properties after a mechanical treatment. The total dough system retards the process to some extent. The exact composition of this surface is not known but will be a mixture of lipids and proteins. Gluten and gliadins retard disproportionation hardly or not at all in the concentration tested.

In the consideration above it was assumed that no biaxial stress will be built up around the gas cells before and during the disproportionation process. However, at a certain strain the biaxial stress around the expanding larger bubbles can become so high that it exceeds the Laplace pressure and thus will counteract disproportionation as well. In order to get information on the stage of the breadmaking process in which this will happen we must consider data of the Laplace pressure and the biaxial stress for the different stages during the breadmaking process (table 5.2). The data of the biaxial strain rate and the biaxial strain have been calculated using the equations 5.2 and 5.3.

For the calculation of the values given in table 5.2 some assumptions have been made apart from the one that directly after mixing the strain of the dough around the gas cells is zero. 1) After mixing the volume fraction of the gas in the dough is 10% (relative volume is 1.1). 2) The radius of the gas cells that will grow out at the beginning of first proof is 100 μm. 3) We assumed that no intermediate moulding and rounding steps take place. The biaxial stresses at the strain (rates) indicated are results obtained from the biaxial extensional experiments on Spring dough.

Table 5.2 *Comparison of Laplace pressure and biaxial stress around expanding gas bubbles in a fermenting bread dough (Spring)*

stage	bubble radius r (μm)	biaxial strain rate $\dot{\epsilon}_B$ (s^{-1})	biaxial strain ϵ_B (-)	Laplace pressure ΔP (N/m^2)	biaxial stress σ_B (N/m^2)
after mixing	5-50	-	-	1.6×10^4 - 1.6×10^3	-
first proof	100-135	1.1×10^{-3} -	0 - 0.3	800-600	0- 700
	150-200	2.7×10^{-4}	0.45-0.75	530-400	700-1000
final proof	230-300	3.8×10^{-4} - 8.6×10^{-5}	0.85-1.15	350-270	1000-2000

From table 5.2 it may be concluded that initially the disproportionation process is influenced only by surface properties. However, for bubbles with a radius of more than 150 μm, which are present already during first proof, the biaxial stress around these bubbles exceeds the Laplace pressure and this will retard or stop the growth of the larger bubbles during disproportionation. This value of the radius may be an overestimation since some resisting stress will already have developed around the expanding bubbles during disproportionation. So very soon after the first proof period has started, bulk properties will dominate further gas bubble behaviour in dough.

As is also clear from table 5.2 biaxial stress is increasing at further expansion of the gas bubbles due to the strain hardening properties of dough. This implies that the gas bubbles which have expanded relatively more will be retarded in their expansion while the relatively less expanded ones can expand further. This leads eventually to a more regular bubble size distribution of the bubbles that are large enough to grow with respect to the partial carbon dioxide pressure in the dough during first proof. The bubbles that shrank during disproportionation will not, or only in a later stage, grow (see section 2.2). These very small bubbles will give the bread its white color. The wheat cultivars that show the most strain hardening behaviour will end up with the most regular bubble size distribution. This is a favourable situation at the start of the baking step.

Coalescence

During fermentation gas cells grow out to a relative volume of 4.1 (volume fraction of gas in dough approximately 0.75). Tiny gas cells are accomodated between the ones that have expanded to a radius of approximately 200 to 250 μm. Bloksma (1990b) has calculated, assuming spherical gas cells arranged in a cubical array, the volume fraction of gas in relation to the number and distance between gas cells. He concluded that at the end of tin proof gas cells will strongly deform each other. In case of a bimodal bubble size distribution, which will probably be present in dough, the larger cells will certainly have approached each other very closely and some will also deform each other. We estimate the thickness of dough membranes to be between a few hundreds and 35 μm (diameter of starch granules).

By means of equation 2.9 $(2(\gamma_{eq}+E(\Delta A))=h\sigma_B)$ an estimation can be made of the thickness h of a film during thinning at which surface properties become important compared with the bulk rheological ones. For the unknown parameters, data obtained from measurements on Spring dough (suspension) will be taken: $\gamma_{eq}=42$ mN/m, $E=35$ mN/m, $\sigma_B=2\times10^3$ N/m^2. If linear behaviour is assumed, then h is approximately 75 μm. This is probably an overestimation of h because E depends on the change in surface area and may not be linear anymore at the end of final proof where the surface area has been enlarged by a factor of 5.4 (van Vliet et al., 1992).

Added surfactants like SSL can give a water surface a high dilational modulus (chapter 3). However, it is questionable whether these high surface moduli will still exist after the large bubble surface expansions that take place during fermentation. The results of the continuous expansion tests (figure 3.17A) show that the surface tension does not exceed values of approximately 32 mN/m at relative expansion rates of 10^{-3} s^{-1}. The specific structures, held responsible for the existence of the high surface modulus, may have been destroyed during this kind of deformation.

If biaxial stresses are higher or lower than found for Spring dough, bulk properties are dominating the behaviour in thinner or thicker films respectively than 75 μm. In this respect, other bulk rheological properties like extensibility and strain hardening behaviour determine whether a dough film will be resistant against further extension or not. In chapter 4 it was shown that for the different wheat cultivars tested good baking wheat cultivars have the highest resistance to biaxial deformation, the most pronounced strain hardening properties and the highest extensibilities. Poor baking wheat cultivars may have an elevated resistance to extension (Arminda), but when the extensibility of the dough is too low, rupture of the dough membranes occurs too soon leading to a low loaf volume.

In case of very thin films (smaller than the diameter of a starch granule) it is probably more relevant to consider the properties of the material between the starch granules which is for the larger part consisting of a gluten network. Differences in biaxial stress levels as well as in strain hardening are even more pronounced for gluten doughs than for flour doughs from wheat cultivars with differences in baking performance (see table 4.5). This indicates that for cultivars with good baking properties bulk properties will be important up to very thin films.

5.4 Baking

During the final stage in the breadmaking process some major changes occur (Bloksma, 1986). Firstly, the gas cells expand fast in a relatively short time, the so-called oven rise. The relative volume of the gas in the dough changes from 4.1 to 6.5. Secondly, the fluid dough mass is transformed into a solid bread structure which is caused for the larger part by the gelatinization of the starch. Thirdly, the foam structure of the dough is transformed into a sponge structure with interconnected gas cells. Because changes occur rapidly during baking, this stage is the most critical of the whole process and so the properties of the dough at elevated temperatures should be considered as well in order to relate rheological properties to baking performance.

Baking takes about 30 minutes and the temperature of the dough changes from 30 to about 70°C (oven temperature is 230°C). Since a temperature gradient exists in the dough expansion of the gas cells starts sooner at the outside than at the inside of the dough. This implies also that gelatinization of starch occurs sooner at the outside. If we assume gelatinization of the starch to occur at 60°C and a temperature rise of the dough at the outside of 0.1 K/s then the dough membrane should be stabilized for 300 s (5 min).

Stability of the dough membranes towards rupture before gelatinization of starch is the essential property required to get a high loaf volume and a regular crumb structure of the final baked product. As was discussed above, the calculated film thickness at room temperature of the membranes where surface and bulk properties contribute equally to film resistance is about 75 μm or lower. However, at 45°C the surface dilational modulus of a dough suspension is about a factor of 5 lower than at 20°C. Biaxial stresses of flour doughs are roughly similar at 55°C compared with those at 20°C at the same $\dot{\epsilon}_B$ and ϵ_B, but for (Spring) gluten dough biaxial stress is 2 times lower at 55°C. Strain hardening behaviour of both flour and gluten doughs does not change very much due to a temperature increase from 20 to 55°C. In total, and again assuming linear behaviour, it follows that for films down to about 30 μm, bulk properties of (gluten) dough determine for the larger part the stability of the film towards extension at more elevated temperatures.

In films thinner than mentioned above surface properties may become important in stabilizing these films towards further extension. The requirements needed for good baking behaviour were discussed in section 2.3. If spreadable components like e.g. lipids are present in the film then a low surface tension during expansion is favourable. During continuous expansion of a dough suspension at 45°C at a relative expansion rate of $5\text{x}10^{-3}$ s^{-1}, the surface tension is approximately 45 mN/m. This indicates that a small surface tension gradient is present at expansion of this system, which may be favourable for stabilizing thin expanding films. However, the surface tension in expansion is so high that e.g. lipids reaching the surface can spread and may lead to destabilization of the expanding film. If lipids or added surfactants are already present in the surfaces of an expanding dough film, surface tensions in expansion will probably be lower than for the expanding dough suspensions and other components will probably not spread.

It is rather difficult to determine at which film thickness the concentrations of the present surfactants in dough, like proteins, lipids and added surfactants as SSL or DATEM, become so low that the Gibbs film elasticity becomes the relevant parameter for film stability. This will probably be the case in a few very thin films and will not affect final bread quality very much.

No differences in surface properties between dough suspensions and gluten from different wheat cultivars could be found. Therefore it is not very likely that differences in bread making performance are caused by the surface properties of the thin films possibly present during the oven rise before solidification of the dough occurs.

5.5 Conclusions

By considering both surface and bulk rheological properties of bread dough and its different components and comparing the values of the parameters that play a role in determining the behaviour of the gas bubbles in dough the following conclusions can be drawn.

The surface tension of the dough and its apparent viscosity during mixing determine the (minimal) gas bubble size after mixing. Adding surfactants like SSL and DATEM will cause a decrease in the bubble radius and an increase in the amount of the entrapped air bubbles compared to a dough without these additives.

Directly after mixing disproportionation of gas bubbles will occur within a few minutes. This process can be retarded very much by wheat lipids and added surfactants. If the dough has sufficient strain hardening properties, the gas bubbles that are large enough to expand at the existing partial carbon dioxide pressure will get a narrow bubble size distribution. This leads to a regular crumb structure in the final product. In more advanced stages of tin proof bulk rheological properties as strain hardening and extensibility of the dough will determine the stability of the dough membranes towards rupture. These properties differ for wheat cultivars with different breadmaking performance.

Also during the baking process bulk properties determine the stability of the gas bubbles in dough towards coalescence for an important part. Only in fims thinner than the diameter of a starch granule surface properties may become important in stabilizing the dough film. However, no differences in surface properties between wheat cultivars with pronounced differences in baking performance could be found. This indicates that the surface properties of these thin dough films are probably not determining final bread quality.

The last table shows the relevance of surface and bulk properties to breadmaking performance and summarizes the main conclusions of this thesis.

***Table 5.3** Relevance of surface and bulk properties to breadmaking*

stage in breadmaking process	surface properties		strain hardening	resistance to extension	extensibility
	γ	E			
mixing	+	-	-	-	-
first proof	+ +	+ +	+ +	+ +	-
final proof (second half)	-	-	+ +	+	+
baking	?	?	+ +	+	+ +

explanation of symbols: + + very relevant; + relevant; - not relevant

5.6 References

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List of symbols

Greek symbols

Γ	surfactant adsorption	$mol.m^{-2}$
γ	shear strain (bulk rheology)	-
γ_0	maximum strain	-
$\dot{\gamma}$	shear strain rate	s^{-1}
γ	surface tension	$N.m^{-1}$
γ_{eq}	equilibrium surface tension	$N.m^{-1}$
$\Delta\gamma$	surface tension difference	$N.m^{-1}$
δ	loss angle (bulk rheology)	rad
ϵ	strain	-
ϵ_B	biaxial strain	-
$\dot{\epsilon}$	strain rate	s^{-1}
$\dot{\epsilon}_B$	biaxial strain rate	s^{-1}
ϕ	relative volume ($\phi = (V_l + V_g)/V_l$)	-
η	viscosity	$N.s.m^{-2}$
η^*	apparent viscosity	$N.s.m^{-2}$
η_{BE}	biaxial extensional viscosity	$N.s.m^{-2}$
η_d	surface dilational viscosity (dynamic measurements)	$N.s.m^{-1}$
η_s^d	surface dilational viscosity (continuous expansion/compression)	$N.s.m^{-1}$
π	surface pressure (γ-γ_{eq})	$N.m^{-1}$
θ	loss angle (surface rheology)	rad
ρ	fluid density	$kg.m^{-3}$
σ	stress	$N.m^{-2}$
σ_0	maximum stress	$N.m^{-2}$
σ_B	biaxial stress	$N.m^{-2}$
σ_{rr}	normal stress	$N.m^{-2}$
σ_{zz}	normal stress	$N.m^{-2}$
ω	radial frequency	$rad.s^{-1}$

Roman symbols

A	area	m^2
dlnA/dt	relative surface expansion rate	s^{-1}
c	concentration	% w/w
c_b	concentration in the bulk	$mol.m^{-3}$
c_s	concentration at the surface	$mg.m^{-2}$
D	diffusion coefficient	$m^2.s^{-1}$
d	X-ray spacing	Å
E	surface dilational modulus	$N.m^{-1}$
E_d	surface dilational elasticity	$N.m^{-1}$
E_f	Gibbs film elasticity	$N.m^{-1}$
F	force	N
f	frequency	Hz
G	shear modulus	$N.m^{-2}$
G'	storage modulus	$N.m^{-2}$
G"	loss modulus	$N.m^{-2}$
h	film thickness	m
h_0	*original height*	*m*
h_t	height at time t	m
m	power law constant	-
n	power law constant	-
P_0	atmospheric pressure	$N.m^{-2}$
ΔP	Laplace pressure difference	$N.m^{-2}$
r	bubble radius	m
r_0	bubble radius at time 0	m
r_t	bubble radius at time t	m
R	gas constant	$J.mol^{-1}K^{-1}$
R	radius of test piece	m
S	solubility	$mol.m^{-3}$
T	temperature	°C or K
T_c	Kraft point	°C or K
t	time	s
V_l	volume of liquid dough without gas	m^3
V_g	volume of gas	m^3
v	compression speed	$m.s^{-1}$
dv_x/dy	shear rate	s^{-1}
y	strain hardening constant	-
z	strain rate hardening constant	-

Summary

The stability of the gas bubbles in dough towards disproportionation and coalescence throughout the breadmaking process determines for a large part the final appearance of bread with respect to two important bread quality aspects: crumb structure and loaf volume. The rheological properties of the gas bubble-dough surface as well as the bulk rheological and fracture properties of the dough between the gas bubbles may contribute to their stability. The aim of this study is to quantify their contributions in order to establish the relevance of both kinds of rheological properties to breadmaking. Therefore, 1) surface and bulk rheological properties of wheat cultivars with pronounced differences in baking quality were determined, 2) the breadmaking process was analyzed regarding the relevant mechanical processes and 3) the relation was studied between these processes and possible relevant (surface and bulk) rheological properties.

Breadmaking can be regarded as a physical process: air bubbles are entrapped and subdivided in the liquid dough mass during mixing and this makes that dough is a foam. During fermentation yeast cells are producing carbon dioxide that diffuses into the bubbles which will expand as a result. In the last stage of the breadmaking process, baking, further expansion of the gas bubbles occurs due to an increase in temperature causing, among other things, more CO_2 production as well as evaporation of water in the gas cells. If the temperature in the dough has become high enough, starch gelatinizes and the dough films between the expanding bubbles become solid. The dough has been transformed into bread. Some solid membranes rupture at continuing expansion and the gas bubbles become interconnected: bread has a sponge structure.

In chapter 2 general foam making and foam stability principles are introduced and the effect of surface and bulk rheological properties on disproportionation and coalescence is discussed. The behaviour of the gas bubbles in bread dough, their amount, size and size distribution are considered for the main stages of the breadmaking process: mixing, fermentation and baking. After mixing gas bubbles with radii between 5 and 50 μm are present and filled with N_2 and CO_2. During fermentation a part of the smallest bubbles will not grow because, due to their high Laplace pressure; the saturation concentration of CO_2 around these bubbles will not be reached. Instead they will shrink because disproportionation will occur: carbon dioxide, and to a much lesser extent N_2, will diffuse towards larger bubbles with a lower Laplace pressure. During baking the relative volume of the gas becomes so high that the dough membranes between the bubbles can become very thin and part of them will even get thinner than the diameter of the starch granules embedded in the (gluten)protein network. To prevent coalescence of the gas cells, the dough membranes should be stable until the dough gets a more solid character due to gelatinization of starch. At the end of the chapter an attempt is made to formulate the physical (rheological) requirements a dough has to meet for good breadmaking performance.

The surface rheological requirements for good baking performance are formulated as follows. 1) During mixing a low surface tension in expansion and compression is favourable to break up air bubbles into smaller ones. 2) During fermentation a surface dilational modulus that exceeds half the surface tension over the relevant time scales is favourable to retard or stop disproportionation. 3) For the stabilization of an expanding dough film, the building up of a surface tension gradient during expansion is beneficial. To stabilize thin expanding dough films, which are possibly present during baking, against rupture, the surface tension in expansion should be low to prevent materials that have reached the surface from spreading.

The required bulk rheological properties of dough for good baking performance are formulated as 1) viscosity above a minimum value throughout the whole breadmaking process, 2) an optimal resistance to extension, 3) a high extensibility and 4) high strain hardening properties during fermentation and baking.

In chapter 3 surface rheological experiments on different dough components are described. To determine the surface dilational modulus the so-called 'ring trough' was used. The surface properties at large deformations were determined with a Langmuir trough. An important finding of this study was that no significant differences between surface rheological properties of dough suspensions from wheat cultivars with different baking performances were found. Therefore, it is concluded that surface rheological properties are not the main factor in determining bread quality. However, certain dough components like wheat lipids and added surfactants, such as SSL and DATEM, can retard disproportionation to a large extent. These components, if present in the right concentration, provide the surface with a high surface dilational modulus over the relevant timescales. Wheat proteins, total gluten and separate gliadins, do not exhibit the right surface properties to retard disproportionation substantially in the systems tested. A surface tension gradient is built up at continuous expansion of a dough suspension. This is favourable to prevent coalescence. However, surface tension values are such that e.g. lipids reaching the surface can spread and may destabilize the dough film.

Another important finding of this study was that suspensions of SSL and DATEM exhibit very high surface dilational moduli (500-1000 mN/m) after having undergone a mechanical treatment comparable to mixing without preheating the suspension.

In chapter 4 bulk rheological experiments on both flour and gluten doughs of 4 wheat cultivars with different baking performances, as well as of rye flour are described. The relevant deformation of dough around expanding gas bubbles is biaxial extension. Therefore, biaxial extension measurements were performed. Additionally, sinusoidal oscillation tests (dynamic measurements) were performed as well. Alveograms and extensograms of the 4 wheat flours were recorded and baking test were done. Differences in biaxial extension properties are found between the tested wheat flour doughs. The biaxial stresses for the various doughs do not vary much at the strains applied. The water contents of these doughs were similar to those used in breadmaking and not the same for every dough. However, their strain hardening properties are different. At 20°C good baking wheat cultivars show higher strain hardening properties than poor baking cultivars and rye, which is also the case at 55°C. Differences in biaxial stress and strain hardening properties are much more pronounced for gluten doughs at the water content tested than for flour doughs and the differences become even more clear at 55°C. However, additional results from extensibility tests in e.g. the Alveograph and Extensograph are necessary to explain differences in baking quality with respect to crumb structure and loaf volume for all the wheat cultivars tested.

The relevance of surface and bulk rheological properties of dough to breadmaking performance is discussed in chapter 5. The effects of these properties on the foam instability mechanisms, disproportionation and coalescence, during mixing, fermentation and baking are dealt with. Both the surface tension and the viscosity of the dough during mixing determine the (minimum) radii of the entrapped gas bubbles after mixing. It appears that surface properties are primarily dominating gas bubble behaviour during the first stage of fermentation directly after mixing. Certain dough components as wheat lipids and added surfactants can retard disproportionation to a large extent. Already during first proof bulk rheological properties, especially biaxial stress and strain hardening contribute to the formation of a relative small bubble size distribution at the start of bubble growth and to its preservation during further stages. At the baking stage extensibility and strain hardening determine stability of expanding gas bubbles to coalescence. Possibly, surface properties may contribute to dough film stability at the end of oven rise if the films have become very thin.

Résumé

La stabilité au disproportionement et à la coalescence des bulles de gaz dans la pâte lors de la panification détermine pour une grande partie deux aspects de qualité importantes du pain: la structure de la mie et le volume. Les propriétés rhéologiques de surface ainsi que les propriétés rhéologiques de masse et les propriétés de rupture de la pâte entre les bulles peuvent contribuer à leur stabilité. L'objet de cette thèse est de quantifier ces contributions pour établir la pertinance des deux sortes de propriétés rhéologiques. Pour faire cela 1) les propriétés rhéologiques de surface et de masse de la pâte de farines de blé de qualité boulangère très differentes ont été déterminées, 2) la panification a été analysée au sujet des processus physiques et 3) la relation entre ces processus et les propriétés rhéologiques éventuellement importantes a été établie.

La panification peut être vue comme un proces physique: des bulles d'air sont prises et subdivisées dans la pâte "liquide" lors du pétrissage ce que signifie que la pâte est une mousse. Pendant la fermentation les levures produisent de l'acide carbonique qui diffuse dans les bulles entrainant leur gonflement. Pendant la phase finale de la préparation du pain, la cuisson, les bulles de gaz continuent à gonfler à cause de l'élévation de la température causant, entre autre, une augmentation de la production de CO_2 et l'évaporation de l'eau dans les bulles. Si la température dans la pâte est assez élévée, l'amidon gelatinise et les films de pâte entre les bulles deviennent solides. La pâte est transformée en pain. Le gonflement continue ce qui cause la rupture de quelques membranes. Les bulles de gaz sont connectées entre elles: le pain a une structure d'éponge.

Au chapitre 2 les principes généraux de la préparation et de la stabilité des mousses ont été introduits et l'effet des propriétés rhéologiques de surface et de masse sur le disproportionement et la coalescence a été discuté. Le comportement des bulles de gaz dans la pâte, leur quantité, leur dimension et la distribution de leur taille ont été considerés pour les phases de la panification: le pétrissage, la fermentation et la cuisson. Après le pétrissage des bulles avec des rayons entre 5 et 50 μm sont présentes et elles sont remplies de N_2 et CO_2. Lors de la fermentation une partie des petites bulles ne gonfleront pas à cause de leur pression de Laplace élevée: la saturation de CO_2 autour de ces bulles n'est pas obtenue. Par contre, elles diminuent de volume suite au disproportionement: le CO_2, et dans une mesure nettement moindre N_2, diffuseront vers les bulles plus grandes possédant une pression de Laplace plus basse. Lors de la cuisson le volume rélative de gaz devient tellement élevé que les films de pâte entre les bulles

peuvent devenir très minces, et une partie des films deviennent probablement plus mince que le diamètre des granules d'amidon qui se trouvent dans le lacis de protéines (de gluten). Pour prévenir la coalescence de bulles de gaz, les films de pâte doivent rester stables jusqu'à la gelatinization de l'amidon qui donnent un caractère solide à la pâte. A la fin du chapitre les conditions physiques (rhéologiques) de la pâte pour obtenir un pain bien expansé et avec une structure de la mie suffisament fine ont été formuleés.

Les conditions rhéologiques de surface pour obtenir un bon pain ont été formulées comme suivent. 1) Lors du pétrissage une tension de surface en expansion et en compression assez basse est favorable pour subdiviser les bulles d'air en bulles plus petites. 2) Lors de la fermentation le module de dilatation de surface qui excède la moitié de la tension de surface pendant les temps pertinants est favorable pour retarder ou arrêter le disproportionement. 3) Le développement d'un gradient de tension de surface est favorable pour stabiliser des films de pâte minces qui expandent. Pour stabiliser des membranes de pâte très minces, peut-être présents lors de la cuisson, contre la rupture, la tension de surface doit être basse pour prévenir que les composants qui atteignent la surface ne s'étalent.

Les conditions rhéologiques de masse nécessaires pour obtenir un bon pain ont été formulées comme 1) une viscosité au dessus d'une valeur minimum lors de toute la panification, 2) une résistance optimale contre l'extension, 3) une extensibilité assez élevée et 4) des propriétés "strain hardening" assez élevées lors de la fermentation et la cuisson.

Au chapitre 3 les expériences rhéologiques de surface sur des composants différents de pâte ont été décrites. Pour determiner le module de dilatation de surface le dit "jauge d'anneau" (ring trough) a été utilisé. Les propriétés de surface à grandes deformations ont été déterminées à l'aide d'un appareil de Langmuir. Un résultat très important de cette étude était qu'il n'y avait pas des différences significatives entre les propriétés de surface des suspensions de pâte faites des farines de différentes qualités boulangères. Pour cela, on a conclut que les propriétés de surface ne déterminent pas la qualité du pain. Pourtant, quelques composants de la pâte tels que des lipides du blé ou des émulsifiants, comme SSL et DATEM, peuvent largement retarder le disproportionement. Ces composants, s' ils sont présents en concentrations adequates, confèrent à la surface un module de dilatation de surface important sur les temps considerés. Les protéines du blé, le gluten total et les gliadines, ne montrent pas de bonnes propriétés de surface pour retarder efficacement le disproportionement dans les systèmes étudiés. Un gradient en tension de surface est développé pendant l'expansion continue d'une suspension de pâte. Cela est favorable pour prévenir la coalescence. Pourtant les valeurs de la tension de surface sont tels que par example des lipides, atteignant la surface, peuvent déstabiliser le film de pâte.

Un autre résultat très important de cette étude était que les suspensions de SSL et DATEM peuvent avoir des modules de dilatation de surface très élevés (500-1000 mN/m) après avoir eu un traitement méchanique comparable au pétrissage sans préchauffement de la suspension.

Au chapitre 4 les expériences rhéologiques de masse sur des pâtes de la farine et du gluten de 4 variétés de blé possédant des qualités boulangères différentes, ainsi que de la farine de seigle ont été déscrites. La déformation pertinante de la pâte autour des bulles expandées est l'extension biaxiale. Ceci est pourquoi les mesures en extension biaxiale ont été faites. Additionellement, des mesures dynamiques ont été faites. Des alvéogrammes et extensogrammes ainsi que des tests de cuisson des 4 farines de blé ont été faites. Des differences en propriétés sur l'extension biaxiale ont été trouvées entre les farines de blé étudiées. Les tensions biaxiales de ces pâtes ne varient pas beaucoup aux déformations appliquées. Les teneurs en eau de ces pâtes étaient les mêmes qu'à la panification et pas la même pour tous les pâtes. Pourtant, les propriétés strain hardening n'étaient pas pareilles. A 20°C les variétés de blé de bon qualité boulangère ont des propriétés strain hardening plus prononcées que les variétés de mauvaise qualité boulangère et le seigle, ceci est également verifier à 55°C. Les différences en tensions biaxiales sont plus prononcées pour des pâtes de gluten à la teneur en eau étudié que pour les pâtes de farine et les differences deviennent plus prononcées à 55°C. Mais les résultats additionels des tests d'extensibilité dans l'Alvéographe et l'Extensographe par example sont nécéssaires pour expliquer les différences en qualité boulangère entre les variétés de blé étudiées.

La pertinance des propriétés rhéologiques de surface et de masse à la panification a été discutée au chapitre 5. Les influences de ces propiétés sur le disproportionement et la coalescence, lors du pétrissage, la fermentation et la cuisson, ont été discutés. La tension de surface et la viscosité de la pâte lors du pétrissage déterminent tous les deux les rayons (minimales) des bulles prises dans la pâte. Il semble que les propriétés de surface sont plus importantes en ce qui concerne le comportement des bulles immédiatement après le pétrissage. Quelques composants de la pâte comme des lipides et certain surfactants peuvent retarder le disproportionement dans une mesure essentielle. Déjà pendant le premier pointage les propriétés rhéologiques de masse, en particulier la tension biaxiale et le strain hardening, contribuent à la formation d'une distribution de la taille des bulles assez étroite au début du gonflement et à sa préservation après. Lors de la cuisson l'extensibilité et le strain hardening déterminent la stabilité des bulles de gaz contre le coalescence. Peut-être, les propriétés de surface contribuent à la stabilité des membranes de pâte à la fin de la phase du pointage au four si les films sont devenus très minces.

Samenvatting

De stabiliteit van gasbellen in deeg tegen disproportionering en coalescentie tijdens het totale broodbereidingsproces bepaalt voor een groot deel het uiterlijk van brood betreffende twee belangrijke kwaliteitskenmerken: kruimstruktuur en broodvolume. De reologische eigenschappen van zowel het gas-deeg oppervlak als de bulkreologische en breukeigenschappen van het deeg dragen bij aan de stabiliteit van de bellen tegen genoemde mechanismen. Het doel van dit onderzoek is om deze bijdrage te kwantificeren en de relevantie van oppervlakte- en bulkreologische eigenschappen voor het bereiden van brood te beoordelen. Daartoe werden 1) van deeg(componenten) van tarwerassen met een duidelijk verschil in bakkwaliteit de oppervlakte- en bulkreologische eigenschappen bepaald, 2) de verschillende stadia in het broodbereidingsproces geanalyseerd op wat de relevante vervormingen zijn en 3) werd het geheel met elkaar in verband gebracht.

Het bereiden van brood kan gezien worden als een fysisch proces: luchtbellen worden in het vloeibare deeg ingeslagen en verkleind tijdens het kneden wat betekent dat deeg als een schuim beschouwd kan worden. Tijdens de rijsperiode produceren de gistcellen koolzuur dat de bellen in diffundeert. Als een gevolg daarvan zullen deze uitzetten. Tijdens de laatste fase van het broodbereidingsproces, het bakken, vindt verdergaande expansie plaats omdat door een stijging in temperatuur o.a. er meer CO_2 geproduceerd wordt en waterdamp de bellen in diffundeert. Als de temperatuur in het deeg hoog genoeg geworden is verstijfselt het zetmeel en worden de deegfilmen tussen de uitzettende bellen vast. Het deeg is brood geworden. Sommige vastgeworden deegmembranen breken bij verdergaande expansie waardoor de gasbellen met elkaar in verbinding komen: brood heeft een sponsstruktuur.

In hoofdstuk 2 worden algemene principes over het maken van schuim en schuimstabiliteit geïntroduceerd en het effect van oppervlakte- en bulkreologische eigenschappen op disproportionering en coalescentie wordt behandeld. Het gedrag van gasbellen in brooddeeg, hun aantal, grootte en grootteverdeling worden bediscussieerd tijdens de drie voornaamste fasen van het broodbereidingsproces: kneden, rijzen en bakken. Na kneden zijn er gasbellen met een straal tussen 5 en 50 μm in het deeg aanwezig. Deze zijn gevuld met N_2 en CO_2. Tijdens de rijs zal een deel van de kleinste bellen niet groeien omdat, als gevolg van de hoge Laplacedruk in deze bellen, de verzadigingsconcentratie van CO_2 rond deze bellen nooit bereikt wordt. In plaats daarvan zullen ze krimpen omdat er disproportionering optreedt: koolzuur, en veel langzamer ook stikstof, zal naar de grotere bellen

diffunderen die een lagere Laplacedruk bezitten. Tijdens het bakken wordt het relative gasvolume in het deeg zo hoog dat deegmembranen tussen de bellen erg dun kunnen worden en een deel hiervan zal zelfs dunner worden dan de doorsnede van de zetmeelkorrels in het (gluten)eiwitnetwerk. Om coalescentie van gasbellen te voorkomen moeten de deegmembranen stabiel blijven totdat het deeg een meer vaste stof karakter krijgt door het verstijfselen van zetmeel. Aan het eind van het hoofdstuk worden de fysische (reologische) criteria geformuleerd die brooddeeg moet bezitten om goede bakeigenschappen te geven.

De oppervlaktereologische criteria voor een goede bakkwaliteit zijn als volgt geformuleerd. 1) Tijdens het kneden is een lage oppervlaktespanning in expansie en compressie gunstig om de ingeslagen luchtbellen tot kleine belletjes te verkleinen. 2) Tijdens de rijs is een oppervlaktedilatatiemodulus die hoger is dan de helft van de oppervlaktespanning over de relevante tijdschalen gunstig om disproportionering te vertragen of te stoppen. 3) Om tijdens het bakken te voorkomen dat de expanderende deegfilmen tussen de bellen breken is het opbouwen van een oppervlaktespanningsgradient tijdens expansie gunstig voor de stabiliteit van de deegfilm. Om te voorkomen dat dunne deegfilmpjes, die mogelijk aanwezig zijn tijdens het bakken, breken moet de oppervlaktespanning tijdens expansie laag blijven zodat voorkomen wordt dat bepaalde componenten in de deegfilm zullen spreiden als ze aan het filmoppervlak komen.

De bulkreologische criteria waaraan deeg moet voldoen voor goede bakeigenschappen zijn geformuleerd als 1) een viscositeit hoger dan een minimum waarde tijdens het hele broodbereidingsproces, 2) een optimale weerstand tegen uitrekking, 3) een hoge vervorming voordat breuk optreedt (ofwel een hoge uitrekbaarheid) en 4) uitgesproken rekverstevigingseigenschappen (strain hardening) gedurende de rijs en het bakken.

In hoofdstuk 3 worden de oppervlaktereologische experimenten met verschillende deegcomponenten beschreven. Voor het bepalen van de oppervlaktedilatatiemodulus werd de zogenaamde 'ringtrog' gebruikt. De oppervlakte-eigenschappen bij grote vervormingen werden bepaald met een Langmuirtrog. Een belangrijk resultaat van dit onderzoek is dat geen significante verschillen in oppervlaktereologische eigenschappen van deegsuspensies van tarwerassen met verschillende bakkwaliteiten werden gevonden. Daarom wordt geconcludeerd dat oppervlaktereologische eigenschappen niet de belangrijkste factor zijn voor het bepalen van de bakkwaliteit van tarwe. Echter, bepaalde deegcomponenten zoals tarwelipiden en toegevoegde emulgatoren als SSL en DATEM (die in de praktijk vaak toegepast worden bij de broodbereiding) kunnen disproportionering in sterke mate vertragen. Deze componenten kunnen, als zij in de juiste concentratie aanwezig zijn, het oppervlak over de juiste tijdschalen een hoge oppervlaktedilatatiemodulus geven. Tarwe-eiwitten zoals het totale gluten of gliadine hebben in de concentratie waarin ze gemeten zijn niet de juiste oppervlakte-eigenschappen om disproportionering wezenlijk te vertragen. Tijdens het expanderen van een oppervlak van een deegsuspensie wordt een oppervlaktespanningsgradient opgebouwd. Dit is gunstig om coalescentie te voorkomen. Echter, de gemeten oppervlaktespanningen zijn zodanig dat bijvoorbeeld lipiden kunnen spreiden en een expanderende deegfilm mogelijk kunnen destabiliseren.

Een ander belangrijk resultaat van dit onderzoek is dat suspensies van SSL en DATEM zeer hoge oppervlaktedilatatiemoduli (500-1000 mN/m) kunnen hebben nadat zij een mechanische behandeling hebben ondergaan die vergelijkbaar is met het kneden van deeg en zonder dat de suspensie vooraf was opgewarmd.

In hoofdstuk 4 worden de bulkreologische experimenten aan bloem- en glutendegen van 4 tarwerassen met verschillende bakkwaliteiten en aan roggebloemdeeg beschreven. De relevante vervorming van deeg rond expanderende gasbellen is biaxiale (tweezijdige) rek. Daarom zijn biaxiale rekmetingen uitgevoerd. Ter aanvulling zijn ook dynamische metingen gedaan. Van de 4 verschillende bloemdegen zijn alveogrammen en extensogrammen bepaald en bovendien zijn bakproeven uitgevoerd. Er werden verschillen gevonden in de biaxiale rekeigenschappen van de 4 verschillende bloemdegen. De biaxiale spanningen varieerden niet zo veel tussen de verschillende bloemdegen als deze een watergehalte zoals dat bij het bakken van brood wordt gebruikt en voor het onderzochte gebied van vervormingen. De mate van rekversteviging is echter wel verschillend. Goed bakkende tarwerassen vertonen bij 20°C meer rekversteviging dan slecht bakkende tarwerassen en rogge, wat ook het geval is bij 55°C. Verschillen in biaxiale spanning en rekversteviging zijn duidelijker voor glutendegen met hetzelfde watergehalte dan voor de bloemdegen en de verschillen worden nog duidelijker bij 55°C. Echter, aanvullende resultaten van rekmetingen in bijv. de Alveograaf of de Extensograaf zijn noodzakelijk om verschillen in bakkwaliteit tussen verschillende rassen betreffende kruimstruktuur en broodvolume volledig te kunnen verklaren.

De relevantie van oppervlakte- en bulkreologische eigenschappen van deeg voor het bereiden van brood wordt besproken in hoofdstuk 5. De invloed van deze eigenschappen op de schuiminstabiliteitsmechanismen, disproportionering en coalescentie, tijdens kneden, rijs en bakken worden behandeld. Zowel de oppervlaktespanning als de viscositeit van het deeg tijdens het kneden zijn van belang bij het bepalen van de (minimale) straal van de ingeslagen gasbellen. Het blijkt dat oppervlakte-eigenschappen voornamelijk het gasbelgedrag bepalen in de periode direkt na het kneden. Bepaalde deegcomponenten als tarwelipiden en toegevoegde emulgatoren kunnen in sterke mate disproportionering remmen. Al tijdens de eerste fase van de rijs dragen ook bulkreologische eigenschappen, met name biaxiale spanning en rekversteviging, bij aan het ontstaan van een relatief nauwe gasbelgrootteverdeling aan het begin van de gasbelgroei. Tijdens het bakken bepalen uitrekbaarheid en rekversteviging de stabiliteit van de expanderende gasbellen tegen coalescentie. Mogelijk dragen oppervlakte-eigenschappen bij aan deegfilmstabiliteit aan het eind van de ovenrijs indien erg dunne deegfilmpjes gevormd worden.

Curriculum Vitae

Johanna Jacoba (Anita) Kokelaar werd op 15 maart 1964 geboren in Oost-en West-Souburg, nu gemeente Vlissingen. In 1982 behaalde zij het Atheneum-B diploma aan de Stedelijke Scholengemeenschap te Middelburg. In hetzelfde jaar begon zij haar studie Levensmiddelentechnologie aan de toenmalige Landbouwhogeschool te Wageningen. De laatste fase van de studie bestond uit de afstudeervakken Levensmiddelenmicrobiologie en Zuivelkunde. Stages werden uitgevoerd bij Melkunie Holland te Woerden en bij het INRA - Station Expérimentale Laitière te Poligny, Frankrijk. In november 1988 nam zij haar ingenieursdiploma in ontvangst.

Van 1 januari 1989 tot 9 april 1993 was zij werkzaam bij de sectie Zuivel en Levensmiddelennatuurkunde van de Landbouwuniversiteit. In deze periode heeft zij als assistent in opleiding het in dit proefschrift beschreven onderzoek uitgevoerd. Ook is zij in deze periode 3½ maand aangesteld geweest als toegevoegd docent bij dezelfde sectie met als taak het mede opzetten en begeleiden van de PHLO-cursus 'Bepaling van de mechanische en breukeigenschappen in de levensmiddelenindustrie'.

Vanaf 1 maart 1994 zal zij als post-doc gaan werken op het 'Laboratoire de Biochimie et Technologie des Protéines' van het INRA in Nantes, Frankrijk.


GEGARANDEERD MET 100% CHLOORVRIJ GEBLEEKTE CELLULOSE GEPRODUCEERD