The rheological and fracture properties of Gouda cheese

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STELLINGEN

1. Voor veel materialen bepalen de vloeieigenschappen het gedrag bij breuk.
   Dit proefschrift.

2. Het bestuderen van het reologisch gedrag van melkgelen is zeer nuttig voor het begrijpen van de consistentie van kaas.
   Dit proefschrift.

3. Materiaaleigenschappen van levensmiddelen kunnen heel goed bestudeerd worden met compressie-, buig-, rek- en/of afschuifmetingen, mits de uitvoering van de experimenten en de berekening van de resultaten goed gebeurt.
   Dit proefschrift.

4. Kaas kan beschouwd worden als een composietmateriaal: de matrix bestaat uit gezwollen eiwitdeeltjes, vetbolletjes gedragen zich als vulstof.
   Dit proefschrift.

5. De kortheid van kaas wordt voornamelijk bepaald door de eiwitafbraak, de pH en het zoutgehalte. Hoogstwaarschijnlijk is vergaande afbraak van het eiwit tot kleine brokstukken hierbij wezenlijk.
   Dit proefschrift.

6. De vloeieigenschappen van Goudse kaas zijn maximaal in het pH-gebied 5,15-5,35. Bij deze pH's worden daarom gemakkelijker ronde ogen en minder scheuren gevormd dan bij hogere of lagere pH.
   Dit proefschrift.

7. De toename van de vervorming bij breuk met toenemende vervormingssnelheid, zoals o.a. gevonden door Ross-Murphy en door Dickinson en Goulding, zou verklaard kunnen worden doordat breuk met een eindige snelheid voortschrijdt.
   Dickinson, E., Goulding, I.C., J. Text. Stud., 11 (1980) 51-63
   Ross-Murphy, S.B., In: Biophysical methods in food research, ed. H.W-S. Chan (1984)

8. Het ontbreken van een algemeen te gebruiken onderzoeksvoorschrift bij het COST-90 projekt 'Reologie van kaas', veroorzaakt dat er alleen zeer voor de hand liggende informatie uit verkregen kan worden.
   Masi, P. In: Physical properties of foods-2, eds. R. Jowitt et al. (1987)

9. Het zou nuttig zijn om de omstandigheden in model-experimenten waarin de vorming van lysinoalanine bestudeerd wordt, meer overeen te laten komen met die van levensmiddelen.

10. Het is niet noodzakelijk dat bacteriecellen volledig gelyseerd zijn, willen hun intracellulaire enzymen in een substraat kunnen werken.

11. Het feit dat chocolademelk beschouwd kan worden als een vaste stof en kaas als een vloeistof, hoeft het genoegen in het consumeren ervan niet te bederven.

12. Bij de bestudering van macroscopische materiaaleigenschappen zou het zeer zinvol zijn meer aandacht te besteden aan onregelmatigheden in de struktuur groter dan moleculaire schaal.

13. Het gebruik van a-calorische vetvervangers in voedsel lost het eigenlijke probleem, het te veel en te vet eten, niet noodzakelijkerwijze op. Dit probleem is meer van psychologische dan van levensmiddelentechnologische aard.

14. Gelukkig voor de Nederlandse economie heeft de toevoeging 'manager' aan een funktiebeschrijving niet altijd ook een inhoudelijke betekenis.

proefschrift van Hannemieke Luyten
The rheological and fracture properties of Gouda cheese.
Wageningen, 10 mei 1988.

ABSTRACT

Luyten, H. (1988), 'The rheological and fracture properties of Gouda cheese.' Ph.D. thesis, Laboratory of Dairying and Food Physics, Department of Food Science, Wageningen Agricultural University (223 pp, English and Dutch summaries).

key-words: rheology, fracture, fracture mechanics, consistency, visco-elasticity, Gouda cheese, composition, maturation, eye formation.

The rheological and fracture behaviour of Gouda cheese was studied. Methods for determining these properties of visco-elastic materials are described. Application of the theory of fracture mechanics, after modification and expansion, to visco-elastic materials with a low or no yield stress is discussed. For such materials, of which Gouda cheese is an example, the flow properties greatly affect the fracture behaviour.

From the effect of variation in composition (fat, water, NaCl and Ca content, pH) and maturation on the behaviour of Gouda cheese, it may be concluded that this cheese may be considered as a composite material. Fat particles act as a filler in a swollen protein matrix. The amount of fat and the rigidity of the fat particles affect the rigidity of the cheese. Factors like pH, water and NaCl content, that change the properties of the protein matrix, clearly affect the rheological and fracture behaviour, e.g. the rigidity and the shortness, of the cheese. The trends of these changes on the protein matrix are similar to those on rennet and acid skimmilk gels under various conditions.

As an example of the importance of the experimental results for cheese manufacturing, the relation between the pH of cheese and eye or slit formation was studied.

CONTENTS

1. INTRODUCTION

Besides taste, consistency is an essential quality mark of cheese. In this context consistency means the resistance of a material to permanent as well as recoverable deformation. The consistency of cheese does not only influence eating properties, but also the behaviour of cheese during handling, cutting, curd fusion, hole formation etc. These properties concern the behaviour of the material during deformation and breaking, that are the rheological and fracture properties under different conditions and time scales. During eating, for example, cheese is quickly deformed until it fractures; the time scale of this deformation is less than a second. During hole formation, on the other hand, the cheese mass is slowly stretched around the growing hole; it must flow and may not fracture. The time scale of this deformation is of the order of magnitude of a week. The desired material properties, the relevant type of deformation and the relevant time scale thus depend on the property considered.

By knowing and understanding more about the rheological and fracture properties, it would be possible to better regulate cheese consistency and to solve problems with, for instance, undesired slit formation.

Some results of experimental work concerning these properties of cheese can be found in the literature. Recent reviews have been published by Eberhard (1985), Walstra et al.(1986) and Prentice (1987). For several (semi) hard cheeses like Gouda, Cheddar or Emmentaler it has been found (as will be discussed further in the chapters 4 and 5) that:

- a cheese with a lower water content is firmer,
- fat softens a cheese at room temperature,
- a low pH makes a cheese shorter and firmer,
- a high NaCl content makes a cheese shorter and firmer,
- ripening causes the cheese to become shorter and firmer.

Such results have been observed by correlating intrumentally obtained parameters (for instance the force needed to compress a given sample to a certain extent at a given speed) of different cheeses with sensory parameters (for instance the firmness) or chemical composition. Some remarks on this approach can be made:

- Because the cheeses will always differ in more than one factor, correlations found are not necessarily causative.
- The relevant time scales of the properties mentioned above is different. Because the behaviour of cheese depends on time, one has to adjust the time scale of an experiment to the property studied.
- For most parameters used in the literature to characterize the rheological and fracture behaviour of cheese, it was not proved that they were true material properties, i.e. independent of the method used. This has to be done before they can be used to describe cheese behaviour and for establishing causative relations between other cheese properties (e.g. composition) and mechanical behaviour.

The purpose of this study is:

1. To establish methods for determining the rheological and fracture properties of Gouda cheese. Therefore in chapter 2 a description of methods (like compression, tension, bending and shear) that can be used for measuring rheological and fracture properties of visco-elastic materials (for example cheese) and a discussion of the experimental results obtained from these different methods will be given. In the literature, theories to relate the rheological and fracture behaviour of a material with composition and structure are available. But, because these theories are only applicable in the linear region and for elastic or elastic-plastic behaviour, and cheese is not such a material, we can not use them directly. This will be discussed in chapter 3.
2. To determine and understand the rheological and fracture behaviour of Gouda cheese and the influence of composition and maturation on this behaviour. The material behaviour of standard Gouda cheese will be described in chapter 3. The influence of composition (water, fat, NaCl and Ca content, pH) and

maturation are discussed in chapter 4 and 5, respectively. A general discussion of the material behaviour of cheese will be given in section 6.1. The relation with the behaviour of milk gels will be discussed in section 6.2.

3. To relate the usage properties of Gouda cheese to experimentally obtained rheological and fracture parameters. As an example of this, the relation between eye or slit formation and experimentally parameters will be discussed in section 6.3.

When talking about cheese in this study, a Gouda type cheese is meant, unless mentioned otherwise.

2. METHODS FOR DESCRIBING RHEOLOGICAL AND FRACTURE PROPERTIES OF VISCO-ELASTIC MATERIALS

Rheology may be defined as the study of the deformation of a material in relation to the applied stress (force per unit of area) and the time scale. Depending on these relations, materials may be divided into 3 groups:

- elastic materials
- viscous materials
- visco-elastic materials

For the first two the relation between deformation (or deformation rate) and stress does not depend on the time scale; for the last it does. Ideally elastic materials deform immediately to a constant shape when a stress is applied on them and after the stress is removed they return immediately to their original shape. In practice this means within the response time of the measuring unit, in theory at the speed of sound in the material. For linearly elastic or Hookean materials the ratio of stress to deformation is constant and this constant is called the modulus ($N\ m^{-2}$). Viscous materials under stress will deform at a certain rate. This deformation is lasting. For linearly viscous materials or Newtonian fluids the ratio of stress to deformation rate is constant and this constant is called the viscosity ($N\ s\ m^{-2}$).

A material is visco-elastic when its reaction to a stress consists partly of a viscous component and partly of an elastic one. The ratio between the two depends on the time scale of the experiment. At short time scales, more bonds between the particles contributing to the structure of the material (in cheese mostly protein molecules and aggregates of them) are permanent and elastic energy is stored in these bonds and so in the material when deforming it. At longer time scales more of this energy can be dissipated by bond breakage, a process which takes time. The elastic or stored energy is eventually available for fracture of the material. The dissipation of viscous energy results in flow of the material and lasting deformation.

Cheese is a visco-elastic material (Mulder, 1946). Its behaviour therefore depends on the time scale considered. Because of its importance for the interpretation of the observed rheological and fracture behaviour of cheese, we shall discuss the theory of visco-elasticity and the influence of time on cheese further in chapter 3.

This chapter will start with some introductionary remarks on the measurement of rheological and fracture properties in general (2.1). After that the material and apparatus used are described (2.2), followed by an extended description of the methods used for determining the rheological and fracture properties of cheese (2.3). In 2.4 we will compare the methods used and check whether we measured real material properties of the cheese, independent of the experimental method.

2.1 Introduction

In this section an introduction into some rheological and fracture-mechanical concepts will be given.

2.1.1 Deformation of a material; stress and strain

For measuring rheological properties of a material, it is necessary to deform it. Methods for doing this are various. They can differ in (Whorlow, 1980):

1. Nature of the test.

   The relation between stress and strain (rate) can be studied in various ways. One may apply a certain stress and measure the deformation (for not low viscous materials this gives a so-called creep curve from which it is possible to calculate the elasticity and viscosity of the material), or apply a certain deformation or a rate of deformation and measure the stress. To measure the relaxation time (= the time necessary to decrease the stress at a certain deformation to the 1/e part (36.8%) of the original value), one has to measure the (decreasing) stress at a certain deformation. By applying a constant deformation rate, for example a constant compression rate, and measuring the necessary force, a force deformation curve is obtained from which it is possible to calculate the stress needed for a certain deformation at that rate.

2. Type of deformation.
   There are three different types of simple deformations: viz. all-sided compression, simple shear and uniaxial extension or compression. In many tests the deformation is not just one of these simple types but a combination, which makes it difficult, or even impossible, to find out the extent of deformation. This will be discussed further for the different modes of deformations applied in section 2.3.
3. Time scale of the measurement.
   The applied stress or deformation can be constant or monotonically changing (static experiments), or fluctuating with a certain frequency (dynamic experiments). The time scale of a measurement is the time during which a certain stress is exerted on a material. It can be varied, e.g. by changing the frequency in a dynamic experiment or the deformation rate in a static experiment. For visco-elastic materials the observed rheological properties will depend on this.

The results obtained in all these kinds of experiment are easy to explain only when they are achieved at small deformations in the so-called linear region. In this region the ratio of stress to strain depends on time only; it thus is independent of the stress and strain level. When applying larger deformations the ratio changes, the material may even yield and/or fracture, which makes explanation more difficult (see 2.1.2 and 3.2).

For quantitative comparison of results, a size-independent measure of deformation has to be defined. Usually the strain is taken, defined as the deformation relative to the original dimensions as the original distance between the considered different points approaches zero (Whorlow,1980).

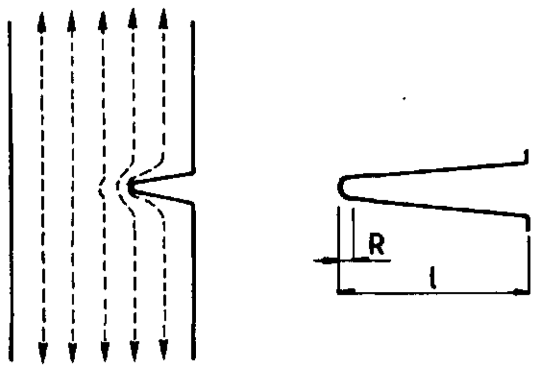
2.1.2 Fracture

In the theory of fracture mechanics one usually assumes that all materials are inhomogeneous and have defects. A material fractures when a crack, slit or other kind of defect grows and new surfaces are formed. Fracture starts if the (local) stress is higher than the adhesion or cohesion forces in the material; and it propagates spontaneously if the deformation energy that is released when the material fractures is at least equal to the energy needed to create the new surfaces.

Fracture always starts at an inhomogeneity or irregularity in the material, because here the stresses are locally higher (Gordon, 1968). The extent of concentration of stress depends on the shape of the irregularity (Gordon, 1968) and on material properties (Atkins and Mai, 1985). We will describe this further in section 3.1.1. According to Inglis the stress concentration due to a semi-circular notch of length l and radius at the tip r (see figure 2.1) in an ideal, isotropic, elastic material is (Gordon, 1968)

$$\sigma = \sigma_0 (1 + 2 \surd(l/r)) \qquad (2.1)$$

Fig. 2.1 Stress trajectories in a bar containing a crack, loaded in tension (after Gordon, 1978).



The stress at the tip of the notch (σ) is the remote stress (σ_0) multiplied by the stress concentration factor. Because the fracture stress at the point where the fracture starts is constant, one can determine the notch-sensitivity of a material by measuring the remote stress at fracture for different sized notches.

A defect spontaneously propagates only if the strain energy released by progress of a crack suffices the energy needed to create new crack surfaces. Only the deformation energy that is stored in the material (=elastic energy) is available for fracture, the energy that is dissipated due to flow of the material is not available. (Although flow is also a kind of bond breakage, new bonds are immediately formed; hence, it does not lead to the formation of new surfaces inside the material.) One may distinguish between elastic and plastic fracture. For essentially elastic conditions, when the amount of dissipated (flow) energy can be neglected, a theory of linear elastic fracture mechanics (LEFM) has been developed. For limited flow (this means a flow region that has the same order of magnitude than the inhomogeneities) the fracture parameters can be estimated using elastic-plastic fracture mechanics (EPFM). Cheese, however, is completely visco-elastic, the material even has no perceptible yield stress (Mulder, 1946). The loss of deformation energy due to flow in this material therefore has to be taken into account when studying the fracture behaviour of cheese. No well developed fracture theory for plastic flow is available. We will discuss this further in section 3.1.3.

The start of the fracture of a structure thus can be described by the fracture stress (σ_f) and fracture strain (ϵ_f). Both depend on the material of which the structure is made (σ_f and ϵ_f of the homogeneous, crack free material and the notch-sensitivity of the material) and the kind of irregularities in it. This will be explained further in section 3.1.1.

2.2 Materials and rheological methods

2.2.1 Preparation of cheese samples

Cheese was made specially for these experiments. The process was as usual for Gouda cheese, only for some of the experiments described in chapters 4 and 5 cheese with a special composition was made. An extensive description will be given in chapter 4. Care was taken to avoid making eyes, slits etc. as much as possible, because these will cause stress and strain concentrations inside the stressed sample. Each time 2 - 8 cheeses of about 2 kg (Gouda model) were made from 40 - 200 kg milk (for some experiments 12 kg Goude cheeses made at the Dutch Institute for Dairy Research (NIZO) were used). The methods used for determining the chemical composition are given in table 2.1.

Cheese samples for the different rheological and fracture tests were cut at ripening temperature (13-14°C) with a borer and a wire (cylindrical samples) or with a special formed mould ('dumb

Table 2.1 Methods used for determining the chemical composition of cheese.

property	method
water content	FIL-IDF standard 4 (1958)
protein content	micro-Kjeldahl, the protein content was .38 times the N-content
fat content	Gerber, NEN 3059
salt content	FIL-IDF standard 17 (1961)
pH	estimated directly in ground cheese with a combined electrode
Ca + Mg content	complexometric titration with *complexon* III
proteolysis	polyacrylamide gel electrophoresis; de Jong (1975)

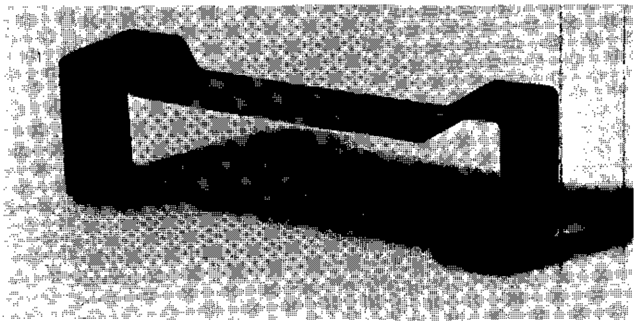


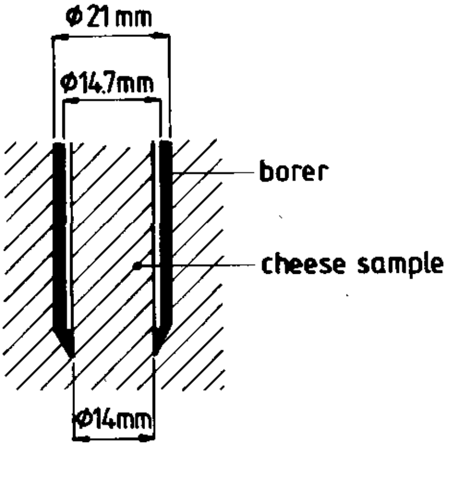
Fig. 2.2 Mould for tension test-pieces.

bell' shape, see figure 2.2). To prevent deformation of the sample during boring or cutting the hard rind was removed beforehand and the test-pieces were cut as slowly as possible. The size of the samples depended on the kind of experiment and was about:

compression:	diameter 15 mm; height 20-30 mm
bending :	diameter 15 mm; length 70-100 mm
shear :	diameter 15 mm; height 9-10 mm
tension :	thickness 10 mm; width 20 mm; length 90 mm

The actual size of the test pieces depended on the properties of the cheese and was measured with a micrometer just before testing. To prevent compression and erosion at the sides of the test-piece inside the borer, the inner diameter of the borer was somewhat larger than the sample diameter as is shown in figure 2.3. This

Fig. 2.3 Borer for cutting cylindrical test-pieces.



resulted in an extension of the cheese in tangential direction around the borer of at most 0.20 (d(sample)=14.0 mm, d(borer)=17.1 mm, ϵ_t=ln(17.1/14)= 0.20 see section 2.3.1) while the cheese is compressed in radial direction. Very old and short cheese therefore fractured around the borer while taking samples. Because of this deformation, samples taken from one piece of cheese should be taken at least several mm from each other.

The long cylindrical samples were cut with a wire to the desired height. As will be shown in section 3.2.4 a wire always disturbs part of the cheese material around it, it does not only cut. To minimize this effect a thin wire was chosen (diameter .3 mm).

Most of the experiments were done at 20°C. During temperature adjustment (about 1½ h) the cylindrical samples were gently rolled over to minimize change in shape due to viscous deformation.

2.2.2 Rheological apparatus

For most kinds of experiments we used an Overload Dynamics material testing instrument, table model S 100, fitted with a 100 or 2000 N load-cell (figure 2.4). Essentially, this apparatus consists of a fixed bottom plate and a moving bar containing the load-cell. The moving bar can be raised or lowered at various fixed speeds (0.1-500 mm min^{-1}, in steps of 0.1 mm min^{-1}). The force needed for the deformation is directly recorded as a function of time. The recorder speed and calibration used depended on the rigidity and shortness of the sample measured. The apparatus was mounted in a temperature-controlled box (± 0.5°C). By using different measuring geometries (see below), uniaxial compression, uniaxial tension and three-point bending tests could be performed.

Creep measurements in compression were made with the apparatus described by Mulder (1946). Essentially with this instrument a constant load is placed on a cylindrical sample and the change in height is measured as a function of time with a displacement transducer (Hewlett Packard). Different stresses were applied by using different weights.

For the shear experiments we used a Deer PDR 81 Rheometer, in

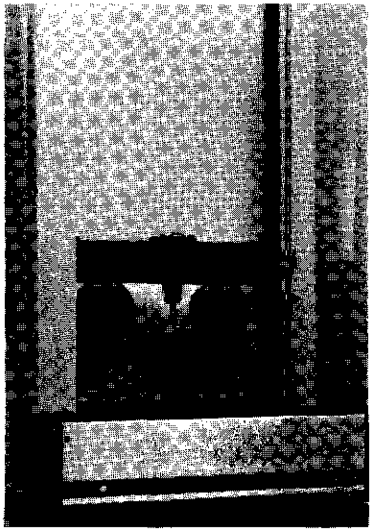
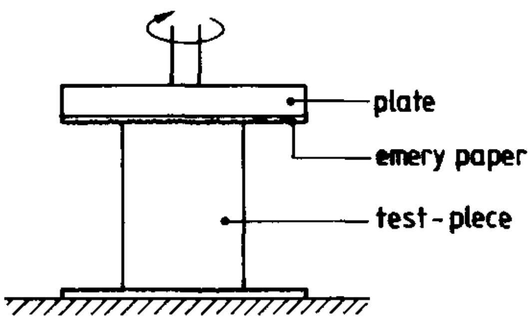


Fig. 2.4 Overload Dynamics materials testing instrument.

which the strain of the sample is monitored as a function of time during application of a constant or sinusoidally varying stress. The Deer was fitted with 2 parallel plates covered with emery paper (figure 2.5). The upper, moving plate (radius 5 cm) was made of perspex to minimize its moment of inertia. It was fixed

Fig. 2.5 Measuring geometry as was used for cheese test-pieces in the Deer Rheometer.



to a linear induction motor with an air bearing support. Angular displacement was determined by a non-contacting electronic sensor, which measured the distance between a circular ramp and the sensor. The temperature could be adjusted by a thermostatting bath below the lower plate (standard = 20°C). Around the cheese sample some wet cotton wool was placed to prevent drying out of the sample. In this way, weight loss during an experiment (3/4 h) was limited to at most 0.4% (results not shown). The strain was monitored with a recorder. For calculations of the dynamic rheological parameters the stress and strain data were directly taken from the instrument and processed by an AIM 65 computer.

2.3 Methods for measuring rheological and fracture properties of cheese

Rheological and fracture tests on Gouda cheese were performed with different methods. To check whether the results are real material properties and are not (greatly) influenced by the method used, more than one kind of test has to be done and the results compared. Only if the results are independent of the method, one can be fairly sure that real material properties have been measured. Only then it is possible to apply the rheological and fracture parameters in, for example, calculations about eye or slit formation in cheese (section 6.3). In this section we will describe the various test methods: compression (2.3.1), extension (2.3.2), bending (2.3.3) and shearing (2.3.4). In the next section (2.4) results obtained by these methods will be compared.

2.3.1 Uniaxial compression

Compressive deformation of foods is a principal technique in the textural evaluation of food materials (Peleg, 1977). It has also often been used for cheese (e.g. Culioli and Sherman, 1976; Creamer and Olson, 1982; Eberhard, 1985). One of the reasons for

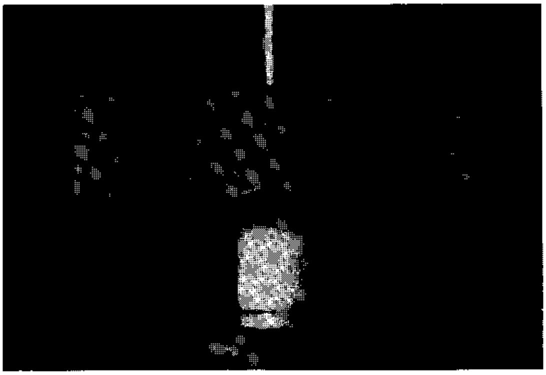
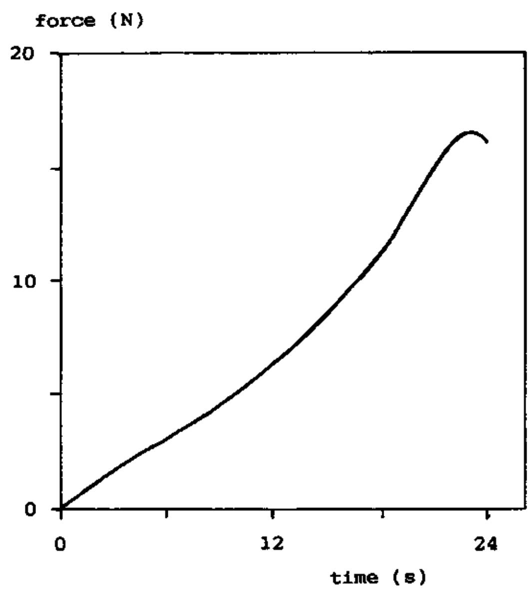


Fig. 2.6 Compression equipment for Overload Dynamics as was used for cheese test-pieces.

its popularity probably is the ease of performing this type of test. In this study uniaxial compression tests were done with the Overload Dynamics machine equipped with parallel plates (figure 2.6) on cylindrical samples of cheese. The force needed for compression was recorded as a force-time diagram. An example of this is shown in figure 2.7. From this curve the relative deformation and the stress can be calculated.

Fig. 2.7 Example of a force (F) - time (t) curve obtained in a compression test. T=20°C; $\dot{\varepsilon}_c$=2.8·10^{-2} s^{-1}; 4 weeks old Gouda cheese with pH 5.18 and 44.8% water.



The relative deformation at a certain point (Peleg, 1977 and 1985) can be given as the Cauchy or engineering strain ϵ_c (-)

$$\epsilon_c = \frac{\Delta h}{h_0} \tag{2.2}$$

or as the Hencky, true or natural strain ϵ_h (-)

$$\epsilon_h = \ln \frac{h_t}{h_o} = \ln (1-\epsilon_c) \tag{2.3}$$

where h_o is the initial height of the sample, h_t the height after a certain deformation and Δh the change in height ($=h_t - h_0$). Both strains are negative for compression and positive for extension. However, as long as the kind of deformation is clear, we will express the strain always as a positive figure. For higher deformations, the Hencky strain is a better estimate of the real strain in the sample, because it is obtained by relating any strain increase (in an already strained sample) to the changed dimensions of the sample. In literature other definitions can be found for the strain at large deformation (Peleg, 1977). We chose for the Hencky strain because it is corrected for the dimensions of the strained sample in a simpler way than the other strain measures (Whorlow, 1980) and very often used. Because the height of the sample decreases during compression, the relative rate of deformation according to the Hencky definition ($\dot{\epsilon}_h$ in s^{-1}) will increase when using a constant compression rate (v):

$$v = \frac{dh}{dt} \tag{2.4}$$

$$\dot{\epsilon}_h = \frac{d\epsilon_h}{dt} = \frac{dh}{h_t \, dt} = \frac{v}{h_t} \tag{2.5}$$

When examining time dependent materials this certainly affects the results.

Formulae 2.2 to 2.5 concern only the overall compressive strain and strain rate in a uniaxial compressed sample. Locally, however, the three-dimensional strain and strain rate can be different due to friction, barreling etc. This will be discussed further in section 2.3.1.2 and 2.3.1.3.

The average stress (σ) in the sample is equal to the force (F) per unit of area (A)

$$\sigma = \frac{F}{A} \tag{2.6}$$

During compression of a sample the actual contact area between the compression plates and the sample will increase, the amount of increase depends on the friction between the sample and the compression plates. For the calculations of the real stress in the sample we have to take this into account. This will be discussed below.

The ratio between the stress and the strain gives the modulus of the material. At strains higher than about 0.03 we observed a change in the stress to strain ratio with increasing strain (see for example figure 2.8). Below this strain this ratio was apparently constant as were the moduli in dynamic experiments (see section 2.3.4.2). Because the structure of cheese is influenced by deformation even at relatively small strains this modulus is meaningful only at small deformations, where it will be a good estimate for Young's modulus (E in N m^{-2})

$$E = \left(\frac{d\sigma}{d\epsilon}\right)_{\epsilon \to 0} \tag{2.7}$$

The apparent uniaxial compression viscosity η^* (N s m^{-2}) or the ratio between the stress and the strain rate is given by (Whorlow, 1980):

$$\eta^* = \frac{\sigma}{\dot{\epsilon}_h} \tag{2.8}$$

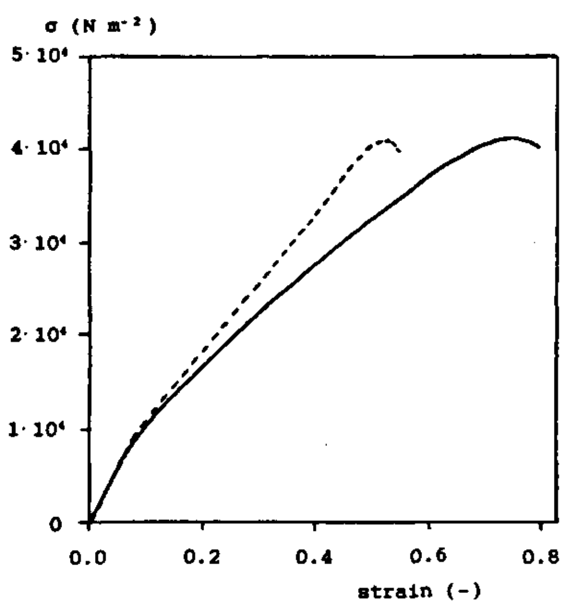
For calculation of the biaxial extensional viscosity (Chatraei et al., 1981; Casiraghi et al., 1985), one has to use the elongational strain rate instead of the compressive strain rate (see below).

The stress and the Hencky strain at the point where the force is at maximum will be denoted as σ_f and ϵ_f respectively.

Because the real stress and strain are not directly related to the force and the time, all curves were recalculated to real stress-strain curves. An example is given in figure 2.8. By doing this the form of the curve changes because:

- the increase of the contact area causes less increase in stress than in force.
- the Hencky strain strongly increases compared with the Cauchy strain, for example, the increase in Hencky strain by a compression by 1 mm of a sample with an original height of 20 mm

Fig. 2.8 Stress-Cauchy strain (---) and stress-Hencky strain (——) curves for the same test-piece as in figure 2.7.

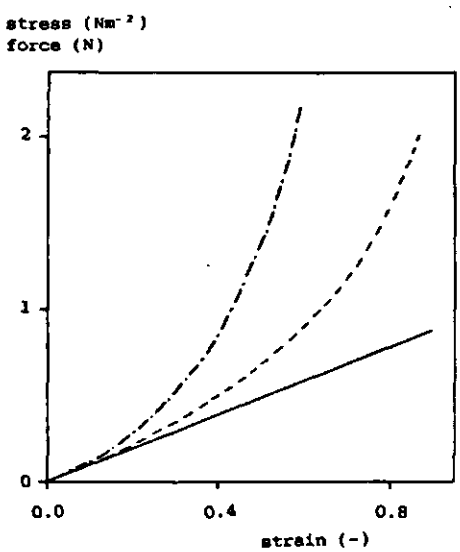


is twice the initial value when h_t is 10 mm, while the increase in the Cauchy strain is the same for both. In fact this automatic correction for the changed dimensions is the major advantage of the Hencky strain above the Cauchy strain. Therefore we shall always use the Hencky strain, except when mentioned otherwise.

- owing to the decrease in height the relative deformation rate increases during the compression. For time dependent materials this may cause an increase in stress.

Knowing the shape of the stress-strain curve is important because only this curve can in principle represent the material properties. If the slope of this curve is decreasing, energy dissipating processes (like yielding or (local) fracture) take place inside the material (Calzada and Peleg, 1978). If the slope of the stress-strain curve increases, other structural changes take place, like for example the straightening of coiled chains in a rubber-like material (Treloar, 1975). Whether the latter or the former effect occurs can not be seen in the force-time curve, but it may be noticed directly from the stress-strain curve. A clear example of the difference in shape between the stress-strain and the force-time curves is shown in figure 2.9. The slope for the

Fig. 2.9 Force-Cauchy strain (-·-·-), σ-ϵ_c (- - -) and σ-ϵ_h (——) curves for a linearly elastic material. E=1; A(t=0)=1.



force-Cauchy strain curve of a linear elastic material is constantly increasing, while the ratio of stress to strain is, by definition, constant. For visco-elastic materials, the stress-strain curve may also be influenced by the increase in relative deformation rate during compression.

2.3.1.1 Influence of sample size and shape

The exact magnitude of the different types of strains and the stresses produced when compressing a sample, depend on the size of the sample and the friction between the sample and the compression plates. Even if the energy per unit area of the crack needed to fracture a material (=the toughness) is constant and fracture is purely elastic, the stresses to cause fracture become smaller as the size of the test-piece increases (Atkins and Mai, 1985). As long as no fracture occurs, the stress strain curves are the same. But because the fracture energy needed for elastic fracture for a test-piece of unit depth is proportional to l (l= some characteristic length of the sample) and the available energy at a certain stress is proportional to l^2, larger bodies will fracture at smaller stresses and strains. On the other hand, the (local) stress at which plastic flow starts is constant and the yield stress at a certain time scale is a real material property (Atkins and Mai, 1985). For larger samples there is also a greater probability that there will be an irregularity or inhomogeneity inside the test-piece that lowers the experimental fracture stress and strain. All these effects cause larger samples to fracture more preferably in a elastic way and small samples in a plastic way.

If the friction between the compression plates and the sample is high, more energy than is needed just for deformation is necessary. This implies higher compressive stresses than would be found in the absence of friction. The relative effect of friction is higher for flatter samples with the same contact area (Chu and Peleg, 1985). The influence of frictional differences due to differences in the surface of the compression plates will be discussed further in sections 2.3.1.2 and 2.3.1.3. The influence of the height to diameter ratio will be discussed in this section.

For compression tests of cheese we were not free to choose any possible size. The test-pieces had to be small compared to the size of the cheese to exclude inhomogeneity due to dry rinds etc. (Eberhard, 1985) and to avoid eyes and holes in the sample. The samples must be large compared to inhomogeneities such as fat globules, curd particles etc. (Walstra and van Vliet, 1982). Moreover, the relative inaccuracy in the determination of the force and the sample size increases with decreasing sample size. To find out whether there is any size effect in the compression tests, we performed several series of experiments. The results of compression tests on samples of one Gouda cheese with a height to diameter ratio of 1.1 to 1.6 but with different sized test-pieces are given in table 2.2. The relative deformation rate was kept constant. No significant influence of the size of the sample on the rheological parameters could be found. Culioli and Sherman (1976) found lower forces for bigger samples, but they compressed at a constant speed which means that the relative deformation rate was smaller for the bigger samples. The results found in deformation tests of cheese are indeed significantly rate dependent (see chapter 3.2.1). Therefore the influence of sample size found in literature can at least partly be ascribed to different strain rates (Peleg, 1977).

If the height to diameter ratio is not kept constant some influence on the results of compression tests can be found. Chu and Peleg (1985) found that flatter test-pieces were stiffer and had a higher strength and strain at failure. They ascribed this to the increased effect of the end constraints for a flatter sample. Using their correction formulas and their data for processed American cheese the error in the modulus in our experiments (h_0=20 mm, r_0=7 mm) due to friction effects should be less than 5%. Possibly it is even less because Chu and Peleg did not use the same strain rate for all experiments. If the strain rate were been kept constant, E (the slope of the σ-ϵ curve for $\epsilon \to 0$), being

Table 2.2 Influence of the size of the sample on the compression curve for 2 different Gouda cheeses. T=20°C; $\dot{\varepsilon}_c$=2.8·10^{-2} s^{-1}.
1. 13 months old Gouda cheese: pH 5.69, water content 26.1%
2. 6 weeks old Gouda cheese: pH 5.41, water content 39.6%

cheese	diameter (mm)	height (mm)	E (Nm^{-2})	ε_f (-)	σ_f (Nm^{-2})
1	19.65	31.8	2.14·10^6	.20	1.59·10^5
	19.55	30.7	2.47	.18	1.53
	19.35	30.3	2.78	.18	1.48
	4.9	6.65	2.10	.17	1.49
	4.9	6.85	2.42	.17	1.79
mean value			2.4·10^6	.18	1.6·10^5
relative st.dev.			11.6%	6.8%	8.1%
2	13.8	20	2.13·10^5	1.33	7.94·10^4
	14.1	19.8	2.51	1.14	5.88
	14.05	19.95	2.92	1.27	8.84
	13.8	19.75	2.95	1.26	8.76
	14.35	20.8	3.31	1.09	9.62
	19.7	30.0	2.02	1.05	8.08
	19.4	30.0	2.47	1.01	8.99
	19.55	30.05	2.62	1.34	6.25
	9.6	10.5	2.45	1.13	7.07
	9.1	9.6	2.60	1.12	8.39
	8.1	10.0	1.94	1.12	6.54
	8.0	10.6	2.41	1.09	6.99
mean value			2.5·10^5	1.16	7.8·10^4
relative st.dev.			15.7%	9.5%	15.5%

least influenced by friction, would be constant, although the fracture stress and possibly the fracture strain as well may then depend on the relative friction, i.e. on h/d. We indeed found no clear influence of h/d on the modulus E, but a higher fracture stress was observed for flatter pieces (table 2.3 and figure 2.10). There was no effect on the fracture strain. It was impossible to increase the height to diameter ratio to more than 2.5, because then the sample buckled during compression and stress and strain calculations could not be made. Because of the increasing influence of friction when using samples with a height to diameter ratio of

Table 2.3 Influence of the height to diameter ratio on several compression parameters measured for a 1 month old Gouda cheese.
T=20°C; $\dot{\varepsilon}=2.1 \cdot 10^{-2}$ s^{-1}.

contact surface	h/d (-)	E (10^5 Nm^{-2})	ε_f (-)	σ_f (10^5 Nm^{-2})
plunger diameter much larger than sample diameter				
perspex	.31	1.74		
	.40	2.44		
	.52	1.65		
	.67	1.70	1.39	1.12
	.70	1.69	1.49	1.03
	.85	2.73	1.34	1.21
	1.04	1.24		
	1.04	1.97	1.39	.85
	1.44	1.07	1.25	1.02
	1.45	1.86	1.27	.78
	1.49	1.97	1.08	.74
	2.08	1.33	1.51	.74
oil	.68	1.01	1.39	.90
	.71	.63		
	1.04	1.70	1.27	.79
	1.09	.84	1.25	.82
	1.47	1.55	1.11	.73
	2.14	1.23	1.42	.61
	2.22	1.74	1.17	.89
emery paper	.51	1.36	1.22	.97
	.70	.89	1.31	.85
	.82	1.07	1.24	.92
	1.10	1.10	1.26	.87
	1.43	1.28	1.18	.74
plunger diameter the same size as initial sample diameter (=20 mm)				
perspex	.53	2.27	1.33	1.75
	.80	1.39	1.37	1.29
	.86	2.16	1.23	1.39
	1.09	1.56	1.36	1.43
	1.56	1.98	1.05	1.11
oil	.52	1.66	1.34	1.50
	1.06	1.71	1.33	1.52
	1.58	1.78	1.25	1.27

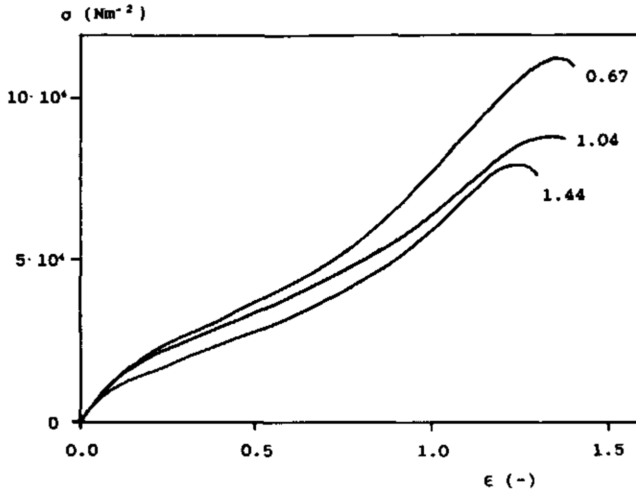
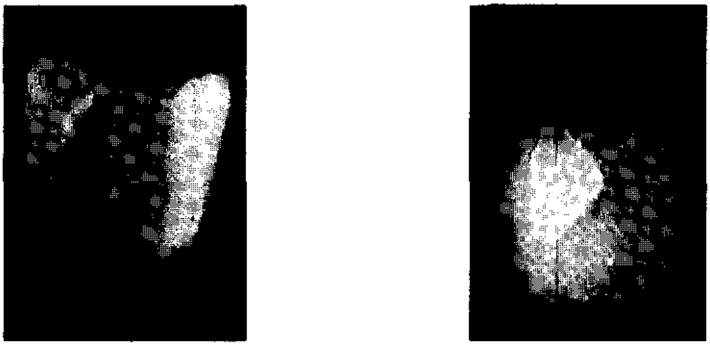


Fig. 2.10 Influence of the height to diameter ratio on the stress strain curve in compression. Same cheese as in table 2.3.

less than 1, we used for all subsequent compression experiments samples with a h/d ratio of 1.3-2. The effect of friction on the measured stress possibly increases with increasing deformation because h/d decreases during compression.

2.3.1.2 The fracture mode

Uniaxial compression will give rise to different kinds of deformation within the sample. As a consequence of this, the way of fracturing may be different (viz. Gordon, 1978). The local, triaxial deformation inside the test piece depends on the structure of the material (Gordon, 1978) and on the friction between the compression plates and the sample (Atkins and Mai, 1985). For anisotropic materials the deformation also depends on the direction of loading (Gordon, 1978). These different ways of deformation can be seen in the fracture behaviour when compressing different samples of cheese. A younger Gouda cheese will show vertical slits at the outside; it fractures in tension. A more mature cheese will show fracture planes inside the sample at an angle of 45° to the direction of compression; it fractures in shear (figure 2.11). To explain this we will calculate the different strains



A B

Fig. 2.11 A. A young Gouda cheese fractures in tension.
B. A mature Gouda cheese fractures in shear.

inside a compressed sample of an isotropic material below.

No friction.

If the friction between the sample and the compression plates is neglectible, a cylindrical test-piece will remain cylindrical. The two main strains are the extension of the radius and the shear inside the sample. If the volume of the sample is constant (which implies a Poisson ratio μ of 0.50; this will be discussed in section 2.4.2), the deformation in tension (ϵ_t) can be calculated as a Hencky strain from the decrease in height of the sample (Chatraei et al., 1981).

$$h_o \pi r_o^2 = h_t \pi r_t^2 \tag{2.9}$$

$$r_t^2 = r_o^2 \frac{h_o}{h_t} = r_o^2 \left(\frac{1}{1-\epsilon_c}\right) \tag{2.10}$$

$$r_t = r_o \sqrt{\left(\frac{1}{1-\epsilon_c}\right)} \tag{2.11}$$

$$\epsilon_t = \ln \frac{r_t}{r_o} = \ln \left(\frac{h_o}{h_t}\right)^{\frac{1}{2}} = -0.5\ \epsilon_h \tag{2.12}$$

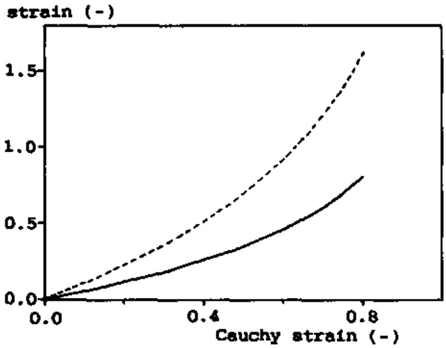


Fig. 2.12 Tensile strain (——) and Hencky compression strain (- - -) as a function of the Cauchy compression strain, assuming no change in volume and no friction.

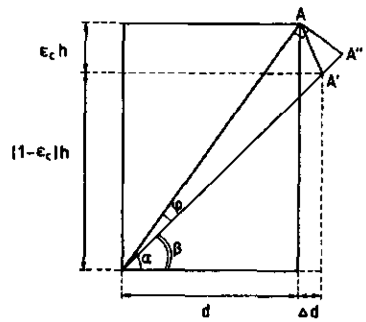
This result does not depend on the height to diameter ratio of a cylindrical sample. The tension as a function of the compression is shown in figure 2.12.

The shear (γ) inside the compression sample can be calculated according to figure 2.13. A point A in a compression test-piece moves to A' due to shear (A to A") and rotation (A" to A'). The shear is equal to tan φ and can be calculated according to

$$\tan \alpha = \frac{h}{d} \qquad (2.13)$$

$$\tan \beta = \frac{(1-\epsilon_c)\ h}{d + \Delta d} \qquad (2.14)$$

Fig. 2.13 Shear in a compression test-piece. For explanation see text.



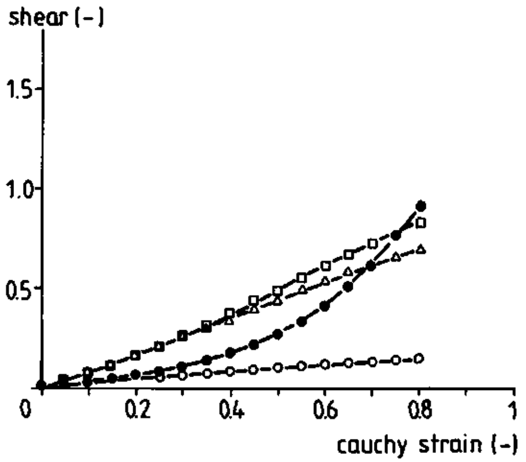


Fig. 2.14 Shear strain as a function of the Cauchy compression strain for various height to diameter ratios: h/d = 0.17(○); 1.0(△); 1.43(□); 6.0(●).

$$\varphi = \alpha - \beta \tag{2.15}$$

This formula only applies for small deformations. The additional shear at larger deformations can be calculated with the dimensions of the sample at that deformation. Some results are drawn in figure 2.14 where the shear is calculated in steps of $\epsilon_c = 0.05$. The magnitude of the shear in the sample does depend on the height to diameter ratio. This is shown for some dimensions in figure 2.14. The shear seems to be maximum when the height to diameter ratio is about 1, which implies shear to occur at an angle of 45°.

Friction acting.

If the friction between the sample and the compression plates prevents any increase of contact area, the middle part of the sample will bulge: the extension in the sample is at a maximum in this central part of the sample and zero at the compression plates. The radius in the central part is $(r_o + \delta)$ and the apparent tension strain is $\ln((r_o + \delta)/r_o)$. The magnitude of δ depends on the shape of the bulge. It can be approximated by assuming a parabolic shape of the bulged part (see figure 2.15, which corresponds quite well with the form obtained from pictures) and a constant volume of

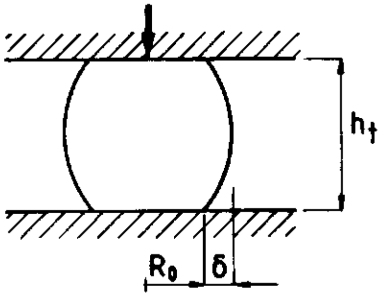


Fig. 2.15 Shape of an uniaxial compressed test-piece if there is friction between the test-piece and the compression plates. For explanation see text.

the sample during compression (Gent and Lindley, 1959):

$$\text{area of section of parabola} = \frac{4}{3}\,\delta\,\frac{1}{2}\,h_t \qquad (2.16)$$

$$\pi\, r_o^{\,2}\, \Delta h \approx 2\,\pi\, r_o\, \frac{4}{6}\,\delta\, h_t \qquad (2.17)$$

$$\delta = 3/4\; r_o\; \Delta h/h_t \qquad (2.18)$$

The maximum tension then is

$$\epsilon_t = \ln \frac{r_o + \delta}{r_o} = \ln\left(1 + \frac{3\Delta h}{4h_t}\right) \qquad (2.19)$$

At the same compressive strain the tension strain is markedly higher than in the absence of friction. The amount of tension for both situations is shown in figure 2.16 as a function of the relative compression of the sample (Cauchy strain).

If the friction between the sample and the compression plates causes a limited increase in contact area while the sample still bulges, the tension strain in the sample will be in between both extremes.

Christianson et al.(1985) found that starch gels in bonded

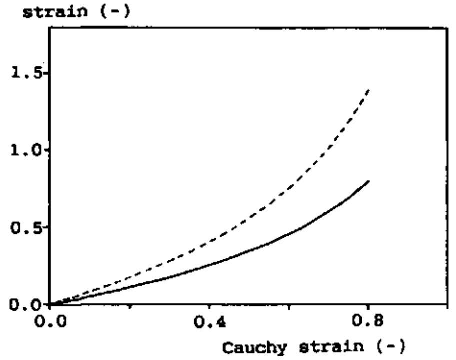


Fig. 2.16 Tension strain in absence (———) and presence (- - - -) of friction as a function of the Cauchy compression strain.

compression fractured at smaller overall compression stresses and compression strains than unbounded samples due to the barreling of the sample. Also Atkins and Mai (1985) mentioned that samples in bonded compression show smaller fracture strains than non bonded samples. Also the way of fracturing was different: the bonded samples had a greater tendency to fracture in tension than the unbounded ones, these fractured mostly in shear. This is in accordance with the calculated curves in figure 2.14 and 2.16; for the used sample shape the tension strain in the bonded case is higher than the shear strain inside the sample, while in the absence of friction at the compression plates the shear strain is always higher than the tension strain inside the compression sample.

It is very difficult to calculate exactly the stress in bonded compressive samples, because the stress bearing area changes with height in the sample. Its average value is certainly larger than the contact area, because the stress lines will bulge within the sample (figure 2.15).

Because it is very time consuming to calculate always the exact contact area (for example from pictures), sometimes plungers with the same diameter as the initial sample diameter were used. Then the stress is calculated from the recorded force and this diameter. This too is also an approximation, because more material is stressed than only that between the compression plates and the sample is not only compressed but the plunger will also penetrate

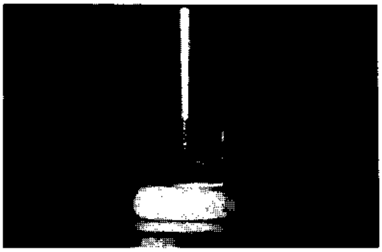


Fig. 2.17 Test-piece compressed with a plunger with the same diameter as the initial sample diameter.

somewhat into the sample (figure 2.17). The calculated stresses are therefore higher than the real stresses in the material. In table 2.3 can be seen that the calculated fracture stress of samples compressed with a small plunger with nearly the same diameter as the sample indeed are higher than the fracture stress for samples compressed with larger plungers.

2.3.1.3 Effect of friction

As is calculated in section 2.3.1.2, friction between the sample and the compression plates influences the experimental determined rheological parameters. If one wants to compare different materials it is important to be sure that differences in rheological and fracture parameters are determined and not differences in friction.

To determine the importance of friction in our experiments, we compressed different samples of the same Gouda cheese. The friction between the sample and the compression plates was varied by using the normal perspex/stainless steel plates either covered with emery paper (high friction) or a thin layer of mineral oil (low friction). The samples were photographed during compression and the size was measured afterwards. This also allowed us to calculate the different deformations inside the test-piece. The results for the increase in contact area are shown in figure 2.18, the results for the rheological parameters are shown in table 2.3 and some examples of experimental σ-ϵ curves in figure 2.19. From

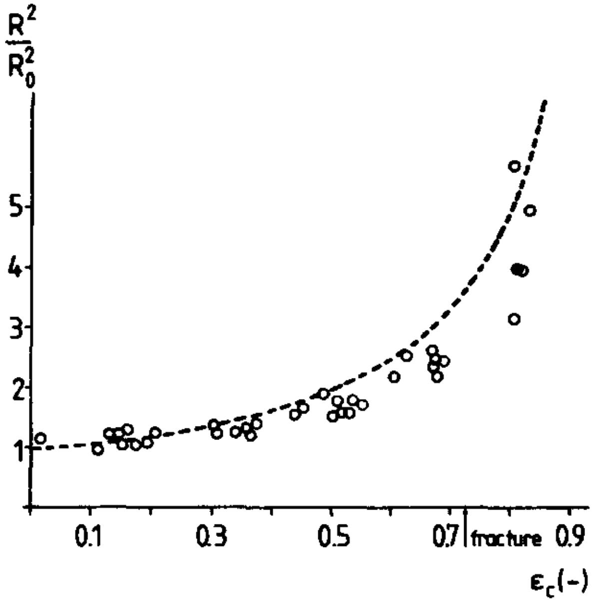
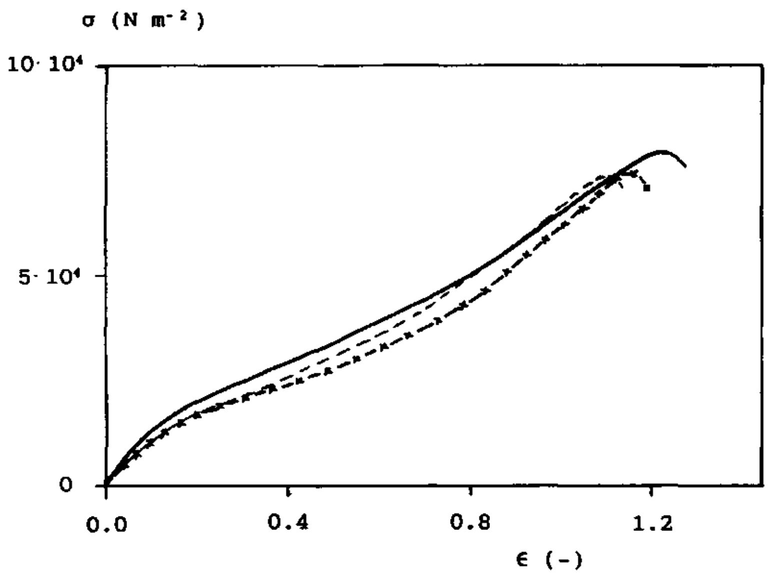


Fig. 2.18 Increase in contact area during compression as measured from pictures for different test-pieces of a 1 month old Gouda cheese (O). The increase in contact area according to formula 2.9 (no friction; no change in volume) is shown as a dotted line.

Fig. 2.19 Stress - strain curves in compression for the same cheese as in table 2.3. The friction between the compression plates and the test-piece was varied:
oil (- - -), perspex (——), emery paper (-x-).

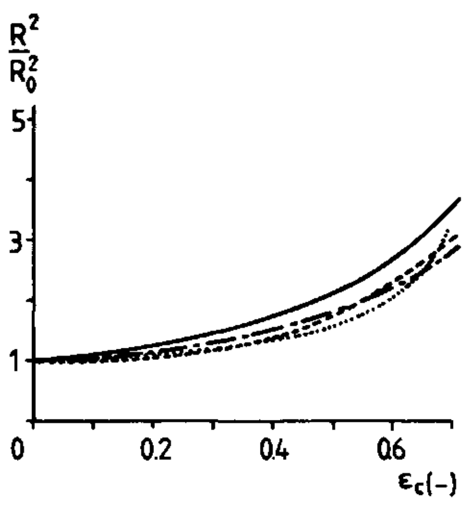


these results it can be concluded that:

- The increase of contact area is less than expected when calculated by assuming a constant cylindrical form; the sample bulges somewhat.
- There is no clear difference between the stress-strain curves obtained by using oil, emery paper or clean perspex or stainless steel plates. The compression parameters for the various imposed frictions were also not significantly different.
- The increase in contact area is the same at either side of the sample (results not shown).

Culioli and Sherman (1976) also compressed Gouda cheese samples with a h/d ratio of 1 and changed the friction by covering the compression plates with emery paper or oil. They found that with emery paper the forces were somewhat lower at the fracture point. The complete stress strain-curve, on the other hand, was higher, even the slope in the beginning (complex modulus), even though there was an increase in contact area if emery paper was used, but, according to Culioli and Sherman, much less than with oil. We recalculated the increase of the contact diameter of their

Fig. 2.20 Increase in contact area between compression plates and test-piece. Calculated from the results of Culioli and Sherman (1976). Friction was varied: oil(——); emery paper(·······); metal(- - -). The increase of the central part when used oil is shown as (—·—).



results (figure 2.20) and found that the differences with different frictions were within the same range as found by ourselves. However, we were not able to recalculate the stresses from the diameters and forces given by them.

Because there seemed to be no measurable difference in the results when using oil or emery paper, we do not expect differences in results between cheeses due to natural frictional variation (e.g. release of moisture or fat). This implies that experimental differences can be ascribed to other differences among cheese or circumstances (e.g. temperature).

The increase in circumference in the central part reasonably agrees with the calculated increase for a cylindrical shape (no friction, see figure 2.21), although the sample bulged somewhat. The reason for this is that the volume of the sample is not constant during a compression; it decreases by up to about 9% at fracture. Because the maximum tension strain in the sample agrees well with the tension strain in the absence of friction, the tension strain will always be smaller than the shear strain (see

Fig. 2.21 Tension strain of the central part of compression test-pieces as a function of the Cauchy compression strain (O). Same test-pieces as in figure 2.18. The shear and the tension strain according to formula 2.15 and 2.12 are given as —— and ----, respectively.

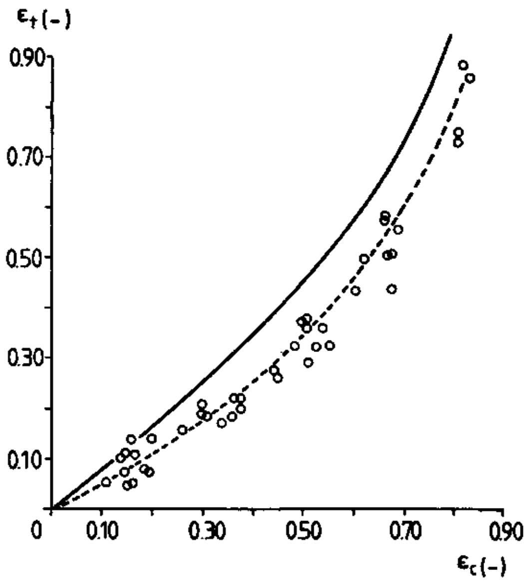
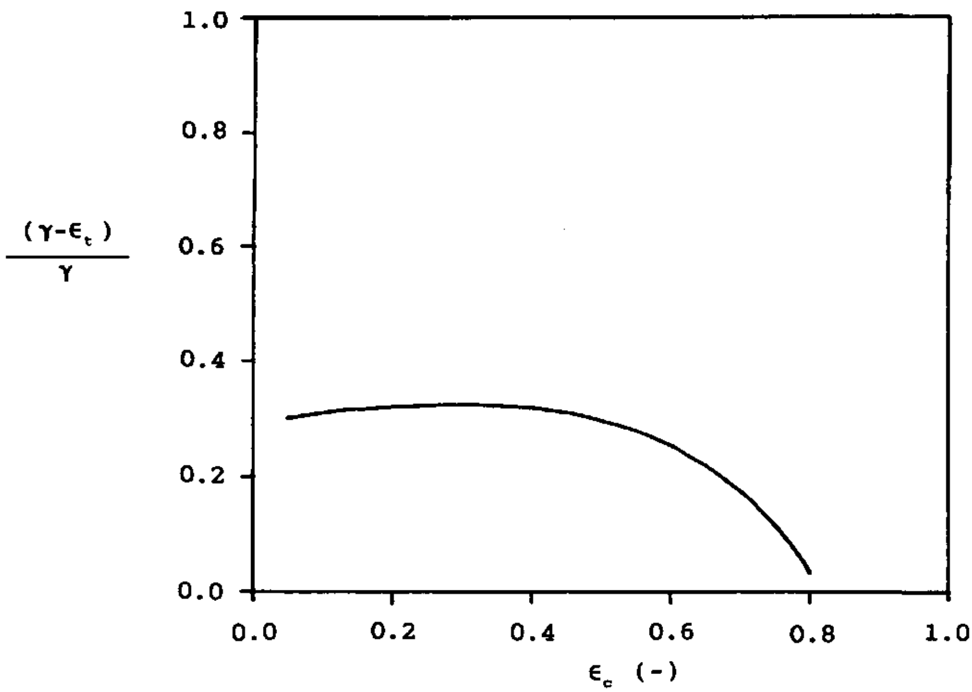


figure 2.21).

For all cheese samples measured in this study we found that a rather more mature or a low pH cheese tended to fracture in shear. Only cheese being young and not acid (for example pH>5.05 at one week old) fractured in tension. The kind of fracture seemed to depend on the compressive strain at fracture. Above a Hencky strain of about 1 ($\epsilon_c \approx 0.63$) all samples fractured in tension when tested in uniaxial compression. When the strain at fracture was 0.8 ($\epsilon_c \approx 0.55$) or lower all samples fractured in shear. Between a Hencky strain of 0.8 and 1.0 the actual mode of fracture was difficult to recognize. According to the calculated tension and shear at different compression strains (figure 2.12 and 2.14) this difference in fracture behaviour can not be explained directly; the shear in the sample is always higher than the tension strain. The difference between γ and ϵ_t relative to γ is, however, higher

Fig. 2.22 The relative difference between the shear and the tension in an uniaxial compressed test-piece as a function of the overall Cauchy compression strain. (no friction; μ=0.45).



for strains at which the samples fractured in shear, than at higher ϵ_c where the samples fractured in tension (see figure 2.22). But it is not clear why this change in fracture behaviour takes place at that particular strain difference. Fracture strain in shear and in tension of a material of course does not have to be the same.

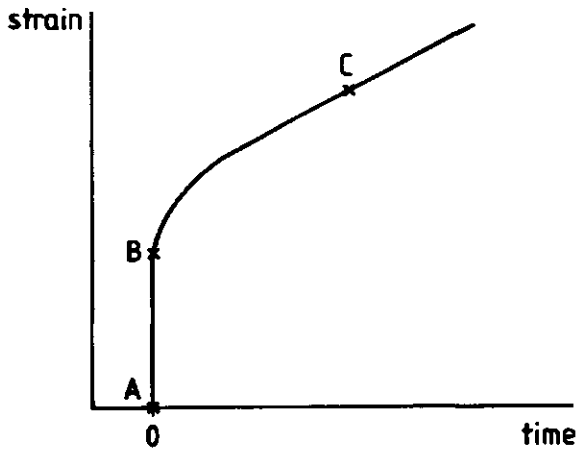
2.3.1.4 Creep measurements in compression

To obtain the viscosity of cheese we did some creep measurements by monitoring the compression of a sample under a resting weight. The stress can be calculated from the weight and the sample area, assuming constant volume and cylindrical shape. The strain and strain rate are expressed according to Hencky. The modulus can be estimated from the elastic part of the creep curve (figure 2.23)

$$E = \left(\frac{\sigma}{\epsilon}\right)_{t=0} \qquad (2.20)$$

and the apparent compression viscosity η^* from the slope of the "viscous" part of the curve

Fig. 2.23 Example of a creep curve. A-B is the elastic part of the deformation from which the modulus can be calculated. The viscosity can be calculated from the slope at C.



$$\eta^* = \frac{\sigma}{d\epsilon/dt} \qquad (2.21)$$

The stress is not constant because, due to the compression, the specimen's contact area increases. The stress therefore decreases which can cause a faster decrease in $\dot{\epsilon}$ than expected for constant stress (Peleg, 1985). Besides, the strain rate can not directly be calculated from the slope of the curve, because the height decreases ($\dot{\epsilon}$=dh/($h_t$dt)). In section 2.4 the results of these measurements will be compared with those of other methods.

2.3.1.5 Conclusions

Summarizing, the conclusions of the previous sections are:

- There is no clear influence of the size of the sample on the rheological and fracture parameters as long as the height to diameter ratio is more than 1 and less than 2.5.
- In our experiments ($h/d \approx 1.5$) variation in friction has little effect on the experimentally determined parameters.
- The different ways in which fracture can occur can possibly be explained by the different kinds of strain (tension and shear) inside the compression sample.

Considering all these results, we used compression samples of about 15 mm diameter and 20 to 30 mm height. They were compressed with a perspex plunger on a teflon coated stainless steel compression plate, which both were cleaned between experiments. Some standard deviations found with this method are shown in table 2.4. The scatter in the calculated modulus is higher than that in the fracture stress and strain, possibly because the end sides of the cylindrical sample are not always exactly flat and parallel (especially for very young cheese this is difficult to achieve), which interferes with the precise calculation of E. We found much higher standard deviations than Eberhard (1985) found. This may have been caused by the cheese used: an Emmentaler is much bigger

Table 2.4 Standard deviations in % for compression testing as found for different standard cheese. T=20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}; diameter=14 mm; height=20 mm; n=number of samples.

ripening time	n	E	ϵ_f	σ_f
1 week	4	15.7%	8.6%	12.7%
	4	22.3	7.8	17.4
	4	20.7	7.7	11.1
	4	7.2	3.7	10.5
	4	13.1	6.9	9.1
1 month	4	10.8	6.9	11.7
	6	13.5	10.2	5.3
	4	6.5	4.9	3.7
1.5 month	11	14.4	6.3	8.9
2 months	5	11.5	5.4	15.8
	8	5.6	6.5	5.0
	7	16.5	5.6	7.0
	10	13.6	4.0	9.4
3 months	4	12.1	7.0	10.7
	13	14.0	8.0	8.8
	12	14.5	5.5	12.4
	10	17.4	6.6	13.4
10 months	4	16.0	6.1	8.0
13 months	5	11.6	8.8	7.9
mean standard deviation		13.5	6.4	10.2

than the 2 kg Gouda we used and therefore there is less influence of the rind-centre inhomogeneity. Possibly the higher flow properties of an Emmentaler cheese (the ripening temperature during the first weeks is higher) also caused it to be more homogeneous. The scatter in our results, on the other hand, is comparable to that found for other materials (e.g. Andersson et al.,1973; Chu and Peleg, 1985; Olthoff et al., 1986).

2.3.2 Tension

Deformation in tension is often applied in materials testing (Gordon, 1968, 1978; Atkins and Mai, 1985) because

- The real deformations follow quite simple.

- Energy is used only for the deformation of the specimen and not for friction.
- The start of the fracture mostly can be determined more exactly because the cracking often starts at the outside of the specimen.
- It is possible to determine the notch sensitivity of a material.
- Differences in fracture strain are more clear because of the smaller increase of the Hencky strain with the displacement in tension as compared to compression (see formula 2.3).

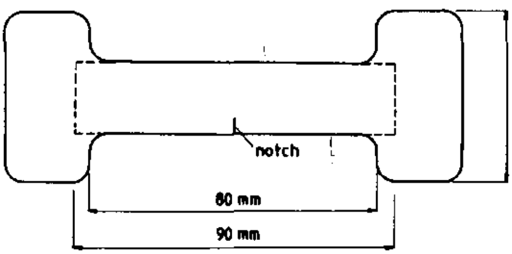
Tensile testing is not common for foods, probably because it is difficult to grip the specimen without breaking it. Gillet et al. (1978) used a tensile test to measure the adhesion between the pieces in processed meat. Schoorl and Holt (1983) estimated the strength of apple tissue by tensile testing. They applied this kind of deformation because it is more related to the bursting of apples, which they wanted to investigate. These authors did not mention any difficulties in gripping the samples.

2.3.2.1 Specimen shape

To avoid fracturing near the grips due to (unknown) stress concentrations, tensile samples are normally made with wide outer ends and a narrow central part (Gordon, 1968); they have a so-called dumb-bell shape (see figure 2.24A). We used 10 mm thick slices shaped like this. The stresses in the central part then are larger than in the outer ends. To enlarge this effect a small notch (l= 0-5 mm) may be made in the central part to determine the site where the fracture will start. With unnotched samples the complete central part of the test-piece was made narrower to prevent fracture starting at the grips.

By applying different sized notches and measuring the overall stress needed to fracture the specimen it is possible to determine the notch-sensitivity of the material. This will be described further in section 3.1.1.

A



B

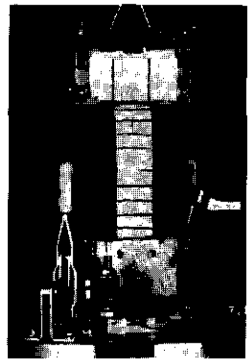


Fig. 2.24 A. Shape and size of a test-piece for tensile testing.
B. Tension test-piece with grips fixed to the Overload Dynamics.

To prevent the specimen from slipping out of the grips or to fail in the outer ends, the inner part of the grips were made of a high-friction, soft and pliable plastic foam material. In figure 2.24B the grips used are shown.

2.3.2.2 Stress and strain calculations

The strain and strain rate cannot be calculated directly from the displacement of the grips, because the shape of the elongated test-piece is not exactly known. The strain and strain rate therefore were calculated from the distance (a) between some lines drawn on the sample, as determined by photography. With elongation of the sample this distance increased in time (da/dt). From the so determined strain rate ($\dot{\epsilon}$) and the speed of the Overload Dynamics (v) the approximate stretched volume can be calculated, assuming that the total volume is constant during the experiment and that there is a clear distinction between the stretched part of the specimen and the undeformed part.

$$\dot{\epsilon} = \frac{da}{a\,dt} = \frac{dh}{h_t\,dt} = \frac{v}{h_t} \qquad (2.22)$$

From several experiments (results not shown) we calculated the apparent length (h) of the tensile specimen to be 90 mm with a standard deviation of 6-11%. In view of the real dimensions of the specimen (see figure 2.24A), this is a likely result. These results were independent of notch length, deformation rate and age of the cheese used. The strain rate was homogeneous throughout the visible part of the specimen.

From this starting length (h_o), the actual strain in tension (ϵ_t, calculated as a Hencky strain) and the stress (σ) can be calculated:

$$\epsilon_t = \ln \frac{h_o + \Delta h}{h_o} = \ln \frac{h_t}{h_o} \qquad (2.23)$$

$$\sigma = \frac{F}{A} \qquad (2.24)$$

The actual stress-bearing area can be calculated, assuming constant volume of the elongated part of the test-piece ($h_o \cdot A_0 = h_t \cdot A$). With these formulas the stress-strain curve can be recalculated from the force-time diagram. However the volume of a test-piece of Gouda cheese does change when deforming it. The Poisson ratio has found to be about 0.45 (section 2.4.2), the decrease in volume up to fracture is about 9%. This implies that the actual stress bearing area is smaller than calculated when assuming constant volume and the actual stress in the sample is higher. The error is maximum at the point of fracture and is not higher than 10%.

For small notches and the same relative rate of deformation no differences in the results of the rheological and fracture parameters were found between test-pieces of 90 and 50 mm initial length. The thickness (b) and the width (w) of the sample were not varied. For deeper notches, for example 10 mm, the 50 mm specimens gave poor results. A reason for this could be that part of the unstretched specimen volume (around the notch) as would exist in a larger test-piece tends to be outside the narrow part of the specimen. This would result in less energy for crack propagation.

2.3.2.3 Execution of the method

Samples with the dimensions shown in figure 2.24A were fixed in the tension grips of the Overload Dynamics and a notch (l = 0-10 mm) was made in it. By raising the upper bar of the apparatus the sample was elongated and ultimately fractured. The start of the fracture at the tip of the notch was noted visually and marked on the force-time curve. Samples with different sized notches were measured.

The reproducibility of the results is not as good as with compression tests possibly due to several factors, e.g.:

- The specimen is bigger which implies that there is a higher chance of having an appreciable inhomogeneity inside the specimen.
- Because it was impossible to measure the notch length before the test without damaging the sample, this was done afterwards, when the sample was already fractured. This can cause differences between experiments.

2.3.2.4 Creep measurements in tension

With eye formation in cheese, a small gas nucleus grows to a large eye due to the gas pressure in it. Hereby the circumference is extended. In section 6.3.1 we will show that it is possible to imitate this by blowing gas through a needle into a cheese. The growth of the circumference of the "artificial" eye is a deformation in tension and a biaxial tensile strain can be calculated as a Hencky strain. The gas pressure is the stress applied on the cheese. This test is a kind of creep measurement and it is possible to calculate an apparent elongational viscosity from the stress and the increase in strain during a certain time according to formula 2.21. In section 2.4.1.4 we will compare this viscosity with the values found with other methods.

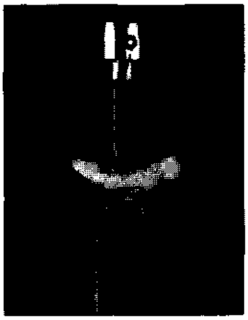


Fig. 2.25 Bending equipment for Overload Dynamics as was used for cheese test-pieces.

2.3.3 Bending

In traditional grading of cheese consistency, long cylinders of cheese are bent by hand up to fracture. In this way, the firmness and shortness of the cheese probably are judged as the force needed to bend the sample and the amount of bending at fracture, respectively. It is possible to imitate this type of deformation with the Overload Dynamics by pressing on a cylindrical test piece supported on two bars as shown in figure 2.25.

Bending tests are used often in material testing (e.g. Atkins and Mai, 1985), possibly because they are easy to perform and it is not necessary to fix the specimen to the apparatus. This type of test is not much used for testing food materials, the reason for this being unknown. Andersson et al.(1973) performed a 3-point bending experiment for testing the fracture properties of crisp bread, but we know of no other published experiments. It is also possible to do notch sensitivity tests with bending (e.g. Birchall et al.,1981).

2.3.3.1 Stress and strain calculations

The actual strain during bending depends on the place in the specimen. One half of the specimen is compressed while the other half is elongated as is shown in figure 2.25. Between these two halves there is a neutral axis which is neither compressed nor elongated. The stress and the strain in the sample can be calculated from the force and the deflection, assuming that (Roark, 1965):

- the material is isotropic and has the same modulus in tension as in compression
- the beam is straight and has a uniform cross section
- the ratio of the distance between the supporting bars to the diameter of the sample is large
- the load is perpendicular to the neutral axis
- stresses and strains are very small and in the linear or Hookean region

The bending moment (M) of a section due to an applied force F (see figure 2.26A) can be calculated with respect to the supported bars (see e.g. Roark (1965) for all calculations);

$$M = \tfrac{1}{2}L \cdot \tfrac{1}{2}F \qquad (2.25)$$

or with respect to the neutral axis

$$M = \int_0^{\frac{1}{2}D} \sigma\, q\, dA \qquad (2.26)$$

With a three point bending test the tensile and compression strain in the sample can be calculated according figure 2.26B.

$$\epsilon_{max} = \frac{(R + \frac{1}{2}D)\tan\alpha - R\tan\alpha}{R\tan\alpha} = \frac{D}{2R} \qquad (2.27)$$

Assuming a Hookean material ($\sigma = E \cdot \epsilon$) and a cylindrical beam (which has I=second moment of inertia=$(1/64)\pi D^4$) this gives

$$\tfrac{1}{4}\, L\, F = \frac{E}{R}\int_0^{\frac{1}{2}D} q^2\, dA \qquad (2.28)$$

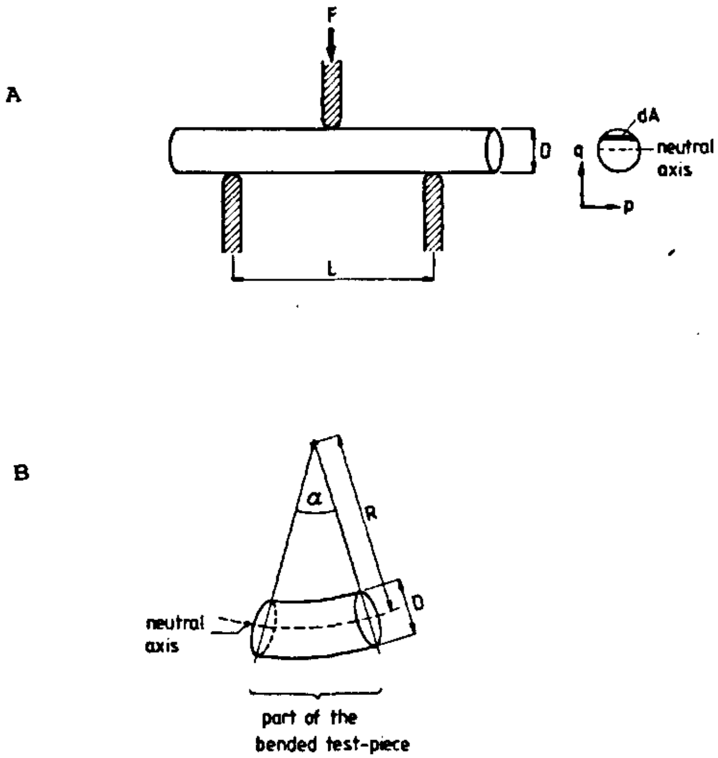


Fig. 2.26 Calculation of bending stress (A) and strain (B). See text for further explanation.

and

$$\sigma_{max} = \frac{8\ F\ L}{\pi\ D^3} \qquad (2.29)$$

Because the moment of bending is also equal to:

$$M = E\ I\ \frac{d^2q}{d\ p^2} \qquad (2.30)$$

the displacement of the centre of the beam, y_{max} or the deflexion, is equal to:

$$y_{max} = \frac{F\ L^3}{48\ E\ I} \tag{2.31}$$

this gives, using 2.29, for the maximum tensile strain ϵ_{max}:

$$\epsilon_{max} = \frac{6\ D\ y_{max}}{L^2} \tag{2.32}$$

Due to the weight of the sample the test-piece will deflect somewhat without an extra force acting on it. Assuming an uniformly weight distribution the maximum strain can be calculated

$$\epsilon_{max} = \frac{5 \cdot 9.81\ \rho L^2}{4\ E\ D} \tag{2.33}$$

where ρ is the density of the material. This means that the strain in the sample (cheese: ρ=1100 kg m^{-3}; E=10^5 N m^{-2}) due to its weight is less than 0.02, much less than the strain at which cheese fractures. Therefore we neglected this effect in our calculations. All calculations above are valid only for small strains and are thus only an approximation for the circumstances we are studying.

2.3.3.2 *Execution of the method*

For standard bending measurements we used samples with a diameter of about 1.5 cm and 7-10 cm long. The distance between the supports was 5 cm (=L). Holders and bending plunger were perspex cylinders with a diameter of 5 mm. We could not find an influence of L on the stress-strain curve (results not shown) although the length of the sample was not large in respect to the diameter. The reproducibility of the results was comparable to those of compression testing (see for example table 2.5).

Bending of samples to study the behaviour of cheese is easily done for more mature or acid cheese with a small strain at fracture. This bending method, however, can not be used for studying the fracture properties of cheese with a high ϵ_f, for example young cheese, because the test-piece will slide from the supports before it fractures.

Another disadvantage of this bending method is that the required sample size is large compared to compression test-pieces, which implies that the probability of having inhomogeneities in the test-piece is higher.

The plunger which bends the sample also penetrates somewhat into the sample and thereby compress it. When assuming a penetration of 1 mm, the contact area is about 0.35 cm^2 and the maximum compressive stress due to this penetration is 0.6 times the value of the maximum bending stress. This certainly is not negligible, and makes it, again, difficult to apply a bending method for soft and deformable materials.

2.3.4 Shear

Shearing deformation differs in kind from that in compression or tension (see 2.1.1) and may therefore give additional information about the properties of a material. We found no literature about experiments in shear on cheese, but milk gels have been studied extensively with this type of deformation (e.g. Roefs, 1986; Zoon, 1988).

2.3.4.1 Calculation of stress, strain and moduli

Small cylindrical pieces of cheese were sheared between two parallel flat circular discs, covered with emery paper as described in section 2.2.2. The upper disc could rotate around its axis. From the angular displacement (α) and the distance between the plates (h) the shear strain γ at radius r can be calculated (Whorlow, 1980) as:

$$\gamma = \frac{\alpha\ r}{h} \qquad (2.34)$$

The strain is not uniform throughout the material, but zero in the centre and maximum at the circumference. A torque (T) applied on the upper plate causes a stress in the test-piece, dependent on the size of the sample (Whorlow,1980).

$$\sigma = \frac{2\ T}{\pi\ r^3} \qquad (2.35)$$

With our apparatus we were able to apply constant or sinusoidally varying torques on samples. When using a constant stress a creep curve is obtained, from which it is possible to calculate the instantaneous shear modulus G ($=\sigma/\gamma_o$) and the apparent shear viscosity η^* ($=\sigma/\dot{\gamma}$). The strain and strain rate used in these calculations are the maximum strain (rate) in the test-piece. Because the viscosity of a non-Newtonian material depends on the strain rate and is thus not equal throughout the test-piece, the calculated $\eta^*(\dot{\gamma})$ is only an approximation of the apparent viscosity at that shear rate. The results are discussed in chapter 2.4 and compared there with those of other tests.
In dynamic experiments the stress is varied sinusoidally at a frequency ω:

$$\sigma_t = \sigma_o \sin(\omega t) \qquad (2.36)$$

where σ_o is the maximum stress and σ_t the stress at a certain time. This stress causes a sinusoidally varying shear

$$\gamma_t = \gamma_o \sin(\omega t-\delta) \qquad (2.37)$$

where γ_o is the maximum deformation and δ the phase difference between the stress and the shear (figure 2.27). This phase difference originates from the viscous properties of the material

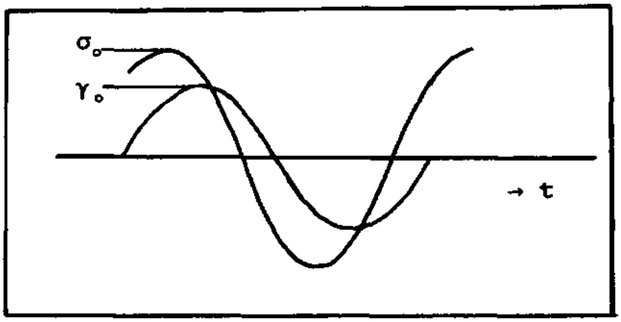


Fig. 2.27 Example of the sinusoidal variation of stress and strain as a function of time for a visco-elastic material.

(Whorlow, 1980). If the strain is taken as the reference, these formulas change into

$$\gamma_t = \gamma_o \sin(\omega t) \tag{2.38}$$

$$\sigma_t = \sigma_o \left(\sin(\omega t)\cos\delta + \cos(\omega t)\sin\delta\right) \tag{2.39}$$

The first term on the right hand side of formula 2.39 represents the part of the stress that is in phase with the deformation, or the elastic part. The second term is that part which is out of phase, or the viscous part. These parts correspond to the elastic or storage modulus (G', a measure of the energy stored in the material) and the viscous or loss modulus (G", a measure of the energy dissipated in the material), respectively:

$$G' = \frac{\sigma_o}{\gamma_o} \cos\delta \tag{2.40}$$

$$G'' = \frac{\sigma_o}{\gamma_o} \sin\delta \tag{2.41}$$

This gives:

$$\sigma_t = G'\gamma_t + G''\frac{1}{\omega}\frac{d\gamma_t}{dt} \qquad (2.42)$$

The ratio between these moduli gives the loss tangent

$$\tan\delta = \frac{G''}{G'} \qquad (2.43)$$

wich is a measure for the viscous-like behaviour of the material. In the Deer Rheometer, a sinusoidally varying torsion is applied to the specimen. This causes a place dependent stress in the test-piece.

$$T_t = \int_0^R 2\pi r^2 \sigma \, dr = \int \frac{2\pi r^3}{h} \left(G'\alpha + G''\frac{1}{\omega}\frac{\alpha}{dt}\right) dr \qquad (2.44)$$

In the Deer a certain mass rotates and thus has a moment of inertia (I), partly due to the mass of the moving parts of the apparatus, partly to the mass of the test-piece. This moment of inertia cause an error in G' that increases with frequency (Jones et al., 1984). In addition, the stiffness and energy dissipating properties of the apparatus (C, and A respectively) can cause an error in the experimental moduli. The moduli can be corrected for these effects (van Vliet, personal communication) by gauging the apparatus with materials with known rheological properties.

$$G' = \frac{2\,h}{\pi R^4}\left(\frac{T_o \cos\delta}{\alpha_o} + I\,\omega^2 - C\right) \qquad (2.45)$$

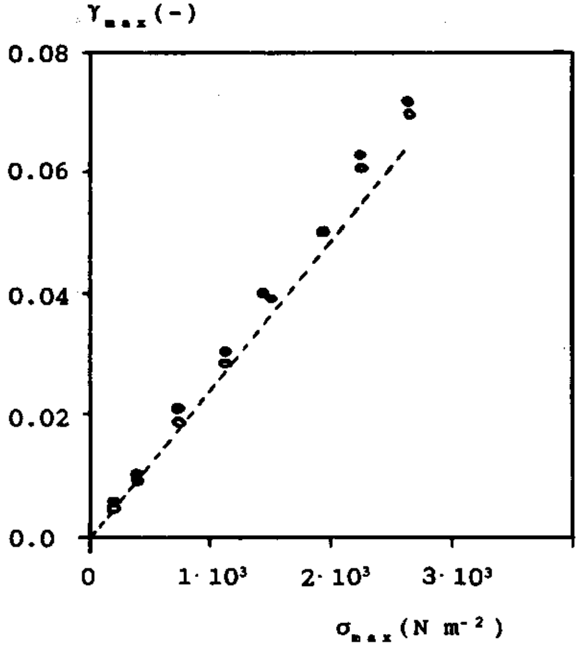
$$G'' = \frac{2\,h}{\pi R^4}\left(\frac{T_o \sin\delta}{\alpha_o} - A\omega\right) \qquad (2.46)$$

2.3.4.2 Execution of the method

All shear experiments were done with test-pieces of 9-10 mm height and about 15 mm diameter. For bigger specimens the stress and strain at the torsions which can be applied by the Deer would be much lower than in the other kinds of experiments. Static experiments were done at several torsions. From the resultant creep curves the modulus (G) and the apparent shear viscosity (η^*) were calculated in the same way as in section 2.3.1.4 for the apparent compression viscosity.

The results of dynamic measurements can be interpreted easily in terms of cheese structure only if done in the linear region, i.e. where strain is proportional to stress (Whorlow, 1980). We found for several kinds of cheese that the maximum shear was proportional to the maximum stress for a shear smaller than about

Fig. 2.28 Maximum shear in dynamic experiments as a function of the maximum applied stress. Example for a 2 weeks old standard Gouda cheese, measured at 10^{-1} Hz (O) and 10^{-2} Hz (●).



0.02 (figure 2.28). G' and G" then were independent of the applied stress. We therefore measured only at smaller strains and corresponding stresses ($\sigma \approx 400$ N m^{-2} and $\gamma < 0.02$). At higher stress tan δ mostly increased and ultimately the upper plate slipped over the cheese sample. This can also be seen very clearly from the shape of the stress-strain curves as obtained on a XY recorder: if there is no slip the curves are elliptical, with slip they are not.

The frequency used in the dynamic measurements must not be too high, because of the moment of inertia of the system. Therefore the upper, rotating plate was made of perspex (low mass) and the frequencies used were low (0.05-0.005 s^{-1} ≈ 0.3-0.03 rad s^{-1}). At still lower frequencies the sample tended to dry out during the experiment.

We found a wide variation in the results of G' and G", presumably because the measurement of the radius of the sample is not exact enough (R^4 in the formula!). This variation is not found in the results for tan δ. When measuring on one test-piece for a long time the stability is very good. During an experiment of 1½ hour on a two week old cheese ($\sigma = 465$ N m^{-2}; 10^{-1} Hz) the maximum shear decreased from 0.019 to 0.018 and the tan δ from 0.358 to 0.345. The decrease may have been due to the drying out of the sample. The weight loss was 0.5%. During a normal experiment of 3/4 hour this was at most 0.4%.

2.4 Comparison of the different rheological and fracture measurements

In previous paragraphs it was shown that stressing a material mostly causes various kinds of deformation inside the test-piece. Moreover, in compression tests on test-pieces with a low h/d ratio, part of the measured stress is due to friction. To compare different materials, it is important to know whether real material properties are measured; this may be so if the results do not depend on the experimental conditions. Therefore several kinds of experiments were performed with the same material, e.g. with samples taken from one cheese. Some of the results are shown in the tables in this chapter.

In the first part of this section (2.4.1) we will compare the results for the force-deformation curves of compression, tension and bending experiments at the same Cauchy strain rate (only constant speed could be applied by the Overload Dynamic machine). In the second part (2.4.2) we will compare compression (and tension) experiments with shear experiments.

2.4.1 Comparison of compression, tension and bending tests

There is no general relationship between the behaviour of materials in compression and in tension, because there are different ways in which a material can run away from a compressive load and because other effects (e.g. friction) can contribute to the compression stress (Gordon, 1978). For our material (Gouda cheese) we found that the deformations in compression, tension and bending have much in common; the circumference of a sample in compression is elongated, the bottom side of a bending sample is stretched while the topside is compressed (see section 2.3.1 and 2.3.3). Some failures in compression have been analyzed as tensile fractures caused by a tensile stress perpendicular to the crack plane. The strength thus calculated for such a material can agree very well with the results of tensile measurements; therefore a compression test is sometimes called an indirect tensile test (Atkins and Mai, 1985). In section 2.3.1.1 and 2.3.1.3 we indicated that friction does not significantly contribute to the compression stress. In this section we will compare the results of different methods, i.e. the modulus (2.4.1.1), the stress-strain curve (2.4.1.2) and the fracture stress and strain (2.4.1.3).

Table 2.5 Comparison of compression, tension and bending experiments of a 6 weeks old Gouda cheese. T=21°C.

kind of deformation	$\dot{\epsilon}_c$ (s^{-1})	E (10^5 Nm^{-2})	ϵ_f (-)	σ_f (10^4 Nm^{-2})
tension (l=0.2-0.3mm)	$1.39 \cdot 10^{-2}$	1.89	.33	3.05
		2.01	.31	2.64
		2.21	.31	2.89
		2.30	.28	2.24
			.29	2.35
bending	$1.81 \cdot 10^{-2}$	1.88	.48	4.13
		1.73	.43	4.08
		1.69	.47	3.76
		1.88	.62	4.36
		1.65	.54	4.41
compression	$1.67 \cdot 10^{-2}$	2.02	.87	4.97
		2.03	.80	4.57
		1.73	.89	4.58
		1.54	.96	4.53
		2.44	.82	5.33

2.4.1.1 The Young modulus in compression and in tension

The first small deformation in compression as well as in tension goes along with very small changes in the distance between the structural elements of the material compared to the equilibrium distance (Treloar, 1975). Because of this the Young modulus for compression and for tension should be equal. In table 2.5, results are shown for compression, tension and bending tests on one cheese. The tests were done at about the same Cauchy strain rate. Because the modulus is measured as the initial slope of the force-time curve, the Hencky strain rate is also about the same. As can be seen, the moduli are not significantly different. In table 2.6 the Young moduli measured in compression and in tension for different cheese are shown. The compression modulus is the mean result of 2-4 tests, the tensile modulus was measured only once on a test-piece without a notch. The results are very comparable.

__Table 2.6__ Comparison of E (table 2.6A) and fracture stress and strain (table 2.6B) as determined in compression and tension experiments of different cheese. For a further description of these cheese see chapters 4 and 5. Fracture stress for compression is recalculated according to formula 2.47 to the value expected to occur at the moment of fracture in tension test. Mean values of experimental results for 5-10 test-pieces are given. The value for ϵ_f in tension was only for one test-piece without a notch. Standard deviation was comparable to table 2.4. t=tension; s=shear.

__2.6A__

no.	cheese	E ($\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}) (10^5 Nm^{-2}) compression	tension
	standard		
1	½ month	1.40	1.28
2	1	2.20	2.15
3	2	2.59	2.48
4	4	3.19	4.27
5	6	4.09	2.86
6	10	24.1	16.6
7	12	12.8	10.6
	pH influence 1 week		
8	pH 5.04	.63	.63
9	5.22	1.28	1.38
10	5.26	1.01	1.63
11	5.08	.98	1.14
12	5.03	.57	.50
	4 weeks		
13	pH 5.18	1.06	1.45
14	5.30	1.62	1.30
15	5.35	1.96	2.31
16	5.12	1.81	1.75
17	5.01	.77	.82

__2.6B__

no.	$\dot{\epsilon}_h$ (10^{-3} s^{-1})	σ_f (10^4 Nm^{-2}) compr.	tension	ϵ_f (-) compr.	tension	mode of fracture
1	1.7	2.9	2.5	1.16	.49	t
2	1.9	2.9	2.7	1.05	.36	t
3	2.1	3.2	2.7	.98	.26	s/t
4	2.5	4.6	3.4	.74	.12	s
5	2.3	5.4	5.5	.56	.21	s
6	2.4	21	23	.38	.13	s
7	2.5	9.4	15.5	.34	.11	s
8	2.1	2.1	2.0	1.02	.24	t
9	2.0	5.3	4.5	1.12	.35	t
10	1.9	4.3	3.0	1.24	.37	t
11	2.4	2.8	2.3	.83	.16	s
12	2.5	1.6	1.2	.55	.11	s
13	2.3	2.3	2.8	.84	.18	s
14	1.9	4.2	4.0	1.02	.36	t
15	2.3	5.6	3.8	1.01	.18	t
16	2.4	3.7	2.4	.52	.14	s
17	2.5	2.1	1.6	.39	.09	s

2.4.1.2 The stress-strain curve

As mentioned above, stress-strain curves in compression and in tension do not have to be identical because of the different ways in which the deformation occurs. Because several cheese samples tested in compression actually fractured in tension, we did expect some similarities in the deformation behaviour.
In figure 2.29(A to D) the stress-strain curves for different cheese tested in compression, tension and bending are shown. As can be seen the curves are similar, but not identical. Reasons for this could be:

- Some of the tension samples had a notch. This causes locally higher stresses and strains in the sample. The highest stress is found at the tip of the notch and can be estimated with the stress concentration factor given in section 2.1.2

  $$\sigma = \sigma_o \ (1+2\surd(1/r)) \qquad (2.1)$$

  As will be shown in section 3.2.3 the strain concentration does not significantly differ from the stress concentration.
- The formulas given for the stress and strain calculations in bending are valid only for small deformations and linear elastic behaviour. For higher strains, the Hencky strain rate will no longer be the same on the compression and the tension side of the sample. This is one of the reasons for a different stress distribution at either side of the neutral plane. Other causes for the difference between the actual and the calculated stresses and strains were given in section 2.3.3.
- The deformation rates for the measurements of figure 2.29(A to D) were chosen such that the strain rate at the start of the experiment was equal for all tests. For compression testing at a constant speed, the Hencky strain rate constantly increases due to the decrease in height of the sample. For tensile testing $\dot{\epsilon}$ decreases and for bending tests the change in $\dot{\epsilon}$ depends on the position in the test-piece. For visco-elastic materials, the stress needed to obtain a certain strain depends on the strain rate. Cheese is a visco-elastic material

and this change in strain rate will therefore influence the results.

- The formula for stress concentration given above is derived for a single notch, perpendicular to the direction of applied tensile strain or stress. The direction of loading with respect

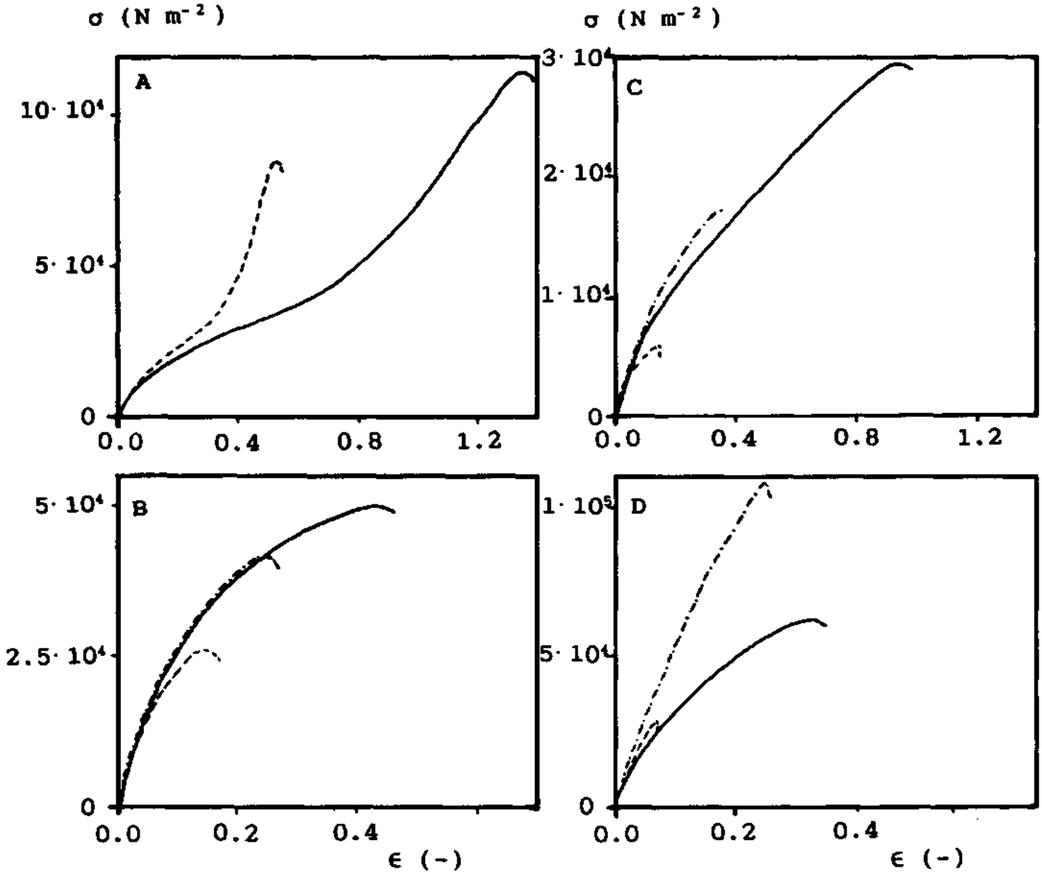
Fig. 2.29 Stress-strain curves for different cheese (A to D) tested in compression (—) and tension (---) (and bending (-·-·-)). Strain rate at start of the experiment was the same for the different deformations.

Cheese: A. 2 weeks old; $\dot{\epsilon}_c = 2.8\ 10^{-2}\ s^{-1}$

B. 6 weeks old; $\dot{\epsilon}_c = 1.6\ 10^{-2}\ s^{-1}$; tension test-piece had a notch of 0.2 mm.

C. 2½ month old; $\dot{\epsilon}_c = 2.8\ 10^{-2}\ s^{-1}$; tension test-piece had a notch of 3.6 mm; the bending test-piece did not fracture.

D. 10 month old; $\dot{\epsilon}_c = 2.8\ 10^{-2}\ s^{-1}$; tension test-piece had a notch of 0.75 mm.



to the direction of the irregularity does influence the stress concentration in the material (Atkins and Mai, 1985). Because Gouda cheese appears to be essentially isotropic, there is no mean direction of the irregularities as there is in a fibrous material, and the direction of loading may not significantly influence the behaviour.

- The magnitude of the different strains relative to one another depends on the way of deformation. In a tension test-piece the two compression strains are perpendicular to the tensile strain, each being equal to half the tension strain. In a compression test-piece, however, two tension strains are perpendicular to the compressive strain, being equal to half the compressive strain. This means that the triaxial strain at a certain ϵ_h in compression and in tension is different.

The curves in figure 2.29A to 2.29D can be corrected for some of the above mentioned phenomena. The tension curves from test-pieces with a notch can be recalculated to the stress strain curves at the tip of the notch using the Inglis concentration factor of formula 2.1. The results are in figure 2.30A to D. The tension and compression curves can be recalculated to a stress strain curve for a constant strain rate using the relation

$$\log \sigma = \text{const} + 0.17 \log \dot{\epsilon} \qquad (2.47)$$

This formula will be derived in section 3.2.1. For the other phenomena mentioned no correction factors are known. The results are given in figures 2.31A to 2.31D and it can be concluded that

- The overall shape of the stress-strain curve does not depend on the mode of deformation. The curves for the younger cheese (figure 2.31A) are convex for small strains and concave for high strains. The deformation curves for the other cheeses tested are all convex.
- The initial slope (the Young modulus) does not depend on the mode of deformation, as was already mentioned in 2.4.1.1.
- For higher strains, especially near the point where macroscopic fracture occurs, the stress needed to reach a certain strain

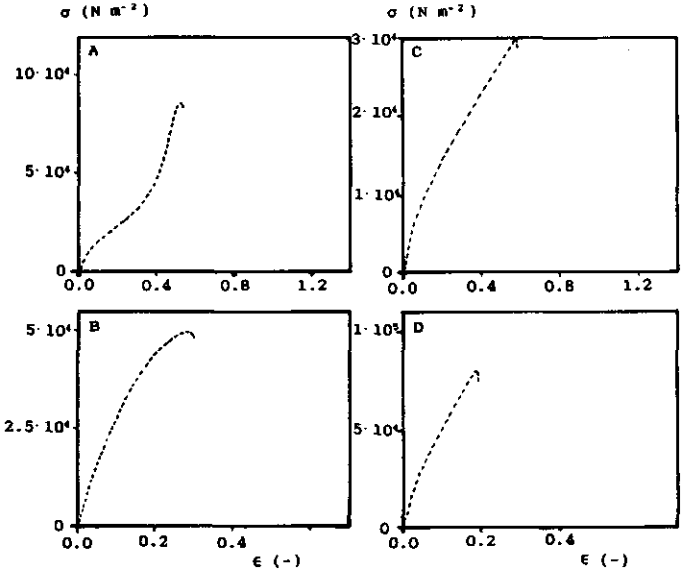
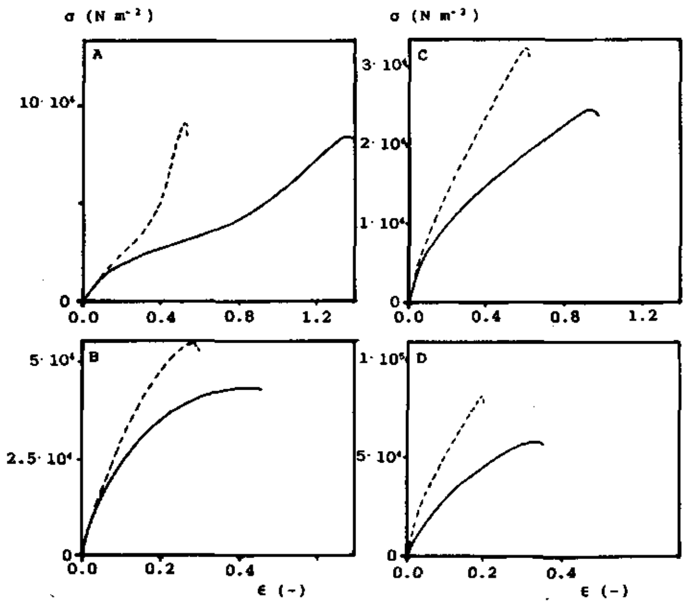


Fig. 2.30 Tension curves for the same test-pieces as in figure 2.29 but corrected for stress and strain concentration due to the notch. (The test-piece of figure 2.29A had no notch, figure 2.30A is thus identical to the tension curve of 2.29A)

Fig. 2.31 Compression and tension curves of figure 2.29 recalculated to constant strain rate.



depends somewhat on the way of deformation even after correction for the strain rate and stress concentration, but the differences become somewhat smaller if the stresses are corrected for these effects. The reason for the discrepancy may be the difference in the three-dimensional state of strain at a certain overall strain. This will be discussed further in 2.4.1.3. The differences in stress at a certain overall strain are highest for very young cheese.

2.4.1.3 Fracture stress and strain

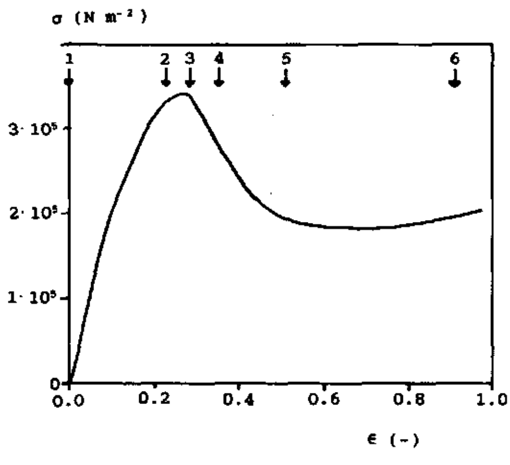
As can be seen in the figures of the previous section (2.4.1.2) the stress-strain curves for the different deformations do agree quite well for small strains. At the point of maximum stress, which is roughly the point where fracture starts, there is a large difference between the curves. It is remarkable that after correction the maximum stresses are closer than are the strains at maximum stress. To check this, we compared the fracture stresses and strains of different cheeses in tension and in compression. In table 2.6B the mean experimental results for a standard cheese of different ages and for several special cheeses (pH influence see section 4.3.2) is shown. The fracture stress in compression was recalculated to the stress that would have been found at the strain rate where the samples tested in tension fractured. As can be seen in this table the fracture stress in tension is about the same as, or somewhat less than, the stress found in compression. The agreement is best when the compressed sample failed in tension.

The strains at maximum stress for different deformations are not at all the same. This can be seen in the figures in the previous section and in table 2.6. Differences in fracture stress between tension and compression in table 2.6A and figure 2.31 were comparable. Differences in fracture strain, however, were found to be larger for the experiments in table 2.6B. The reason for this discrepancy is unknown. The ϵ_f in compression testing is always much higher than the ϵ_f found in tension or bending experiments. Reasons for this may be:

- The actual tensile strain in compression is roughly half the Hencky strain ($\epsilon_t \approx \frac{1}{2}\epsilon_h$, see section 2.3.1.2). When taking this into consideration the difference in ϵ_f decreased, but did not vanish.
- The (local) tri-axial strain at a certain overall strain depends on the mode of deformation (see section 2.4.1.2).
- It is not possible to indicate the exact moment at which fracture starts. With bending and tension, fracture seemed always to start at the outside of the sample and the moment could therefore be quite well observed. If in a compression test failure is in tension, this is also the case and it was observed that fracture started before the maximum in the force-time curve, at or possibly just before the maximum in the stress-strain curve. If the compressed sample fails in shear, fracture starts inside the sample and this is not visible on the outside. It can be seen very clearly on the pictures in figure 2.32. In this experiment pieces of cheese were compressed up to a certain strain after which the plunger was immediately removed. The test-piece then was cut in the direction of

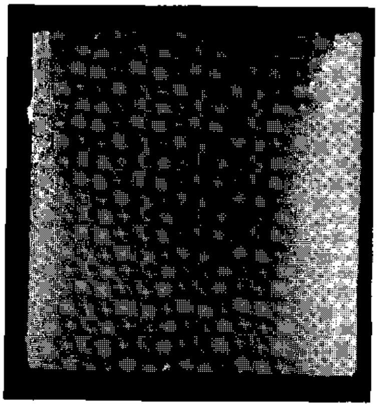
Fig. 2.32 A. Compression curve of a 1 year old cheese. Numbers refer to the pictures in figure 2.32B.
B. Fracture inside the compression test-pieces. For explanation see text.

A



B

1



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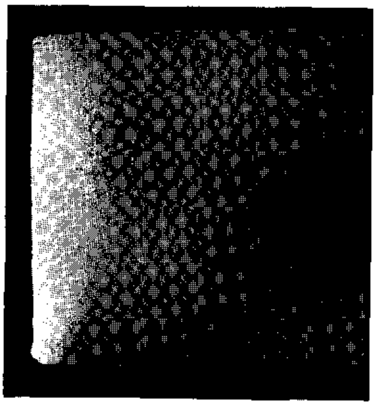

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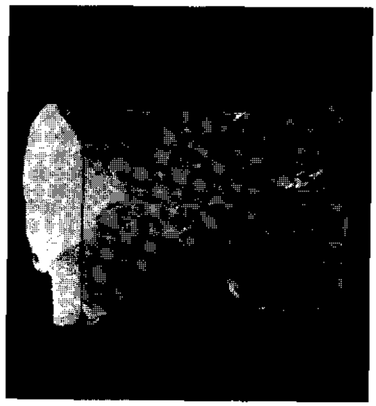

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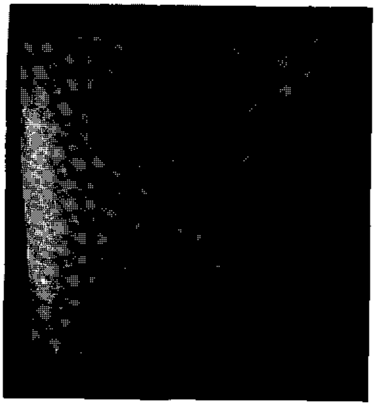
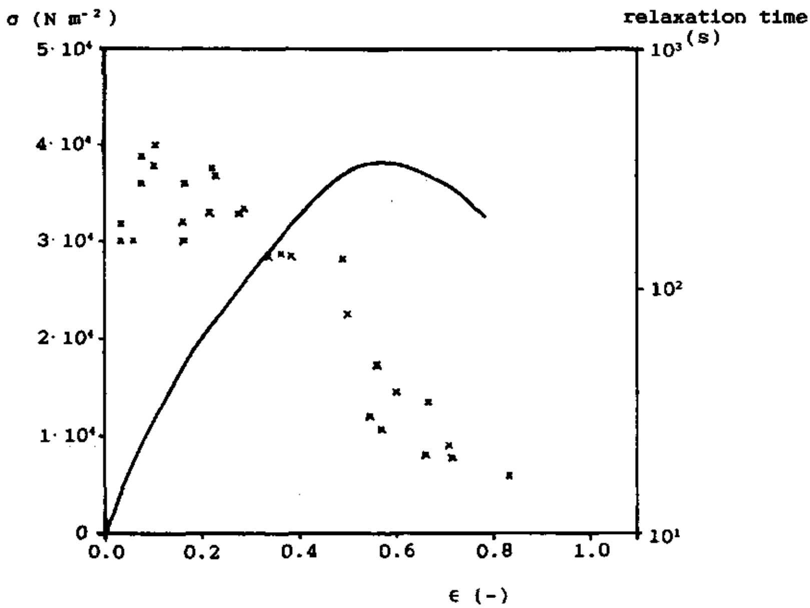


6

compression and the two parts were photographed. This was done after compression to various strains. As can be seen in the pictures, crazes were visible before the maximum in the σ-ϵ curve and long before fracture was visible on the outside of the sample. This means that the actual fracture strain and stress in compression for cheese samples that fractures in shear are smaller than the stress and strain at the maximum of the σ-ϵ curve, which were defined as the σ_f and ϵ_f. This also means that in comparing the σ_f and/or ϵ_f of different cheeses, we not really compare the fracture parameters but some nearby stress and strain. There will be some similarities between the σ_f and ϵ_f and the fracture parameters, but we must be aware that the differences do not have to be the same for all cheeses.

The fact that there are already failure phenomena before the maximum stress occurs can also be made clear when studying the decrease in the relaxation time with increasing strain (Pollak and Peleg, 1980). An example of this is shown in figure 2.33.

Fig. 2.33 Stress-strain curve (——) and apparent relaxation times (X) for different strains, both measured in compression. T=20°C: $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}; 6 weeks old cheese with 60% fat in dry matter.



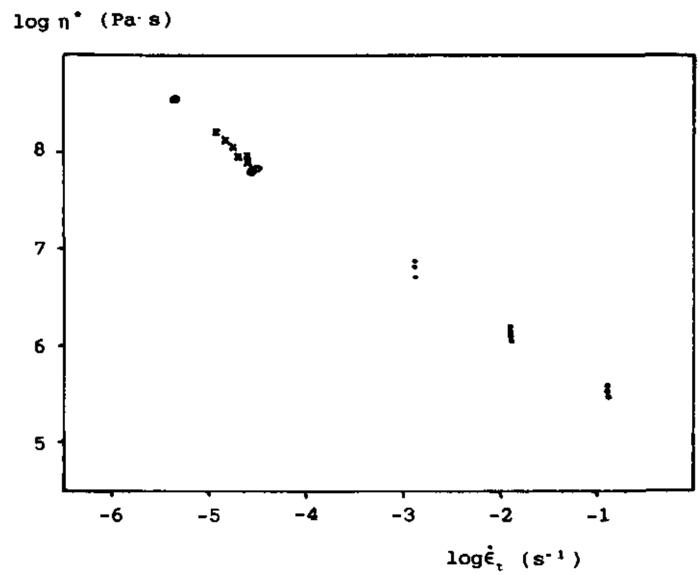
At strains lower than 0.05 the behaviour of the material was no longer (apparent) linear. From ϵ=0.25 on the apparent relaxation time decreased with increasing strain. The stress needed to compress the sample, however, increased up to a strain of about 0.6. These results implies yielding and fracture to occur long before σ_f and ϵ_f has been reached. This behaviour does not have to be the same for the different modes of deformation and deviation in results can partly be ascribed to differences between the actual start of fracture and the measured σ_f and ϵ_f.

2.4.1.4 Elongational viscosity

Elongational viscosities were calculated from creep measurements in tension (see section 2.3.2.4), creep measurements in compression (section 2.3.1.4) and uniaxial compression experiments with the Overload Dynamics (section 2.3.1.1). The tension in compression experiments was calculated as the increase in circumference with decreasing height (section 2.3.1.2.).

In figure 2.34 an example is shown of the apparent viscosity

Fig. 2.34 Apparent elongational viscosity as a function of the tension strain rate for different experiments; creep in compression(X), uniaxial compr. at constant speed(●) and eye formation(○). 1 week old Gouda cheese with pH 5.2.



of a cheese as a function of the tension strain rate. From this can be concluded that

- Cheese is a shear thinning material; the apparent viscosity decreased with increasing strain rate. We will discuss this further in section 3.2.1.
- The results for the different tests were about the same. This proves, again, that with the different methods we are measuring the same material properties.

In section 6.3 we will further discuss the relation between this test and the actual eye formation in cheese.

2.4.2 Comparison of compression and shear experiments

Deformation in shear is really different from deformation in tension or compression (see section 2.1.1). Compressive and tensile experiments are more easy to perform, but they have the disadvantage that with deformation both shape and volume can be changed (Ferry,1970) which makes it more difficult to interpret the results. A measure for the change in volume (dV/V) is the Poisson ratio μ (Reiner,1971)

$$\mu = \frac{1}{2} \left(1 - \frac{dV}{V\, d\epsilon}\right) \qquad (2.48)$$

With this measure it is possible to relate the values for the different moduli (Reiner,1971). For isotropic, homogeneous materials this is:

$$E = 2\, G\, (1+\mu) \qquad (2.49)$$

$$E = 3\, K\, (1-2\mu) \qquad (2.50)$$

If there is no change in volume ($\mu=\frac{1}{2}$) during compression or tension testing, the Young modulus would be 3 times the shear modulus ($E = 3G$) and the bulk modulus would be infinite ($K=\infty$). If the volume decreases during compression μ is smaller than $\frac{1}{2}$.

In analogy to the Poisson ratio, a Trouton ratio can be defined, which describes the ratio between elongational viscosity (η^*_E) and shear viscosity (η^*) (Reiner,1971)

$$\eta^*_E = Tr\ \eta^* \qquad (2.51)$$

For Newtonian fluids Tr is three. For visco-elastic materials Tr normally is higher than three and depends on the strain rate. Especially for polymer solutions very high values for the Trouton ratio can be found (10^3-10^4), which implies that the resistance against deformation in elongation is much higher than in shear. The Poisson as well as the Trouton ratio thus can tell you something about the material behaviour in deformation.

In the first part of this section (2.4.2.1) we will compare the moduli in shear and in compression and try to calculate the Poisson ratio. In the second part (2.4.2.2) we will compare the shear and compression viscosities.

2.4.2.1 The modulus in compression and in shear

To determine the Poisson ratio for cheese we did a few experiments on standard Gouda cheese of 2 and 4 weeks old :

- comparison of the shear and compression modulus from creep measurements;
- comparison of the shear modulus (G^*) found in dynamic experiments with the compression modulus (E) for compression at different strain rates;
- estimation of the volume reduction during compression by measuring photographic pictures made of the specimen at different strains.

In table 2.7 the results for the compression and shear modulus found with creep measurements are shown. The ratio E to G does not significantly differ from 3. In figure 2.35 the results for the moduli of Overload Dynamics compression tests and of dynamic shear tests are shown. From these results it can also be concluded that

Table 2.7 Shear and compression modulus from creep experiments of a standard Gouda cheese. T=20°C.

	G ($N\ m^{-2}$)	E ($N\ m^{-2}$)	E/G
2 weeks old			
mean value	$5.36 \cdot 10^4$	$1.42 \cdot 10^5$	2.65
st. dev.	$1.57 \cdot 10^4$	$0.11 \cdot 10^5$	
(number of exp.)	(7)	(6)	
4 weeks old			
mean value	$7.99 \cdot 10^4$	$2.15 \cdot 10^5$	2.69
st. dev.	$0.61 \cdot 10^4$	$0.31 \cdot 10^5$	
(number of exp.)	(7)	(6)	
4 weeks/ 2 weeks	1.49	1.51	

the ratio E to G does not differ much from 3 and certainly is not much lower than 3.

We estimated the volume reduction by measuring the exact size of samples on pictures of compression tests. Up to fracture (ϵ_f=1.10) we found (results not shown) a decrease in volume between 5.6 and 13.6%, with a mean value of 9.6%. A volume reduction

Fig. 2.35 Compression modulus (E,X) and shear modulus (G^*,●) for a 4 weeks old standard Gouda cheese at different time-scales.

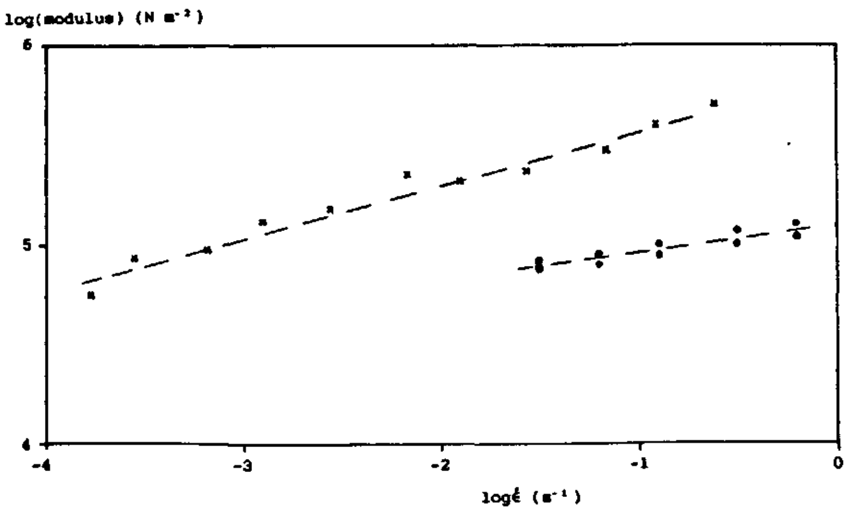


Table 2.8 The Poisson and E-G ratio for different volume reductions.

volume reduction (%)	μ (-)	E/G (-)
5.6	0.475	2.95
mean value = 9.6	0.456	2.91
13.6	0.438	2.88

of 9% has earlier been found for cheese by Calzada and Peleg (1978). The consequence of this for the Poisson ratio and the E to G ratio is shown in table 2.8.

From the results in this section it can be concluded that there is a small change in volume during the compression of Gouda cheese, i.e. up to about 9% at fracture. The ratio between E and G therefore is somewhat lower than 3, but a difference between E/G and 3 can not be established significantly by measuring the moduli because of the large scatter in the results.

2.4.2.2 The apparent viscosity in compression and in shear

To determine the Trouton ratio for cheese we compared the shear and the elongational viscosities found for the same cheese.
The slope of the creep curve was determined for various strains and from this $\dot{\epsilon}$ (or $\dot{\gamma}$) could be calculated. The apparent viscosity was calculated as the ratio between stress and strain rate. For measurements of η^*_E from uniaxial compression tests with the Overload Dynamics we calculated the stress (= force/contact area) and the tension strain rate for different strain rates. η^*_E then equals $\sigma/\dot{\epsilon}_t$ (Chatraei et al., 1981). The results for η^*_E as a function of $\dot{\epsilon}$ for different strains are shown in figure 2.36.

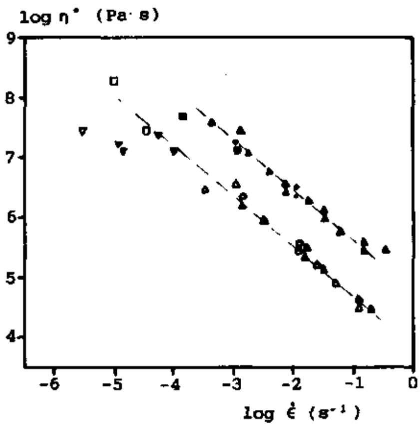


Fig. 2.36 Apparent elongational viscosity as a function of the strain rate for a 2 weeks old Gouda cheese. Measurements were made in compression (Δ,▲) or in tension (○,●) with the Overload Dynamics and in creep measurements in compression (□,■) and in shear (▽,▼), at a strain of 0.02 (open symbols) and 0.25 (closed symbols).

From these results it can be concluded that the apparent viscosity depends on the strain, the strain rate and the kind of deformation.

At small strain, part of the deformation is elastic. This results in lower apparent viscosities than at higher strains, which is virtually only an artefact. If the strain is high enough for failure and fracture to occur, η^*_E will increase little with further increasing strain.

Gouda cheese appears to be a shear thinning material: the apparent viscosity markedly decreased with increasing strain rate. We will discuss this further in chapter 3.2.1.

η^* found for shear experiments was indeed lower than that found for compression and tension experiments. Because we only did a few experiments it is not possible to calculate the exact ratio η^*_E/η^*. We can estimate the Trouton ratio to be about 3. Its value certainly is not much higher as can be found for several polymer solutions (Ferry, 1970). This implies that the network in cheese is a particulate network as also has been found for acid and rennet milk gels (Roefs, 1986; Zoon, 1988).

2.5 Evaluation of the methods used

For studying the rheological and fracture behaviour of materials like Gouda cheese, several methods can be used. Some of these have been discussed in the previous sections. Although the experimental results for the stress-strain curves did not depend on the method used, the information about the material did depend on the method.

Fracture behaviour is best studied with a bending or a tension test, because the start of fracture and the way it propagates can be noticed very well. With both these methods it is also possible to study the influence of *inhomogeneities* in the material. Fundamental information about a soft or deformable material can not easily be obtained by a bending method, because the calculations for stress and strain are only valid for small deformations. Bending tests, however, are much easier to perform than tension tests, because the test-piece does not have to be gripped. For fracture testing of (food) materials we therefore would advise a bending test for hard and brittle materials (like chocolate) and a tension test for softer and more deformable materials (like meat and cheese).

However, practically, tension testing of food materials is most times difficult to perform. The test-piece has to be quite large, which implies more inhomogeneities, and is difficult to grip. Therefore compression tests are often used for these materials. Some of the disadvantages of this method are that the start of fracture can not always be noticed and that the actual strain and stress inside the material are difficult to calculate (due to bulging, friction etc.).However, due to the ease of performing the experiments, the smaller size of the test-pieces and the smaller influence of inhomogeneities, the scatter in the results is smaller than with tension tests.

2.6 Summary

In this chapter various methods for measuring rheological and fracture properties of Gouda type cheese are described. It was shown that the rheological and fracture parameters measured, hardly depended on the type of measurement (nature of test, kind of deformation) and may therefore be considered as (almost) real material properties. Compression, tension and bending experiments gave the same results for the Young modulus and comparable results for the fracture stress, but not for the strain at fracture. The reason for this presumably is differences in the local triaxial strain for the same overall strain. The moduli determined in shear or in compression (and tension) were similar, except for the theoretical factor of about 3. The Poisson ratio of cheese is about 0.45; the Trouton ratio does not significantly differ from 3.

These results imply that it is possible to compare the rheological and fracture properties of different cheese by performing one or more of the experiments described. It is also possible to use the found parameters to calculate flow and to predict fracture phenomena occurring in the cheese, for example during hole formation (eyes or slits).

3. VISCO-ELASTIC AND FRACTURE PROPERTIES OF GOUDA CHEESE

The consistency of cheese is a very important property. It affects quality aspects like

- eating quality
- usage properties, for example ease of cutting, grating, spreading
- handling properties, for example shape retention
- ease of curd fusion and rind formation
- hole formation

If we want to study these phenomena we actually need to know the material properties of cheese related to these aspects. These properties include the rheological properties, which describe the deformability, as well as the fracture behaviour, i.e. why and how a material fractures and under what conditions.
In chapter 2 we showed that it is possible to measure material properties of cheese. In this chapter (in section 3.1) the theory of section 2.1 will be extended. After a description of the rheological and fracture behaviour of Gouda cheese (section 3.2) it will be shown that flow properties are important for the behaviour of this cheese, not only for small deformations but also if fracture occurs.

3.1 Fracture of visco-elastic materials, theoretical considerations

The basic theory for studying fracture properties of materials is known as linear elastic fracture mechanics (LEFM). The basic assumption for this theory, worked out in section 3.1.1, is that all deformation energy is stored in the material and can be used to fracture it. The only irreversible work done is that to fracture the specimen.

For visco-elastic materials, however, part of the deformation energy is not stored but dissipated due to flow (see section

3.1.2). This means that other theories taking into account this loss of energy must be used. At present no theory for combined flow and fracture is available, some lines of attack are discussed in section 3.1.3.

3.1.1 LEFM

As was stated in section 2.1.2 a material fractures when a crack, slit or other kind of defect grows and new surfaces are formed. The fracture starts (initiates) if the (local) stress is higher than the adhesive or cohesive forces in the material. It propagates if the amount of deformation energy that is released when a material fractures (because of the release of elastic strain), is at least equal to the energy needed to create the new surfaces.

Fracture initiation

Near defects, slits or inhomogeneities the local stress mostly is higher than the overall stress in the material. Therefore the maximum stress that a material can sustain is first reached near defects etc. The extent to which the stress right at the crack tip (σ) is higher than the average stress in the cracked specimen far away from the crack (σ_0), is designated as the stress concentration factor. In section 2.1.2 the Inglis concentration factor was given for an elliptical through thickness crack in a large plate with crack length l and with a tip radius r (see figure 2.1), normal to the applied stress or deformation in a linear elastic isotropic material. The stress at the tip of the crack according to Inglis is

$$\sigma = \sigma_0(1+2\surd(l/r)) \qquad (2.1)$$

Besides the fact that materials are often not linear elastic up to the point of fracture, the disadvantage of this concentration factor is that it describes only the stress in one point of the sample. No indication is given of the manner in which the locally

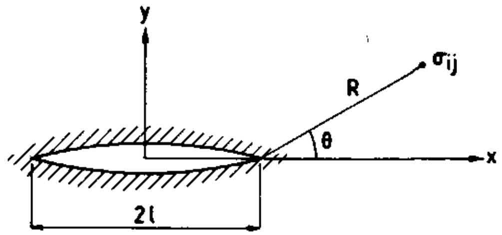


Fig. 3.1 Stresses at a point ahead of the crack tip (from Ewalds and Wanhill, 1984). For explanation see text.

high stress falls off to the stress in regions that are essentially undisturbed by the presence of the defect. To take this into account, Irwin developed the stress intensity factor K, which gives the magnitude of the elastic stress field in the vicinity of a crack tip. The stress at a certain place near the crack tip σ_{ij} (figure 3.1, Ewalds and Wanhill,1984) then is:

$$\sigma_{ij} = \frac{K}{\sqrt{(2\pi R)}} f_{ij}(\theta) \qquad (3.1)$$

where $f_{ij}(\theta)$ determines the place coordinates with respect to the crack tip. Equation 3.1 applies only to isotropic, homogeneous, linear elastic materials at small deformations. At fracture the stress intensity factor K reaches a critical value K_c. Its value depends on the material and the circumstances.
In LEFM formula 3.1 is mostly rewritten to (e.g Atkins and Mai, 1985)

$$K_c = \sigma_o \sqrt{(\pi l)} Y \qquad (3.2)$$

for which σ_o is the overall stress at fracture, Y is a dimensionless geometrical function depending on crack and specimen geometry. Values for Y can be found in several handbooks. As can be seen K_c is not equal to the stress concentration. The advantage of it is that it can be measured and used for several specimen geometries, and not only for a large plate with a through-thickness crack normal to the applied stress.

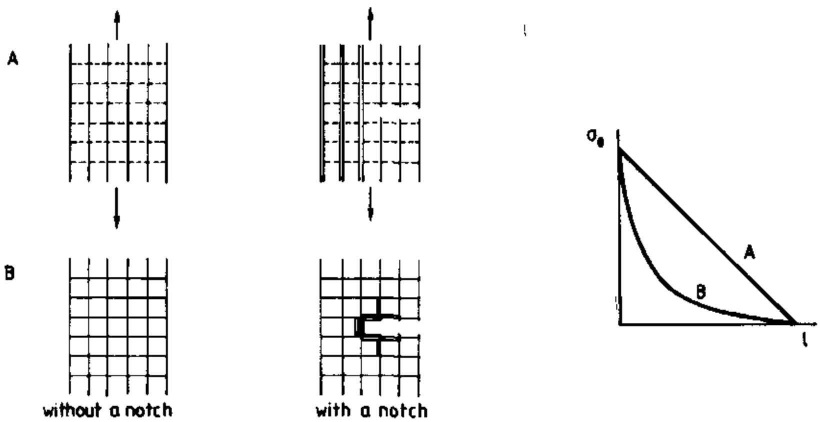


Fig. 3.2 Notch-sensitivity of different materials and the overall stress-notch length curves of these materials.
A. Material with less or no mechanical connections between the elements.
B. Material with shear connection between the elements.

Both for the stress concentration and the stress intensity approach, it can be deduced that the overall stress at fracture (σ_0) decreases with increasing crack length (l). To what extent an irregularity determines the amount of stress concentration depends on the shape of the inhomogeneity, as can be seen most clearly in the Inglis concentration factor ($1+2\sqrt{(l/r)}$), and on the extent of mechanical connections between the structural elements of the material. For instance, by assuming a material to consist of rows (strands) of elements (figure 3.2) one can imagine that, if there is little mechanical connection between these, individual ones may break without greatly influencing the stress acting on other rows of elements (figure 3.2A). The stress concentration equals the width of the sample (w) divided by (w-l) (figure 3.2c): the material is notch-insensitive. On the other hand, if there is strong mechanical connection preventing shear between the rows, fracture of one row of elements greatly influences the stress acting on the other elements and energy released by the fracture of one element can be transmitted to other elements, which, consequently, may break more easy (figure 3.2B). Then the overall stress at fracture is lower than based on the reduction of area alone (figure 3.2). The material is called notch-sensitive. The Inglis and Irwin formulas both apply to isotropic,

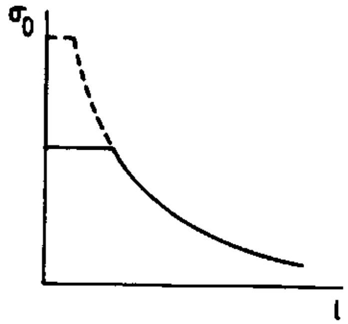


Fig. 3.3 Notch-sensitivity curves for 2 structures made of the same material. Structure 1 (——) has larger defects than structure 2 (---).

homogeneous and notch-sensitive materials. The extent of decrease of the overall stress at fracture with increasing notch length determines the notch-sensitivity of a material.

Therefore the properties of a material determining its mechanical strength can be distinguished on two levels:

1. on a molecular scale these properties are determined by the kind of material (for example the number and strength of the inter-atomic or molecular bonds) and the possibility of energy transport within the material (determining the notch-sensitivity).
2. on a larger scale these properties are determined by the number and shape of the inhomogeneities or defects in the material and, again, the possibility of energy transport (for example the connection between individual rows of elements can vary).

Both factors determine the extent of stress concentration. Test-pieces made of the same material but with different sized defects in it, thus have different strengths, as is illustrated in figure 3.3 (e.g. Birchall, 1981).

Fracture propagation

Initiation of fracture is determined by the local stress as pointed out above. The speed of crack growth, and even the question whether the material fractures spontaneously, is determined by the energy. To fracture something, bonds must be broken and for this energy is needed. By deforming an elastic material, energy

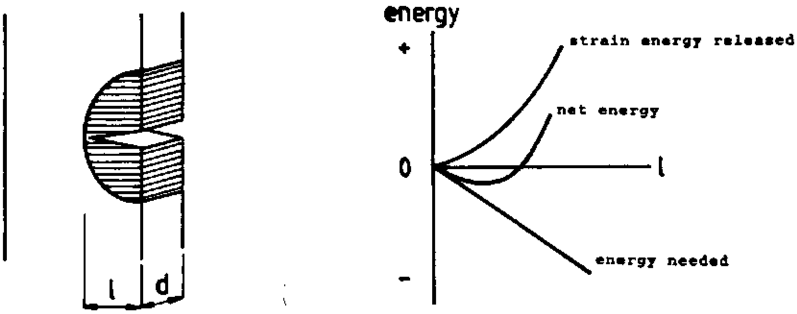


Fig. 3.4 A. Relaxed volume of material around a crack.
B. Fracture energy needed and amount of stored energy available for crack growth as a function of crack length.

is stored in it. When something fractures, the stress in the material just around the crack can relax and the stored deformation energy is released. This energy then can be used for further fracturing if it can be transported to the tip of the crack. Fracture now is spontaneous if the (differential) energy released during crack growth is at least equal to the (differential) fracture energy required (figure 3.4; Griffith, 1920; Gordon, 1978). Consider a large plate of thickness d of a homogeneous, notch-sensitive material, which is deformed, containing an elliptical crack of length l growing to a length l+δl; now the relaxed volume around the crack grows to (Griffith, 1920)

$$\tfrac{1}{2}\pi d(l+\delta l)^2 \qquad (3.3)$$

Then the released strain energy is

$$W'\ \tfrac{1}{2}\pi d\ ((l+\delta l)^2-l^2) \qquad (3.4)$$

for which W' is the stored deformation energy per unit volume. This energy is used to fracture an area of $d\cdot\delta l$ m^2. If the energy needed for fracture is R_s (the specific fracture energy in J m^{-2}), fracture propagates if

$$W'\ \tfrac{1}{2}\pi d\ ((l+\delta l)^2-l^2) \geq R_s\ d\ \delta l \qquad (3.5)$$

The lower limit for spontaneous crack growth is

$$R_s = \pi l W' \qquad (3.6)$$

For elastic materials the stored energy W' equals

$$W' = \int \sigma\epsilon \, d\epsilon \qquad (3.7)$$

for linear, elastic materials this is $\frac{1}{2} \cdot \sigma_f \cdot \epsilon_f$ and the specific fracture energy R_s is

$$R_s = \frac{\pi \sigma_f^2 l}{2E} \qquad (3.8)$$

The disadvantages of this approach are

- Actually the strain energy is not evenly distributed throughout the sample. Near the crack, besides the stress, also the strain energy is higher.
- For non-elastic materials, part of the energy is dissipated in other ways than by fracture. This will be discussed below and in 3.1.3.

Because R_s and E are material constants, the fracture stress σ_f is proportional to $l^{-1/2}$, in accordance with the stress intensity formula 3.2. A curve which shows the stress necessary for crack propagation as a function of the crack length at propagation is therefore similar to the crack initiation line. An example is shown in figure 3.5 (e.g. Ewalds and Wanhill, 1984). The difference between the initiation and propagation lines (and thus the region of slow crack growth) depends on the material tested.

The energy needed to produce a fracture of one unit area (i.e. two units of new surface area) is called the specific fracture energy (R_s in J m^{-2}) of a material. To achieve a deformation, however, additional energy is needed: part of the stored energy is not used for fracture and part of the energy can be dissipated

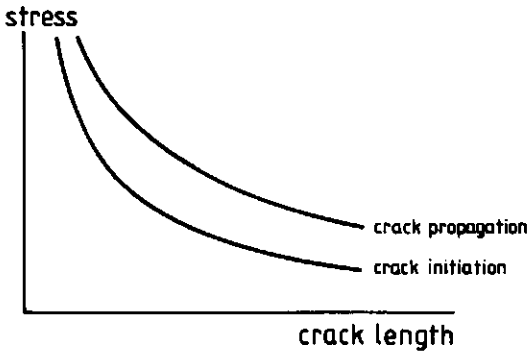


Fig. 3.5 Overall stress at crack initiation and propagation as a function of the crack length.

due to flow. The total energy which has to be supplied to a material to produce a fracture of one unit area is called the toughness R (in J m^{-2}). Its magnitude depends on:

- The energy needed to increase the surface. This is in principal the Gibbs surface energy ($\gamma_s \Delta A$; Chan et al., 1987). This term becomes more complicated if the Gibbs surface energy depends on time and/or on the orientation of the fracture surface in respect to the material structure (as for example in a crystal).
- The amount of stored energy not used for fracture. This depends on the geometry of the test-piece and the crack. By using formula 3.5 this energy is not taken into account.
- The exact size of the fractured surface (Andrews, 1980). The surface can be rough and more material can be fractured than just in the surface layer of the crack (e.g. because of side cracks).
- The amount of dissipated energy not due to fracture. This can be caused by flow of the material giving irreversible deformation (fractured pieces do not fit together; Atkins and Mai, 1985) or by friction because elements of the material are pulled out during fracture (e.g. with a fibrous material; Atkins and Mai, 1985).

If a material has a relatively high yield stress (i.e. not much lower than the fracture stress at the time scale applied and higher than the overall stress far away from the crack), flow of the matrix is limited to the volume of the material just around the crack, and fracture parameters, like R_s, can be estimated using linear elastic fracture mechanics (LEFM) or elastic-plastic fracture mechanics (EPFM). LEFM may be applied if the size of the zone where flow of the matrix occurs is negligible compared to the size of the crack. EPFM may be applied if the depth of the zone where flow occurs is of about the same size as the radius of the crack tip and is small compared to the size of the specimen (<10%; Atkins and Mai, 1985). If the yield stress is much lower than the fracture stress and not higher than the overall stress far away from the crack, energy dissipation due to flow of the matrix occurs throughout the complete material. Besides flow of the matrix, energy dissipation can occur throughout the complete material caused by movement of material relative to each other, for example flow of liquid through the matrix. Different approaches to estimate fracture parameters for materials in which energy is dissipated with deformation will be discussed in section 3.1.3.

All these influences on the toughness causes this property to be very dependent on the nature of the material. For example, for the toughness of glass about 1-10 J m^{-2} has been found and for steel 10^4-10^6 J m^{-2}, while the fracture stress differ less (30-170 and 3000 MN m^{-2}, respectively) (Gordon, 1968). The (theoretical) energy needed to break all chemical bonds in one plane can be estimated from the Helmholtz energy needed to break covalent bonds. Assuming this energy to be 500 kJ mol^{-1} and the distance between adjacent bonds to be 1 nm, about 1 J is needed to fracture an area of 1 m^2. This indeed has been measured for glass.

The specific fracture energy (R_s) can be estimated from force-distance relations as obtained in:

- tensile experiments with a notch in the sample. For calculation of R_s formula 3.6 can be used.
- controlled crack growth (Atkins and Mai, 1985).
- cutting of the material with a wire or a knife (Atkins and Vincent, 1984).

With all these methods, the energy needed for a certain growth of new surface by fracture may be calculated. In practice, however, the calculated values of R and R_s depend on the method used, mostly because the material is not ideal elastic (Atkins and Mai, 1985) or because the depth of disturbance varies (Andrews, 1980; Green et al.,1986).

3.1.2 Visco-elastic behaviour

A material is visco-elastic when part of the strain energy is stored in the material (elastic part) and part is dissipated (viscous part) (see chapter 2). This last process takes time and the consequence is that the material behaviour is time dependent. Moreover the deformations are lasting.

The energy dissipation may be caused by various mechanism depending on the type of material being tested (e.g. flow of matrix material, flow of liquid through the matrix, movement of elements of material relative to each other causing friction etc.).

Cheese can be conceived as a continuous matrix of a swollen protein mass, interspersed with fat globules. The protein mass, in turn, consists of small proteinaceous particles held together by various binding forces into a network throughout the cheese moisture (Walstra and van Vliet, 1982). The fact that cheese is a "time dependent material" has been mentioned by several workers (e.g. Mulder, 1946; Dickinson and Goulding,1980; Creamer and Olson,1982), but little is known about the kind of bonds that cause this behaviour.

For acid milk gels (Roefs,1986) the viscous behaviour at small deformations can be mainly ascribed to the formation and breaking of protein-protein bonds. There may be some effect of liquid movement along and in and out of the strands and conglomerates. Water-water bonds need not be taken into account, because of their very short life-time of 10^{-13} s. Zoon (1988) showed for rennet milk gels that both the deformation and the stress at fracture depended on the time scale. The visco-elastic behaviour in the linear region of these gels depended on van der Waals forces, electrostatic (i.e. calcium-phosphate) forces and hydrophobic interaction; i.e. on flow of the protein matrix.

Several factors, such as pH and salt content, have an effect on the rheological behaviour of cheese that can best be explained by a change in protein behaviour (see chapter 4). Protein breakdown also affects cheese consistency, especially the integrity of the α_{s1}-casein seems to be important (de Jong, 1976; Creamer and Olson, 1982). Therefore we feel that protein-protein bonds are essential for the visco-elastic behaviour of cheese (chapters 4 and 5). Masi and Addeo (1984) supposed that the breaking and reformation of salt and H-bridges in Mozzarella cheese were important for the visco-elastic behaviour, because this behaviour was not affected by the fat and/or water content. We found that cheeses with a higher water content can be more viscous-like (higher tan δ, see section 4.3.2). There is a kind of transition point and water possibly acts as a plasticizer. Because the water content of Mozzarella is high and Masi and Addeo could not find an effect of water content on the viscous behaviour, it may have been beyond the transition point. We will discuss this further in section 4.3.2.

Not only the behaviour of the protein network in cheese determines the energy dissipation process, but also the movement of liquid through this network could be important. We will discuss this further in section 6.1. Besides, friction between such structural elements as fat globules and the protein matrix may play a part.

The visco-elastic character of a material influences its rheological behaviour in several ways (see section 2.1.1):

- The force or stress needed for a certain strain decreases with decreasing strain rate. This results in smaller values for E, G, and G' for smaller strain rates (longer times).
- The amount of stored strain energy per unit of volume decreases with decreasing strain rate.
- Part of the deformation is lasting, i.e. is not recovered when removing the stress.

3.1.3 Influence of flow on fracture

Because the visco-elasticity of a material largely determines the amount of stored strain energy at a certain ϵ and $\dot{\epsilon}$, the visco-elastic behaviour is important for the fracture properties of this material.

For limited flow the fracture parameters can be estimated using elastic-plastic fracture mechanics (EPFM). In this theory one supposes the flow to be limited to small areas just around the crack tip (see section 2.1.2), because only in these areas the yield stress of the material is reached and the material flows. The elastic (part of the) energy then can be measured or estimated. In Gouda cheese, however, no yield stress can be detected (Mulder, 1946) and flow takes place throughout the stressed body. At present no theory for combined flow and fracture is available, but certain lines of attack are possible (Atkins and Mai, 1985) and will be discussed in this section.

The deformation energy that is put in a material can be used for energy storage (elastic), dissipation (flow and friction) and fracture. An energy summation can be made (Atkins and Mai, 1985)

$$W = W' + W'' + W_f \qquad (3.9)$$

W = total energy input
W' = stored energy
W'' = dissipated energy not due to fracture
W_f = energy used for fracture

The problem with combined flow and fracture is the measurement of the energy used to fracture the material. It can be estimated in a number of ways.

- For purely elastic materials W" is zero. The fracture energy can be calculated using formula 3.6 and 3.7.

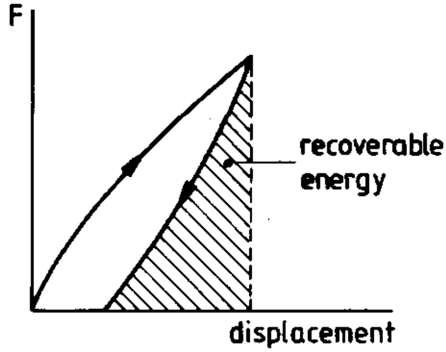


Fig. 3.6 Force-displacement curve for loading and unloading of a test-piece.

- With loading and unloading experiments the change in stored energy can be measured. Then for example, W' can be determined by a graphical method when loading and unloading the sample to different strains. The area under the "unloading" branch of the stress strain curve represents the recoverable energy W'. The difference between the loading and the unloading lines is the dissipated energy, due to flow as well as fracture (figure 3.6). The specific work of fracture then is the release in stored energy with increasing crack length:

$$R_s = \frac{\delta W'}{\delta a} \qquad (3.10)$$

In this way direct use is made of the energy definition of R_s. It is therefore still used as a reference to check the magnitude of R_s found by other methods. The problem is, that this method is difficult to use if there is also energy dissipation during the unloading process; or if the elastic recovery is slower than the unloading process.

- The experiments can be performed in such a way that the amount of stored and flow energy is limited. For instance by tearing or cutting a sample (figure 3.7, Atkins and Vincent, 1984) only some material close to the new formed surfaces is disturbed.

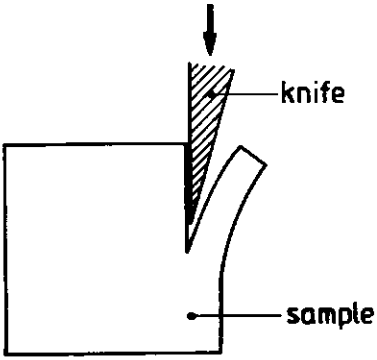


Fig. 3.7 Cutting of a test-piece.

$$W = W' + W'' + W_f + \text{slice curling energy} \qquad (3.11)$$

The energy used for curling of the cut-off slices can be estimated by extrapolation to zero slice thickness. The energy used for deformation of the volume of material directly around the wire can be estimated by extrapolation to zero wire thickness.

The exact effect of circumstances or composition on the W_f can not be measured directly, because the influence can be different for the various types of energy. For example, the effect of temperature on flow does not have to be the same as on the fracture energy.

Flow also influences the fracture stress of a material more directly. Near a defect the local stress is higher. This also means that there are local differences in flow and energy dissipation which affects the actual stress at the crack tip (the stress concentration is probably less, because of flow), as well as the shape of the crack tip (the tip blunts). Both these effects decrease the stress concentration effect of the inhomogeneities and increase the overall stress needed for fracture. This means that a material which exhibits some flow during fracture, will be less notch-sensitive.

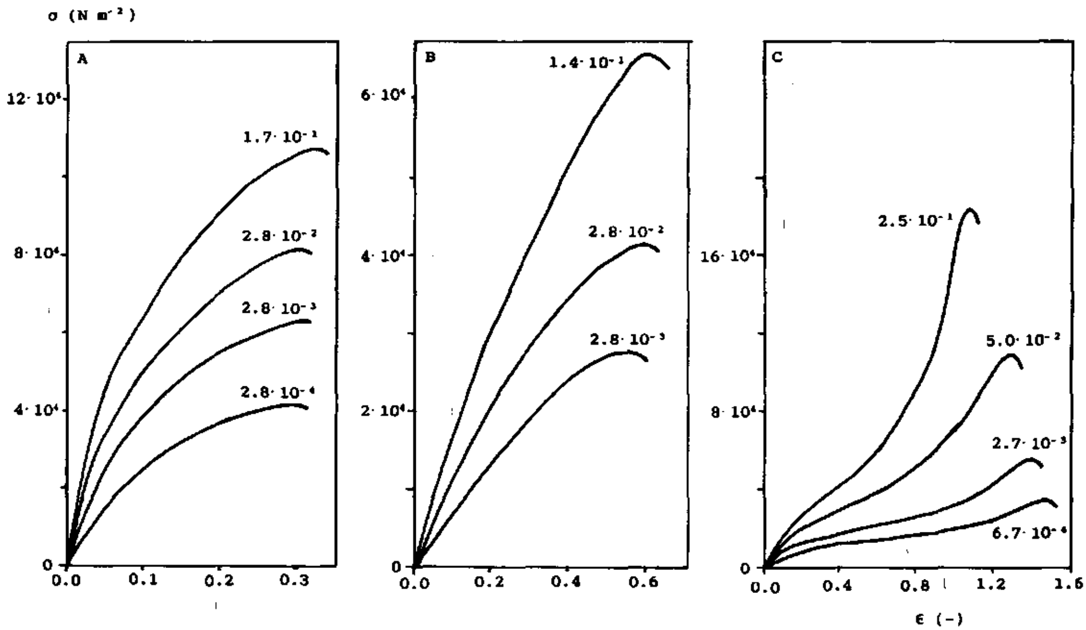


Fig. 3.8 Compression curves for 3 different cheeses measured at different strain rates.
A. 9 month old standard Gouda cheese.
B. 1 week old cheese of low pH (4.94).
C. 2 weeks old cheese of normal pH (5.24).

3.2 Results and discussion

The experimental methods are described in section 2.3.

3.2.1 The influence of the strain rate on the rheological behaviour

Gouda cheese is a visco-elastic material. We found that we can discriminate between two different types of visco-elastic behavior. The type that is found for all cheese older than about 4-6 weeks and for all cheese (irrespective of age) with a low pH will be discussed first. Cheese that is both young and not acid, behaved differently, this will be discussed in the final part of this section. Examples of the influence of strain rate on the stress-strain curves of a mature and a young cheese with a low pH can be seen in figures 3.8A and B. The stress needed to compress a sample is given for various strain rates. Curves like these

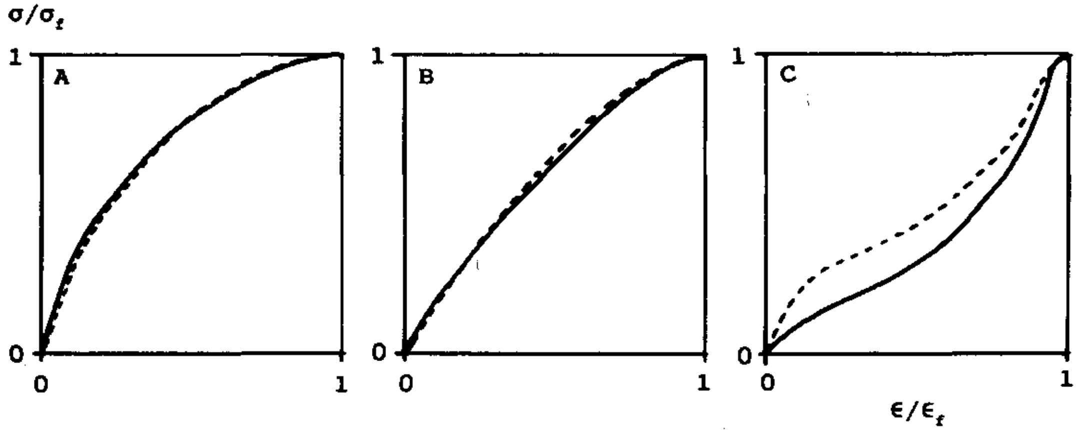
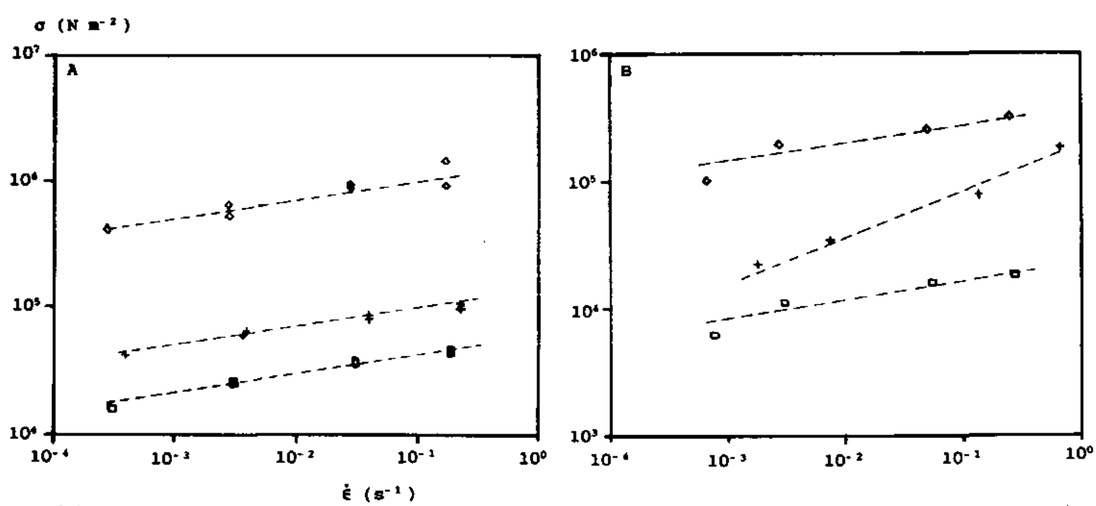


Fig. 3.9 Shape of the compression curves of the same cheese as in figure 3.8 at a strain rate of about 10^{-1} s^{-1} (—) and 10^{-3} s^{-1} (- - -).

were found in compression as well as in tension. With increasing strain rate, the stress needed to reach a certain strain increased. The fracture strain was mostly not dependent on the rate. The shape of the stress strain curve also did not depend on the strain rate as can be seen in figure 3.9A and B. Thus the effect of the rate for these cheeses was independent of the strain and was similar for E, $\sigma(\epsilon)$ and σ_f (figure 3.10). In figure 2.35 it can be seen that the effect of rate on the shear modulus in the

Fig. 3.10 Influence of strain rate on $\sigma(\epsilon=0.10$,□ (A)), $\sigma(\epsilon=1.0$,+ (A)), σ_f (+ (B)) and E (◇ (B)) for a 9 month old cheese (A: same as in figure 3.8A) and a 2 weeks old cheese (B: same as in figure 3.8C).



linear region is also similar. This means that the energy dissipation processes depend on relaxation processes on a molecular scale. The slope of the $\log\sigma(\epsilon)$-$\log\dot{\epsilon}$ curve (n) (figure 3.10A) was calculated for several cheeses and kinds of deformation and found to be 0.15 - 0.20, with a mean value of 0.17.

A similar rate dependence can be found for other types of rheological experiments:

- the apparent viscosity of cheese decreased with increasing strain rate, as can be seen in figures 2.34 and 2.36, with data of different creep experiments as well as of compression tests at constant deformation rate. The slope of the $\log \eta^*$-$\log \dot{\epsilon}$ curve was (-0.80)-(-0.85), in accordance with the results of figure 3.10, because

$$\log \sigma = \text{const} + n \log \dot{\epsilon} \qquad (3.12)$$

and

$$\eta^* = \frac{\sigma}{\dot{\epsilon}} \qquad (2.8)$$

or

$$\log \eta^* = \log \sigma - \log \dot{\epsilon}$$

gives

$$\log \eta^* = \text{const} + (n-1)\log \dot{\epsilon} \qquad (3.13)$$

- In relaxation experiments, the stress needed for a certain deformation decreased with time as can be seen in figure 3.11. The slope of this line (measured for only one cheese) is about -0.20, again in accordance with the other experiments. The still continuing and possibly even relatively faster decrease of the stress with time at large t, implies that the material has no or only a very small yield stress (Blom et al., 1986).

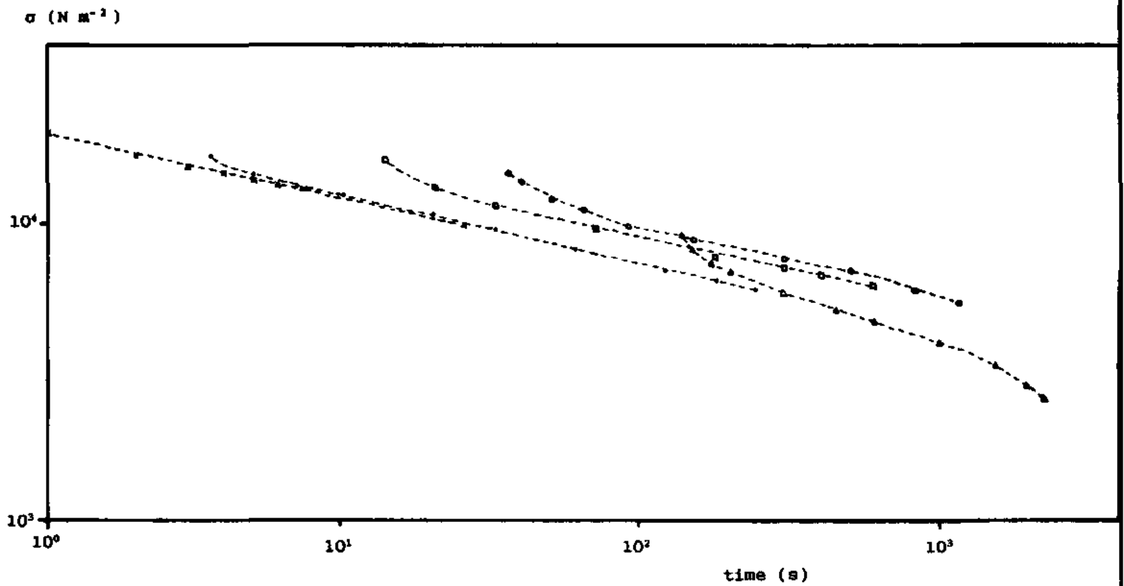


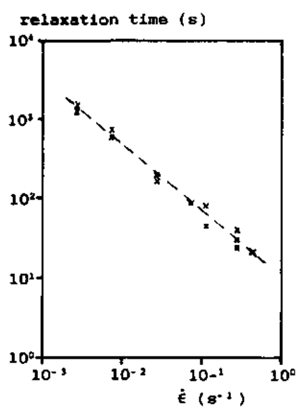
Fig. 3.11 Stress (σ) during relaxation of a young Gouda cheese. A strain of 0.10 was reached for different compression rates. $\dot{\varepsilon}=2.8 \cdot 10^{-1} s^{-1}$(X):$2.8 \cdot 10^{-2} s^{-1}$(•);$7.2 \cdot 10^{-3} s^{-1}$(□):$2.8 \cdot 10^{-3} s^{-1}$(O):$7.2 \cdot 10^{-4} s^{-1}$(Δ);t=time after start of compression.

The same behaviour has been found for rennet milk gels (Zoon, 1988).

- The apparent relaxation time decreased with increasing deformation rate at which a certain deformation was reached. Again, this effect agrees well with the other results for the effect of rate (see figure 3.12).

The decrease of stress and energy needed for a certain deforma-

Fig. 3.12 Apparent relaxation times for a young Gouda cheese as a function of the compression rate. Same cheese as in figure 3.11.



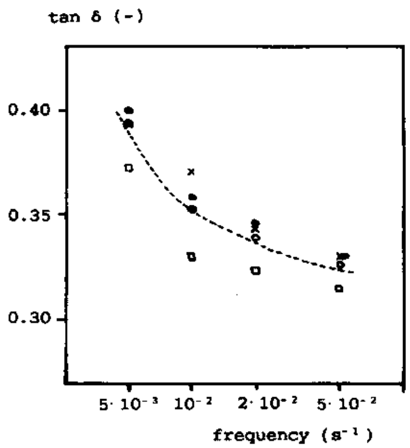
tion with decreasing strain rate is possibly caused by two factors. Owing to the breaking and reforming of matrix bonds (flow) the stress and the energy decrease, and owing to the slower movement of liquid through the matrix (energy dissipated per unit volume and per unit time $\equiv \eta^{*}\dot{\gamma}^{2}$) the energy needed decreases.

The slope of the $\log\sigma$ - $\log\dot{\varepsilon}$ curve (n) is a measure of the relative importance of elastic and viscous contributions in stress relaxation (van Krevelen and Hoftijzer, 1976). In a completely elastic material n is zero, in a more viscous material it is larger. It is therefore closely related to the loss angle δ in dynamic experiments. For linear visco-elastic behaviour, tan δ<1 and a constant slope of the log(modulus) - log(time scale) curve the relation between n and tan δ at the same time scale is (Booij and Thoone, 1982)

$$\tan \delta = \frac{\pi}{2} n \qquad (3.14)$$

A value for n of 0.15 - 0.20 would thus yield a loss tangent of 0.24 - 0.31. This is in fair agreement with the values for tan δ we found for different Gouda cheeses in dynamic experiments (figure 3.13, tan δ=0.31 for short time-scales). For longer time scales tan δ will become larger. An increase in tan δ is noticeable

Fig. 3.13 The loss angle tan δ as a function of the frequency for a standard Gouda cheese of different maturation time; 1 week (X); 1 month (O); 3 months (□); 6 months (●).



at shorter time scales than the accompanying change in slope of the log(modulus) - log(time scale) curve (e.g. Ferry, 1970).

For acid milk gels tested at 30°C, a tan δ of 0.25 was found (Roefs, 1986), independent of the frequency. This was in accordance with the results of the dependency of the storage or loss modulus on the frequency; the log G'(or G") - log ω curves had a constant slope of 0.15.

Differences between the calculated and the experimental values

Table 3.1 Values for n (formula 3.12) for some elastic and visco-elastic materials, calculated from the results of the fracture force or stress (or the viscosity, Dickie and Kokini,1980).

product	$\dot{\varepsilon}$ range (s^{-1})	n	reference
various food materials			
10% gelatine	$3\cdot10^{-3}$-$7\cdot10^{-2}$	0	Bagley et al. (1985)
bread	1.4-$2.8\cdot10^{-2}$	0	Verhoeven (1988)
biscuit	$3\cdot10^{-4}$-$7\cdot10^{-3}$	0	Boode (1985)
chocolate (milk)	$2\cdot10^{-3}$-$2\cdot10^{-1}$	.19	Luyten,H.,not publ.
chocolate (plain)		.14	"
whipped butter	10^{-1}-10^{2}	.06	Dickie and Kokini
whipped cream		.06	(1982)
squeeze margarine		.12	"
tub margarine		.08	"
whipped pudding		.12	"
marshmallow cream		.38	"
peanut butter		.07	"
cheese			
double Gloucester	(factor 20)	.23	Shama and Sherman (1973)
Gouda	$2\cdot10^{-2}$-$3\cdot10^{-1}$	.19	Culioli and Sherman (1976)
cream cheese	$2\cdot10^{-3}$-$5\cdot10^{-1}$	.18	Lee et al (1978)
American	"	.14	"
Cheddar	"	.22	"
Cheddar	$3\cdot10^{-3}$-$6\cdot10^{-1}$	.22	Dickinson and Goulding
Leicester	"	.21	(1980)
Cheshire	"	.14	
Cheddar	$2\cdot10^{-3}$-$4\cdot10^{-1}$	.19	Creamer and Olson (1982)
processed cheese	$2\cdot10^{-4}$-$1\cdot10^{-1}$	.15	Casiraghi et al. (1985)
Provolone	$4\cdot10^{-3}$-$2\cdot10^{-1}$	.19	Pompei et al., unpublished

for tan δ may be due to the assumptions made to calculate formula 3.14 not being fully correct for cheese or milk gels.

In table 3.1 values of n for different (food) materials as found in literature are given. Our results agree well with those found for different types of cheese by other workers.

In the beginning of this section it was mentioned that results like those in figure 3.8A and B were found for nearly all Gouda cheese investigated. An example of a different behaviour found for a young Gouda cheese with a pH between 5.2 and 5.4 is shown in figure 3.8c.

Again, with increasing strain rate, the stress needed to reach a certain strain increased. But the shape of the stress-strain curve depended on the strain rate (figure 3.9C), and was different from the one usually observed. In general, more mature or acid cheeses had a convex-shaped stress-strain curve and young not acid cheeses a more concave shape, especially at higher strain. It seems that these cheeses exhibit more flow during compression, especially at lower deformation rates. The slope of the logσ-log$\dot{\epsilon}$ line depended on the strain and was for larger strains also higher than found for type 1 cheese. This can be seen in figure 3.10B. A value for n of 0.38 at ϵ=1.0 could be calculated. A consequence is that the fracture strain clearly depended on the strain rate, as opposed to the results for the more mature or more acid cheeses. This feature will be discussed further in section 3.2.2.

The different shape of the compression curve and the rate dependent fracture strain (see figure 3.14) are very important for the consistency related properties of young Gouda cheese. This will be discussed further in chapter 5 and 6.

3.2.2 The influence of the strain rate on the fracture properties

The results given in the previous section show that for most Gouda cheese the shape of the stress-strain curve, including the

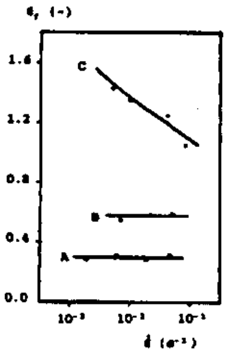


Fig. 3.14 The influence of the strain rate in compression on the fracture strain ϵ_f. Same cheese as in figure 3.8.

fracture region, did not depend on the rate of deformation. Even the fracture strain was independent. This was, however, not so for some younger cheese. To make the next discussion easier we will call the cheese that is more mature, more acid or both type 1, and the other cheese (young with a not too low pH) type 2.

The fracture strain appeared to be a kind of material property for type 1 cheese. This is corroborated by the following observations:

- If the compression was stopped temporarily at a certain strain until the stress in the sample was relaxed to a value of 1/e times the stress at the moment the deformation was stopped, the strain at fracture after proceeding compression did not change significantly, as can be seen in figures 3.15A and C. The stress at fracture, however, decreased significantly (5%) after an intermediate relaxation process (figure 3.15A and C).
- When the deformation is not stopped but a few loading and unloading cycles are performed at a strain smaller than ϵ_f, then the ultimate fracture strain is neither affected (figures 3.15B and C).

Therefore, it may be concluded, that for this type of cheese in the strain rate range tested (10^{-4}-10^{-1} s^{-1}), the strain at fracture ϵ_f is a constant and the stress at fracture σ_f depends on the strain rate and the strain history. Similar results have been

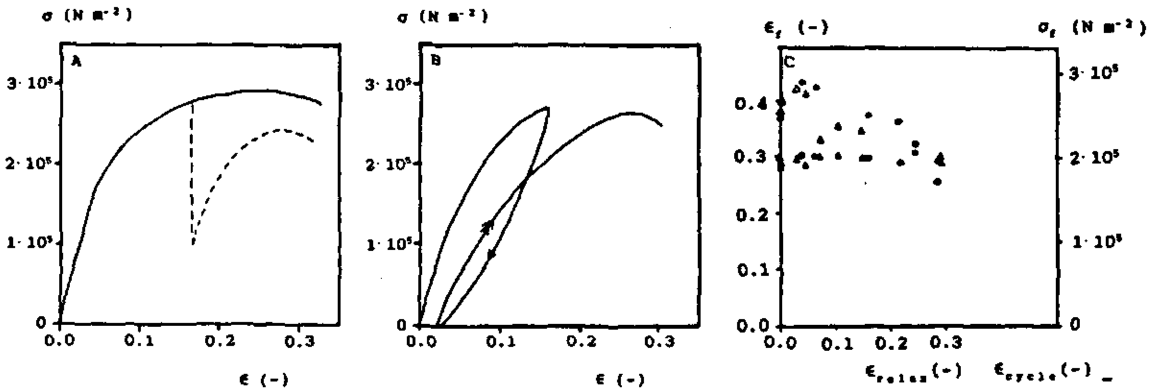


Fig. 3.15 Influence of relaxation (A: σ_f(Δ), ϵ_f(▲)) and unloading (B: σ_f(O), ϵ_f(●)) on compression curve for a 1 year old cheese. See text for explanation. Several results are summarized in fig.C.

found for Danbo cheese (Christensen and Luyten, unpublished results).

For type 2 cheese, the fracture behaviour depended on the applied time scale. The strain at fracture increased with decreasing strain rate (figure 3.8C) or with increasing relaxation before fracture (e.g. by cycling, see table 3.2). The different shape of the stress-strain curve of type 2 cheese and the change of this

Table 3.2 The influence of cycle experiments on the fracture stress and strain for a 2 weeks old standard Gouda cheese. $T = 20^\circ C$; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$. The cheese was cycled twice before it was compressed up to fracture.

ϵ_{cycle} (-)	ϵ_f (-)	σ_f (N m^{-2})
no	1.37	$8.68 \cdot 10^4$
-	1.38	8.64
-	1.35	8.21
-	1.46	7.35
-	1.58	7.83
-	1.53	8.80
-	1.52	9.08
mean	1.46	$8.37 \cdot 10^4$
st.dev.	6.2%	7.3%
0.10	1.55	$7.81 \cdot 10^4$
0.22	1.65	10.5
0.51	1.65	7.54
1.25	1.72	9.85
1.35	1.80	11.3

shape with changing strain rate point to a more pronounced flow character of this cheese. The strain rate influence indeed was higher for type 2 cheese than for type 1 cheese (see section 3.2.1). This flow possibly caused the fracture strain to be dependent on the strain rate in the strain rate range tested.

In the literature, no direct explanation for this fracture behaviour can be found. Ross-Murphy (1984) found for gelatin gels of different concentration (5-25%) that the stress and the strain at fracture increase with increasing strain rate. Qualitatively, this trend was explained by saying that the probability of rupture depended on the amount of stored elastic energy and the faster the deformation, the higher the stress that can be reached before this energy was exceeded. In our opinion, this explanation does not hold, because the amount of recoverable (stored) energy is higher for higher strain rates at the same strain (less relaxation of stress before the strain is reached).

In engineering materials it is sometimes found (Atkins and Mai, 1985) that the effect of time on the modulus and the yield stress is the same (metals, n = 0.1-0.2). Then the fracture strain is also independent of the rate of deformation.

Creamer and Olson (1982) found for Cheddar cheese no influence of the strain rate on the strain at fracture. On the other hand Dickinson and Goulding (1980) found an increasing fracture strain with increasing strain rate for Cheddar, Cheshire and Leicester cheeses. These workers did not give an explanation for their results. A possible explanation may be the difference between the observed moment of fracture and the real start of it (see section 2.4.1.3).

A possible explanation for the difference between type 1 and type 2 cheese will be given in the sections 4.5 and 6.1.

The consequence of the dependence of rheological behaviour and fracture properties on the strain rate is that experiments must be performed at the right strain rate if one wants to use the results for the explanation of certain events. For example, when using the results of rheological and fracture experiments for calculations on hole formation (eyes or slits), the tests have to be done at low strain rates, at a time scale comparable to eye formation in cheese. Only, if it has been proved that a certain aspect of the rheological and fracture behaviour is independent of the strain rate (as for example was found for the fracture strain of type 1 cheese), one may extrapolate experimental results for one strain rate to others within the tested range.

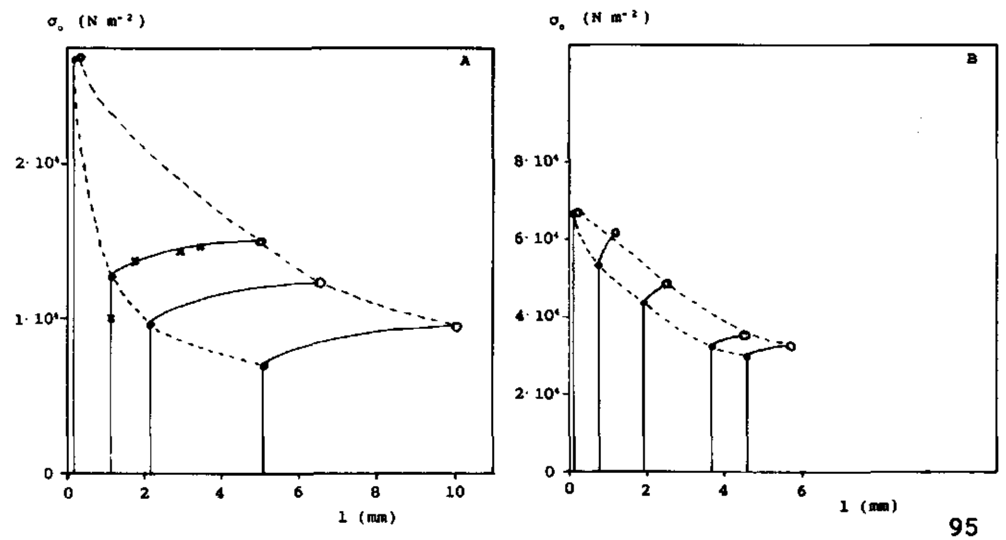
3.2.3 Notch-sensitivity and fracture initiation

Most of the experiments reported in the previous section were performed in compression. With this type of deformation it is very difficult to precisely determine the moment at which fracture starts or propagates. Therefore several other experiments (mostly tension tests) were performed to find out when cheese fractures.

Fracture initiation and propagation.

The stresses needed to initiate and to propagate fracture were determined for several aged Gouda cheeses by tension experiments with and without a notch (see section 2.3.2). In figure 3.16 some

Fig. 3.16 Overall stress(σ_o) - notch length(l) curves for a young (A) and a more mature (B) cheese. Results are given for crack initiation (●) and propagation (○). All calculated σ_o-l points for one test-piece are given as an example (X).



typical results are shown. A young cheese is notch-sensitive in crack initiation. Because of the high work of fracture for this cheese, the fracture does not immediately propagate. A more mature cheese on the other hand is less notch-sensitive, but when the fracture has started it propagates almost immediately. This faster propagation is possibly an important aspect during sensory evaluation of cheese samples: a more mature cheese appears to be more brittle.

This difference was also clear in "bite and wedge experiments" (Vincent et al., 1988). Small cubic pieces of various cheese (2 cm) were bitten with the incisors until they fractured spontaneously. With a young Gouda cheese it was necessary for the teeth to penetrate quite deep, thus putting much energy into the test-piece, before the fracture propagated. A mature cheese broke when the teeth had penetrated far less into the cube. This can be seen clearly in figure 3.17, where the remaining parts of some samples are shown. The penetration of the teeth can be seen, and it is much deeper in young Gouda than in a more mature one. For the "wedge experiments", sharp, perspex wedges (attached to the Overload Dynamics) were penetrated into cubes of cheese with a speed of 1 mm min^{-1} up to the point where the cheese fractured spontaneously and the penetration force decreased. In this way the "bite experiments" were imitated. The results of the "bite

Fig. 3.17 Remainder parts of cubes of cheese which were bitten with the teeth. A young (A), mature (B) and old (C) cheese. The arrows indicate how far the teeth had penetrate into the test-pieces.

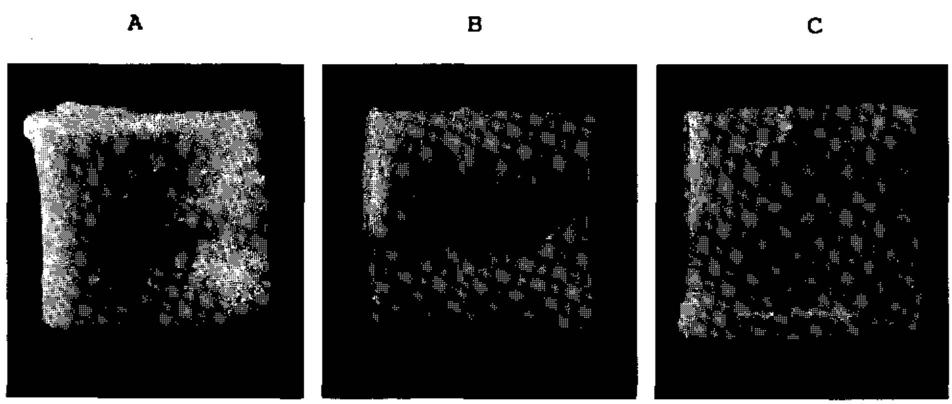


Table 3.3 Distance between teeth or wedges at start of propagated fracture for different cheese. See text for further explanation.

cheese	distance (mm)		R_s (propagation)
	teeth	wedge	($J\ m^{-2}$)
young	3.8	3.5	11.3
young + cumin	5.2		16.2
mature	9.0		1.25
old	13.2	11.5	
old + cumin	13.1	13.0	

and wedge experiments" were fully consistent as can be seen in table 3.3. The difference between initiation and propagation of fracture depends on the fracture energy and on the supply of stored energy. The latter quantity is shape dependent (Atkins and Mai, 1985), but the difference between materials will remain: fracture in mature cheese propagated sooner than in young cheese in all tested methods.

The reasons for this difference between young and more mature cheese are probably related to the protein breakdown in the cheese. We will discuss this further in chapter 5.

Notch-sensitivity.

Flow influences the notch-sensitivity of a material, as was stated in section 3.1.3. In figure 3.18 (example of experimental results) it can be seen that, for a lower strain rate the stress needed to fracture the material decreased relatively less with increasing notch length. This implies that the stress needed to fracture a test-piece, which decreases with decreasing strain rate due to the viscous properties of the material, tends to increase because of to the smaller notch-sensitivity. The effect of the strain rate measured (n) thus is the sum of these two effects.

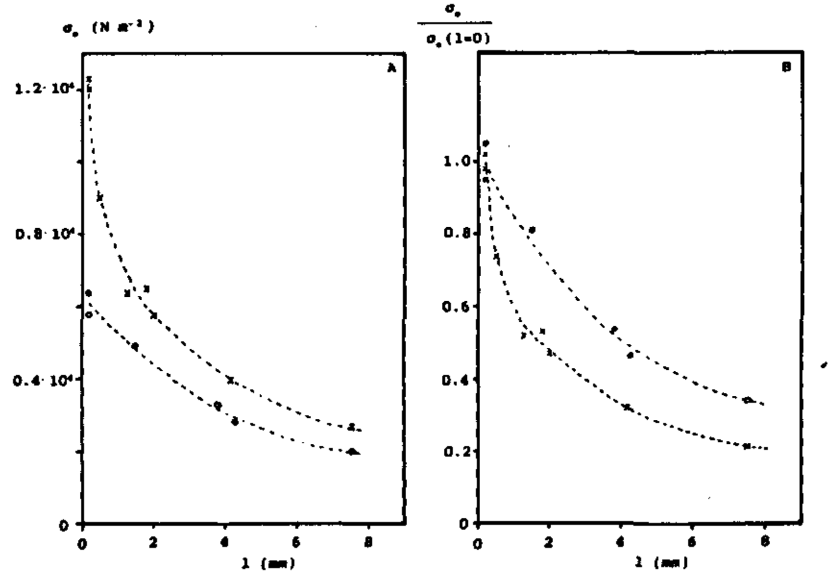
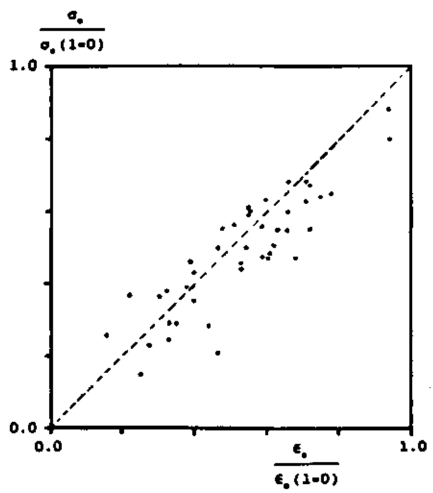


Fig. 3.18 A. Overall stress - notch length curve for a 3 weeks old standard Gouda cheese. Measured at different strain rates in tension, namely $2.8 \cdot 10^{-2} s^{-1}$ (X) and $2.8 \cdot 10^{-3} s^{-1}$ (O).
B. Same but the stress is given relative to the overall fracture stress with no notch.

Strain amplification.

A notch in a material causes a stress concentration and thereby decreases the overall stress needed to fracture the material. But it also decreases the overall strain at fracture. In figure 3.19

Fig. 3.19 Relative decrease in fracture stress (in tension) as a function of the relative decrease in fracture strain for different cheese and notch-lengths. T = 20°C; $\dot{\varepsilon}_c = 2.8 \cdot 10^{-3}$ s^{-1}.



the relative decrease in stress is shown as a function of the relative decrease in strain for different cheeses and notch lengths. For linearly elastic materials, where the ratio stress to strain is a constant ($\sigma = E \cdot \epsilon$), we would expect the stress and strain concentration to be the same. But cheese is not linearly elastic ($\sigma = E(\epsilon) \cdot \epsilon$) and the ratio stress to strain for most cheese decreases with increasing strain. Therefore we would expect the ratio σ_o to $\sigma_o(l=0)$ to be smaller than the ratio ϵ_o to $\epsilon_o(l=0)$. We indeed found this tendency (see figure 3.19), but the difference with equal stress and strain concentration was too small to be significant.

Inherent defects in Gouda cheese.

Because the fracture stress in the notch tip at a certain strain rate is a material constant, the size of the defects in the sample can be estimated from the overall stress at zero notch length, assuming a stress concentration according to formula 2.1 or 3.2. For nearly all cheese a defect length of about 0.1 - 0.3 mm could be calculated in this way. We will elaborate at this when discussing the influence of the fat content (section 4.3.3) and the fusion of the curd particles (section 5.2).

3.2.4 Fracture energy

From the tension experiments with a notch, it is also possible to estimate a value for the fracture energy (R_s) of Gouda cheese. Because cheese is a very deformable, visco-elastic material it is only possible to estimate an order of magnitude. Assuming no energy dissipation in the sample, an upper value for R_s can be calculated using the formulas 3.6 and 3.7. Some results obtained in this way are given in table 3.4. The actual value for the fracture energy is lower because the stored energy in the volume just around the crack tip is lower due to energy dissipation caused by flow of the material.

Possible methods to estimate the part of the energy that is stored (and thus available for fracture) are hysteresis experiments

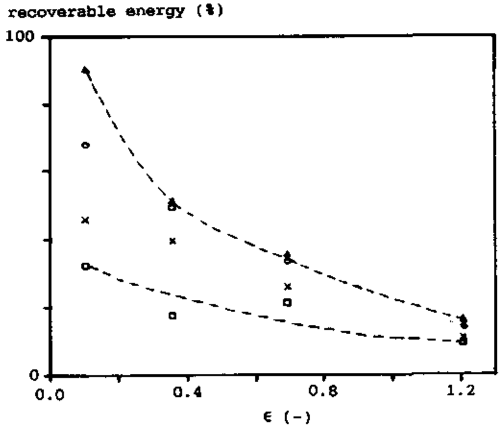
Table 3.4 Fracture energy of several Gouda cheeses (not corrected for energy dissipation). T = 20°C: $\dot{\epsilon}_c$=2.8·10^{-3} s^{-1}.

cheese and age	R_s estimated at fracture (J m^{-2}) initiation	propagation
standard cheese		
2 weeks	6.3-9.2	11.0-12.5
1 month	4.5-8.1	
2 months	2.9-7.8	
4 months	5.3-6.8	
6 months	6.6-9.1	
10 months	1.3-3.1	
12 months	0.6-3.1	0.8- 1.5
with cumin seeds		
young	6.3-6.7	16.2-16.1
mature	1.2-1.3	1.2- 1.3

(Holt and Schoorl,1983; Holt and Schoorl,1984; Atkins and Mai,1985) and dynamic experiments (Andrews, 1980).

With loading and unloading experiments the recoverable energy is represented by the area below the unloading curve in a stress strain diagram (see section 3.1.3). The hysteresis between the loading and unloading line is a measure of the energy dissipated. In figure 3.20 some results from a hysteresis experiment with a 1

Fig. 3.20 Hysteresis for different strains and strain rates. T = 20°C: 1 month old Gouda cheese. 2.8·10^{-4}s^{-1}(□);2.8·10^{-3}s^{-1}(x);2.8·10^{-2}s^{-1}(o);1.7·10^{-1}s^{-1}(Δ).



month old Gouda cheese are shown. Cylindrical samples of cheese were compressed at different rates up to a certain strain and unloaded. Each point in the figure represents a single measurement. The part of the energy that is recovered on unloading decreased with increasing strain and decreasing strain rate. Lee et al. (1978) performed cycle experiments on several cheeses and found that the ratio of the second and first loading cycle decreased with increasing strain but was independent of the strain rate. The effect of rate, however, was measured at 80% compression where all cheeses had already fractured. As can be seen in figure 3.20 we also found much less effect of rate on the hysteresis if the sample was (nearly) fractured. In chapter 2 it was shown that the apparent relaxation time decreased with increasing strain, possibly due to fracture phenomena in the sample before the maximum stress had been reached. This effect has been proved by pictures for a type 1 cheese, but is possibly also important for other cheese. This effect could also be the reason for the increased hysteresis with increasing strain.

The exact amount of recoverable energy is difficult to determine because:

- there is some elastic recovery after finishing the unloading cycle (slower than the unloading),
- if the unloading of the sample is performed slower than the sample would recover "naturally", the sample still flows during the unloading process.

The actual amount of stored energy at a certain strain is larger than measured in an unloading experiment due to the first point, and lower due to the latter point.

Just before fracture (ϵ_h=0.8-1.0 for this cheese, see figure 3.17) according to the hysteresis experiments, about 20-40% of the energy was stored and available for fracture. This implies that the actual specific fracture energy measured in tension would also be 20-40% of the calculated value, thus 2.2-5.0 J m^{-2} for a young, type 2, Gouda cheese.

For some materials it is possible to perform the same kind of experiments with cracked samples. Then the dissipation of energy

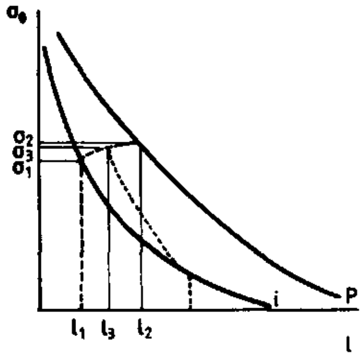


Fig. 3.21 Theoretical stress - notch length curve for complete fracture (- - - - -) and for crack growth during unloading (..........).

is due to flow as well as fracture (Atkins and Mai,1985). With controlled crack growth it is possible to estimate the energy used for this crack growth as the difference in stored energy for different crack lengths and thus calculate R_s. We tried this for cheese but, because the fracture did not stop directly after stopping the elongation, it was impossible to perform the experiments in such a way that the results could be used for calculation of the specific fracture energy. The probably reason for the fracture not stopping during unloading is given in figure 3.21. A tension sample with a notch of length l_1 can be loaded up to a stress σ_1 without cracking and hysteresis experiments can be performed. At stresses higher than σ_1 the notch grows slowly until it reaches a length l_2 at σ_2 and fracture propagates spontaneously. If the loading is stopped at some stress between σ_1 and σ_2, for example σ_3, the notch has grown to a length l_3 under loading, but will continue growing during unloading. This further crack growth depends on

- the rate of unloading
- the rate of crack growth
- the difference between fracture initiation and propagation.

The breaking only stops if the stress and crack length have reached a combination of values corresponding to a point below the initiation line.

Another way to estimate the amount of stored energy is by measuring the loss tangent in dynamic experiments (Andrews, 1980). Tan δ is the ratio of the loss modulus G" to the storage modulus G' (see section 2.3.4.1), i.e. the ratio between the amount of energy that is dissipated during a certain time scale and the stored energy. However, care has to be taken in using this relation, because dynamic experiments are mostly performed (and are only meaningful) in the (apparent) linear region and thus at small stresses and strains. Fracture on the other hand occurs mostly at larger stresses and the flow in the material then can be different. The relation therefore is valid only as an estimate for brittle materials (Andrews, 1980).

For most cheeses it was shown (type 1 cheese, see section 3.2.1) that the effect of rate was independent of the strain; the slope n in formula 3.13 is a constant. The measured loss tangent for these cheeses compared well with this slope (formula 3.14). The experimental loss tangent was about 0.31-0.40, which implies that 71-76% of the energy was stored. On the other hand, the value for n of 0.15-0.20 suggests that 76-81% of the energy is stored. This would result in a work of fracture of 0.6-1.2 J m^{-2} for a 1 year old Gouda cheese. The apparent value for n for young (type 2) cheese was higher, namely about 0.38 at ϵ=1.0 (see section 3.2.1). When assuming that formula 3.14 may be applied, this slope would suggest that about 63% of the energy is available for fracture and that R_s for young and not acid Gouda cheese is 7-8 J m^2. These results are listed in table 3.5.

We do not know what the exact value for the specific work of fracture of cheese is and neither why the results obtained by the use of the hysteresis experiments are not consistent with those derived from the effect of rate and from the dynamic experiments.

When cutting a material and measuring the necessary force, it is also possible to calculate a fracture energy using formula 3.11 which reads as:

$$W = W' + W'' + W_f + \text{curling energy} \qquad (3.11)$$

Table 3.5 Apparent fracture energy of a young (2 weeks) and a mature (12 months) Gouda cheese.

assumptions	% of energy available	fracture energy R_s ($J\ m^{-2}$)	
		young cheese	mature cheese
no energy loss	100	11.0-12.5	0.8-1.5
type 1 cheese			
slope n=.15-.20	76-81		0.6-1.2
tan δ=.31-.40	71-76		0.6-1.1
type 2 cheese			
slope n=.38	63	6.9-7.9	
hysteresis experiments	20-40	2.2- 5.0	

An hypothetical example of a force-time curve for a cutting experiment is shown in figure 3.22. When cutting a test-piece of a width l with a speed v during a time t the input energy is $F_c vt$. This is used to fracture an area lvt and to deform a volume of

Fig. 3.22 Hypothetical force-time curve for a cutting experiment.

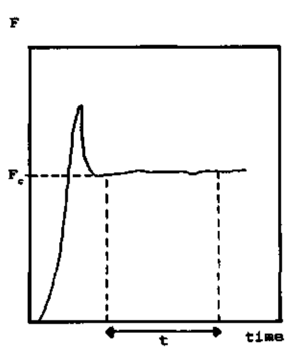
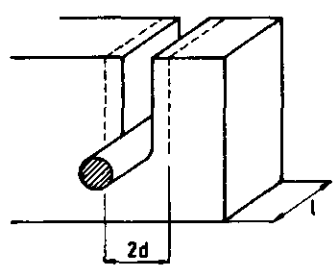


Fig. 3.23 Wire with diameter d cutting a test-piece.



material around the wire of 2dlvt (assuming that the disturbed volume is twice as thick as the thickness of the wire d, see figure 3.23).

$$F_c vt = R_s vtl + (W'+W")2dlvt \qquad (3.15)$$

It now is possible to calculate R_s from the forces necessary to cut a sample of cheese with wires of different diameters by linear extrapolation to d is zero. This was done for a 1 month old Gouda cheese. The results are shown in table 3.6. The order of magnitude of R reasonably agrees with the results derived from other experiments, although the fracture speed is different.

The energy that is not used for cutting is used to deform the material. An apparent viscosity can be estimated when assuming the cutting force to act on an area 2dl and the shear rate to be

$$\dot{\gamma} = \frac{v}{2d} \qquad (3.16)$$

The results for η^* are shown in figure 3.24. The apparent viscosity calculated in this way is somewhat lower than found for compression testing at large strains. A reason for this could be

Table 3.6 Influence of cutting speed (v) on R_s for a 2 months old Gouda cheese. T = 20°C.

v (mm min^{-1})	F_c/l d = 25μm (J m^{-2})	F_c/l d = 300μm (J m^{-2})	R_s d = 0μm (J m^{-2})
1	6.4	22.5	4.9
3	7.0		
10	8.6	29.0	6.7
15	11.0		
20	11.4	31.0	9.6

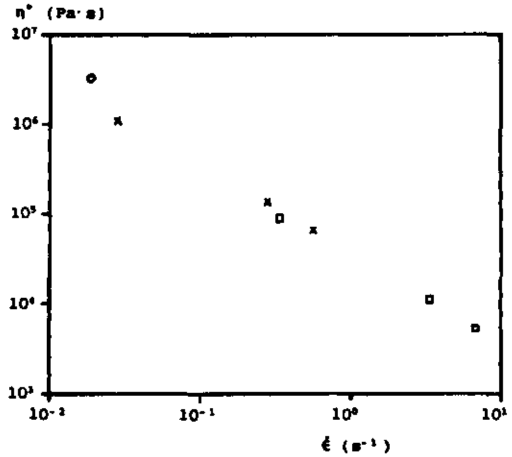


Fig. 3.24 Apparent viscosity η^* calculated from cutting experiments with a 300 μm wire (X) and a 25μm wire (□). The apparent viscosity calculated from compression tests at a high strain is drawn as (○). T = 20°C; young cheese.

the different type of deformation (with cutting a shear viscosity is calculated, with compression an elongational viscosity) and the estimation of the disturbed volume. When assuming the Trouton ratio to be 3 (section 2.4.2.2), the above calculated shear viscosity is somewhat too high. If the disturbed volume would be somewhat larger than 2dvtl, the η^* would be somewhat lower. The strain rate at which it was measured then is somewhat lower as well, and the results would better agree.

The effect of strain rate on the total work of cutting is the same as found for other deformations. Again, this indicates that we measured the same kind of material properties with different methods.

Summarizing all the results of this section we can conclude that the fracture energy of cheese is of the order of a few J m^{-2} for young cheese, decreasing to about 1 J m^{-2} or somewhat less for very mature Gouda cheese. The (theoretical) energy needed to break all chemical bonds in one plane probably is about 1 J m^{-2} (Gordon,1978). For most materials R_s is higher, due to the disturbance of some material in the vicinity of the plane of the new surface. The value of R_s for cheese is probably that low because

Table 3.7 Inhomogeneities in cheese. Very approximate (from Walstra and van Vliet, 1980).

type	scale (m)
casein sub-micelles	10^{-8}
paracasein micelles	10^{-7}
protein network strands	10^{-6}
fat globules	10^{-6}-10^{-5}
unevenness of network	10^{-5}-10^{-4}
curd grains	10^{-3}-10^{-2}
curd pieces (Cheddar)	$2 \cdot 10^{-2}$
"acid spots"	10^{-2}
holes	10^{-2}
precipitates of salts, amino acids	10^{-3}
difference rind-centre	10^{-2}-10^{-1}

the network is not throughout the complete material due to fat particles and protein breakdown. This also could be the reason for the decrease in R_s with increasing maturation.

Because the work of fracture is a material constant (for a given rate of deformation), it is possible to estimate the size of the defects in cheese from the total energy used to fracture a tension sample without a notch (formula 3.8). In this way a defect size of 0.1 - 0.3 mm could be calculated for nearly all cheeses. This result is the same as found from the stress measurements (section 3.2.3). Comparing this defect size with the size of inhomogeneities in cheese (Table 3.7; Walstra and van Vliet, 1980), it can be concluded that in absence of holes and slits, fracture of a sample of cheese is caused by growth of defects which are larger than fat globules and the unevenness of the network and smaller than the curd grains. This will be discussed further in section 5.2

4. INFLUENCE OF COMPOSITIONAL FACTORS ON THE RHEOLOGICAL AND FRACTURE BEHAVIOUR OF GOUDA CHEESE

Composition, manufacturing procedure and maturation very much influence the rheological and fracture behaviour of cheese. In this chapter we will describe the influence of some compositional factors on the behaviour of Gouda cheese, i.e. water, fat, Ca and NaCl content and the pH. In the next chapter (5) the influence of maturation and proteolysis will be treated.

4.1 Introduction

4.1.1 General approach

It is common knowledge among cheese technologists that composition and manufacturing procedure of the cheese affect its consistency. But it is often difficult to interpret the results, because mostly more than one parameter is varied. Several workers tried to determine compositional and rheological parameters of a large number of samples of varying properties and calculated a correlation matrix (e.g. Chen et al.,1979; Eberhard,1985). This poses two problems:

- Due to the wide scatter in the results of rheological measurements and the great number of variables, statistical significance often can not be attained.
- Because the tested cheese did not vary in only one compositional parameter, its is always uncertain whether a found relation is causative.

Non-causative relations frequently occur. For example

1. The pH of a cheese determines the behaviour of the protein and the solubility of the calcium phosphates, which results in a different rheological behaviour and fracture strain of the cheese (section 4.4.1). But variations in manufacturing conditions causing a different pH also affect for instance,

the syneresis (hence moisture content), the rennet absorption (hence proteolysis) and the calcium content. Moreover, the pH as such affects proteolysis.

2. A higher salt content is most times achieved by brining for a longer time, which decreases the water content of the cheese. The salt content affects proteolysis.

To avoid these problems we carried out two different kinds of experiments (for methods see section 4.2):

- Cheese was made with one factor different, trying as good as possible to leave all other compositional parameters constant.
- One compositional parameter was changed later on by absorption of different salt solutions to small test-pieces or by exposion to hydrochloric acid or ammonia vapour.

Not all variations could be achieved by both methods. The fat content, for example, could only be varied by the first method.
The range in which the parameters were studied, was limited to values observed in practice for Gouda cheese. Outside this range, several effects may be much different and results from this study can not be extrapolated and used directly. Nevertheless, we feel that results of this study will be of much use to interpret the behaviour of cheeses with a composition outside the range for Gouda cheese. For cheeses which are quite similar to Gouda cheese, like Edam, Cheddar and Emmentaler cheese, results certainly will be applicable.

4.1.2 Influence of composition

Many variables influences the consistency of cheese. This has been studied by several workers and reviews have been made (e.g. Walstra and van Vliet, 1982; Eberhard, 1985; Walstra et al., 1986; Prentice, 1987). Disadvantages of most methods used to study compositional influence were mentioned in the previous section. In this section we will give a brief review of some trends.

Water content

An increasing water content decreases the force necessary for a certain deformation; water softens a cheese (e.g. de Jong, 1978). The strain at fracture generally does not change (e.g. Eberhard, 1985). Creamer and Olson (1982) found similar effects by adding moisture to small samples of mature Cheddar cheese. By regulation of the dehydration during pressing and maturation it is even possible to control the firmness of a cheese (Wodecki et al.,1984).

Fat content

A low fat cheese is firmer and more elastic (e.g. Emmons et al., 1980). The stress at fracture and the energy needed to cut a cheese at room temperature decrease with increasing fat content (Green et al.,1986). Generally, a lower fat content goes along with a higher water content, but with a lower water content in the fat-free matter.

pH

More acid cheese is shorter and firmer (e.g. Raadsveld and Mulder, 1949B; Creamer and Olson,1982; Creamer et al, 1985). A high-moisture cheese that has undergone sufficient proteolysis "liquifies" at high pH, but not at low pH (Noomen, 1983).

Calcium content

No clear effects have been found. The influence is possibly pH dependent; at high pH, more calcium seems to make a cheese more firm (Lawrence et al.,1983).

Salt (NaCl) content

Longer brining gives a firmer and shorter cheese (e.g. Eberhard, 1985; MPagana and Hardy, 1986), but then the water content decreases with increasing salt content.

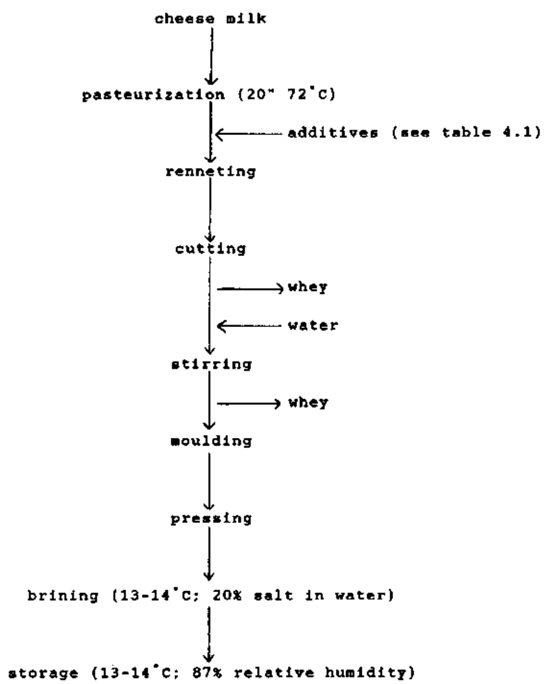
Maturation

High-moisture cheese become softer and more liquid like with ripening (de Jong, 1976). Cheese with a lower water content become shorter and firmer (Mulder, 1946). These changes with maturation are probably related to the α_{s1}-breakdown (de Jong, 1976; Creamer and Olson, 1982), however, the decrease in water content can also be important.

Temperature during maturation

At higher ripening temperatures water loss and protein breakdown occur faster. This decreases the strain at fracture and the springiness of the cheese and increases the firmness and viscosity at a certain age (Raadsveld and Mulder, 1949A; Fedrick and Dulley, 1984; Eberhard, 1985).

Fig. 4.1 Steps in cheese making.



4.2 Materials and methods

The methods used to determine the chemical composition of the cheese are described in section 2.2.1. The rheological and fracture tests are described in section 2.3. In this section we will describe the cheese making process (4.2.1) and the changing of the composition of small pieces of cheese later on (4.2.3).

4.2.1 Cheese making from natural milk

Milk was obtained from the dairy herd of the University. The cheese making process for standard Gouda cheese is shown in figure 4.1. A recent review of the manufacturing of Gouda cheese has been given by Walstra et al. (1987). Deviations from the standard manufacturing procedure to obtain special cheese (for example with a different pH) are shown in table 4.1.

Table 4.1 Cheese making parameters. Values given for 100 l cheese milk. See text for further explanation.

		standard cheese	special cheese			
			fat 10+	fat 60+	pH and Ca	rennet
cheese milk:						
fat	%	4.0-4.6	0.4	5.6		
protein	%	3.0-3.6				
lactose	%	4.3-4.6				
additives:						
35% $CaCl_2$	ml	40	20	45	25-625	18-200
KNO_3	g	20				
starter	ml	900			900-1250	
rennet	ml	20				5-60
renneting:						
time	min	30				20-70
temperature	°C	30				
cutting time	min	20	15	30		
whey off	l	50		45	25-50	
washing water	l	14	16		0-25	
temperature	°C	35	28	37	30-34	
time	min	25	15	40		
extra $CaCl_2$	g/l	-			0-12.5	
whey off		all				
pressure time	h	1.5				
brining	h	32				

The starter was a common one for Gouda cheese making (Bos), cultivated for 16-18 hours at 20°C in sterile skimmilk. The rennet was a commercial calf rennet (strength 1:10 800). The mean composition of the standard cheese after 1 week was mostly about 40-44% water, pH 5.2, 48-50% fat in the dry matter, 4% NaCl in water, 0.8% Ca.

To obtain cheese with varying fat content but with the same ratio of water to solids-not-fat (SNF), the fat content of the cheese milk was adjusted as well as cutting time, cooking temperature and amount of wash water (see table 4.1). The latter adjustments were made because low-fat cheese tended to lose much more water than cream cheese. In spite of these efforts, the low-fat cheese still was (somewhat) dryer than the cream cheese, but we could adjust for this when interpreting the results. Protein breakdown (as determined with gel electroforesis, see table 2.1), NaCl and calcium content were not significantly different from standard cheese (results not shown).

Cheese with varying calcium content was made by adding $CaCl_2$ to the cheese milk and/or to the wash water. The pH of the cheese was varied by varying the amount of first whey and wash water. Also the amount of starter was varied somewhat. The cheese made with different pH and calcium content was tested after 1 and 4 weeks of maturation. No significant variation in protein breakdown and NaCl content was observed.

For the cheese made with different rennet content, the amount of calcium added to the cheese milk was varied to diminish the influence of the rennet concentration on the renneting time.

4.2.2 Recombined and filled cheese milk

Recombined milk was made from milk fat (obtained from Frico) and skimmilk. Filled milk was made from soya oil (obtained from Reddy) or palm fat (obtained from Interback) and skimmilk.
To obtain a cheese milk with fat particles covered with casein, we used the following procedure. Skimmilk was made from a commercial low-heat skimmilk powder (obtained from Krause) in water

(9% solids; 40°C) and was kept overnight at 5°C. A stirred mixture of fat and skimmilk (5.6% fat) was homogenized with a Rannie homogenizer at 40°C and 10^6 Pa. The mean (volume/surface) diameter was estimated by a spectroturbidimetric method (Walstra, 1965) and was found to be 1.5 - 3.5 µm. The recombined milk was used to make cheese with 60% fat in the dry matter according to the method described in section 4.2.1. Renneting time was somewhat longer.

To obtain cheese milk with fat particles not covered with casein, 3.5 kg fat was homogenized in 8.5 kg of a 10% solution of whey powder (obtained from the NIZO). The emulsion was centrifuged to a fat content of 40-50% and washed (1x) with 10 l skimmilk. Subsequently, skimmilk was added up to a fat content of 5.6% and the milk was used for cheese making according to section 4.2.1. Renneting time was somewhat longer. To prevent the cheese from becoming too acid, which may occur because of the extra lactose in the whey, the amount of curd wash water was increased.

4.2.3 Changing the composition of test-pieces of cheese

As mentioned in section 4.1.1, the disadvantage of studying, for example, the pH influence by testing cheese with different pH is that more parameters are varied. To avoid this problem we also tried to change one parameter of the composition of a sample of cheese afterwards. This was done for the water, salt and calcium contents and the pH.

The water, NaCl or calcium content of a sample of cheese were changed by absorption of small amounts of moisture. To do so, a test-piece suitable for compression or dynamic shear experiments (d ≈ 14mm; h ≈ 10 or 20 mm) was placed in a cylindrical box and 0.1-1.0 ml of moisture (standard was 4% NaCl; 0.8% Ca as $CaCl_2$; lactic acid up to pH 5.2) was added. A similar method was used before by Creamer and Olson (1982) to change the water content of test-pieces of Cheddar cheese. The boxes with the cylindrical samples in it were gently rolled over during 3 days at 14°C. Already after 1 day all moisture was absorbed, after 3 days the sample must has been homogeneous. Assuming the diffusion coefficient (D) of water in cheese to be about 0.4 cm^2/day (Geurts, 1972), differences in the water concentration in a cylinder of cheese with a radius (r) of 7.5 mm are decreased to 95% when (Leniger and Beverloo, 1975)

$$\frac{D\ t}{r^2} = 0.6 \tag{4.1}$$

or within 0.84 day. This implies that after 3 days the sample is essentially homogeneous. The water content after 3 days was calculated by weighing the sample and was checked sometimes by drying (see section 2.2.1 for the method). The results were not significantly different and neither was the difference between the central part of the sample and the outside. Only samples which had absorbed all added moisture were used. To change the water content, different amounts of standard moisture were added, to change the salt or calcium content, a constant amount of moisture but with different NaCl or $CaCl_2$ content was used.

The pH of a test-piece was changed by keeping the pieces for 1-20 minutes in HCl or NH_3 vapour in a desiccator. After this, the samples were put separately in small boxes and were kept for 3 days at 14°C. The actual pH was measured after the rheological or fracture testing and was found to be independent of the place in the test-piece. Just after adjusting the pH this was certainly different; the pH of the outer layer then was 1 and 10, respectively, and this layer looked very white (acid) or smooth and shining (high pH). This means that the pH effect on Gouda cheese is reversible. This method of changing the pH of cheese afterwards was only possible with young cheese. For more mature cheese, the time necessary to change the pH increased and for a cheese older than 3 or 4 months it was not possible to change the pH (especially to decrease it) in a time short enough to prevent too much evaporation. Absorption of some moisture before changing the pH did not help. We did not investigate this phenomenon any further and used the method, at least in relation to these aspects, only for cheese up to 3 months old.

4.3 Influence of water and fat content

Cheese may be considered as a continuous matrix of a swollen proteinaceous mass, interspersed with fat globules (Walstra and van Vliet, 1982). These fat particles possibly only act as filler particles in the protein network, which implies that the behaviour of cheese can be described as that of a composite material.

We first will give an introduction to the theory of rheological and fracture behaviour of composites and of the expected influence of water and fat on the behaviour of the composite material cheese in section 4.3.1. Because the cheese tested varied somewhat in water content, which greatly affects the behaviour, the influence of water will be described first (section 4.3.2) and after this the influence of fat content and fat properties (section 4.3.3).

4.3.1 Composite materials and application to Gouda cheese

Theory

The properties of a material are modified by the incorporation of a filler. Both the properties of the filler and the matrix, as well as the adhesion between filler and matrix, affect the material behaviour.

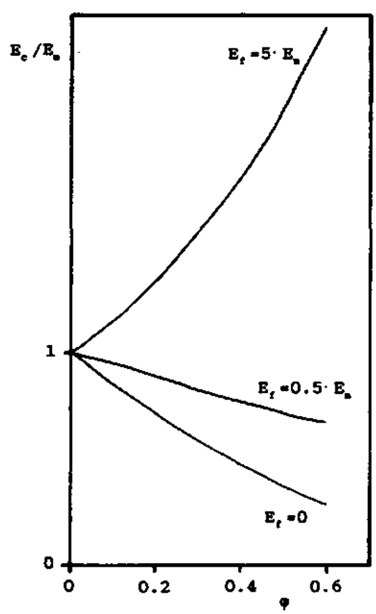
If the filler consists of air bubbles (foam) or particles which have no mechanical connections with the matrix, a smaller volume of material is deformed than in the absence of filler. The modulus of the composite decreases with increasing filler content. If the particles interact with the matrix, they also deform and influence the modulus of the composite: particles which are more rigid than the matrix increase the composite modulus, particles with a smaller modulus decrease the composite modulus. Mechanical interaction between matrix and filler can be caused by bonds between the two phases or by friction between them. Formulas to describe this behaviour can be found in the literature. An often used equation is that of Kerner (1956) for calculation of the composite modulus G_c from the matrix modulus G_m, the matrix

Poisson ratio μ, the filler modulus G_f and the volume fraction of filler φ, if there is perfect adhesion between filler and matrix:

$$\frac{G_c}{G_m} = \frac{\dfrac{\varphi G_f}{(7-5\mu)G_m + (8-10\mu)G_f} + \dfrac{(1-\varphi)}{15(1-\mu)}}{\dfrac{\varphi G_m}{(7-5\mu)G_m + (8-10\mu)G_f} + \dfrac{(1-\varphi)}{15(1-\mu)}} \qquad (4.2)$$

Some theoretical results are shown in figure 4.2. In fact this equation is equal to a second order approximation of the more sophisticated van der Poel theory (1958). Some deviation in the results occurs, especially at high φ and at high G_f to G_m ratios. However, for Gouda cheese (fat content < 60%; temperature ≥ 14°C) the ratio G_f to G_m is never higher than about 5 and φ is below 0.5. Then the difference for the modulus G_c calculated according to formula 4.2 and according to van der Poel (calculations see

Fig. 4.2 Influence of filler volume fraction φ and filler modulus E_f on the ratio of composite modulus to matrix modulus (E_c/E_m), according to formula 4.1.



Smidt, 1975) is less than 7.4%. Because formula 4.2 is much simpler, we used this one.

Because the Poisson ratio may be different for matrix and filler, the compression modulus E_c of a composite can not directly be calculated from formula 4.2 and E_f and E_m. In section 2.4.2.1 was given

$$E = 2\ G\ (1+\mu) \tag{2.49}$$

This has to be taken into account. However, the difference between E_c calculated according to formula 4.2 and 2.49, and E_c calculated with formula 4.2 and replacing the shear modulus by a compression modulus is for cheese less than 1.8% (μ_f=0.50 and μ_m=0.45).

Filler particles also can affect the composite behaviour at higher deformations, because they may act like defects and cause stress and strain concentrations around the filler particles. At high volume fractions of filler, these stress (and strain) concentrations can intensify each other. The strain at fracture then strongly decreases with increasing volume fractions. In the literature several influences have been found, depending on the mechanical interaction between filler and matrix. The strain at fracture ϵ_f always decreases with increasing φ, but the difference between composites with and without mechanical interaction between filler and matrix is not clear. Nielsen (1966), for example, found the decrease in ϵ_f with increasing filler volume to be smaller with no mechanical interaction. Doláková-Svehlová (1982) found the influence of mechanical interaction to be dependent on the volume fraction. For higher values of φ, mechanical interaction decreased the fracture strain more strongly. The decrease in ϵ_f with increasing φ and the increase in E_c with increasing φ results in a not predictable change in the stress at fracture for rigid filler particles.

Because of the presence of filler particles a smaller matrix area has to be fractured for the same specimen cross section. This can cause in a decrease of the toughness R with increasing φ, but additional energy adsorbing processes caused by, for instance, friction between the matrix and the filler or fracture of bonds between matrix and filler can cause an increase in R. The dependence of the toughness on the filler volume therefore depends on the material and can not be predicted by a general theory (Bucknall, 1978).

Cheese as a composite material

The behaviour of cheese possibly can be described as that of a composite material. The matrix consists of swollen protein particles, fat particles act as a filler.

Because the matrix consists mainly of protein and water, the amount of water directly determines the protein concentration and thereby the rigidity of the matrix. A higher water-protein ratio will give a lower modulus of the matrix.

The aqueous phase of a not very young cheese consists of small proteinaceous particles (diameter in Gouda cheese 10-15 nm; e.g. Hall and Creamer, 1972) presumably with some interstitial moisture, which mass completely fills the space between the fat particles. A small change in the water content thus will have a large effect on the friction between these protein particles and thus on the rigidity of the cheese. Moreover, the rheological behaviour of the protein particles (for instance their deformability) may greatly affect the behaviour of the matrix material.

The rheological properties of the protein within the matrix depend on several factors, for instance the pH, NaCl content (this will be discussed in section 4.4), the temperature and the water content. At very low water content, the protein molecules have little freedom to move (vibrate) and the deformability of the protein particles as well as the ratio of viscous over elastic properties (as measured at a certain time scale) will be small. In fact the transition from a more solid-like to a more viscous-like behaviour shifts to longer time scales when lowering the water content (Houwink and de Decker, 1971).

The influence of a filler on the rheological and fracture properties of a composite material depends on:

- the rigidity of the filler in respect to the rigidity of the matrix material
- the amount of filler (volume fraction)
- any mechanical connections between filler and matrix.

The rigidity of fat particles is caused by the interfacial tension and the crystal network inside the particle. At high temperatures, where the fat is completely liquid, the modulus of the fat globules depends on their surface tension and their size. It can be estimated by the Laplace pressure ($2\gamma_s/r$) (van Vliet, 1988) and, since the interfacial tension is 1-2 $mN \cdot m^{-2}$ (Walstra and Jenness, 1984) and the diameter mostly 1-10 µm (Walstra and Jenness, 1984), it can be estimated to be 0.5-4 kPa (van Vliet, 1988). At lower temperatures, however, the milk fat is partly crystallized and the network of crystals inside the fat particles causes the latter to be very rigid.

If the modulus of the fat particles is lower than that of the matrix (this certainly is the case for Gouda cheese at a high temperature), an increase in the fat content will decrease the rigidity of the cheese. If the rigidity of the fat particles is higher than that of the matrix, a higher fat content will cause a higher rigidity of the cheese. The measuring temperature will thus certainly affect the modulus of the cheese. The decrease in firmness of cheese with increasing temperature is, in literature, always ascribed to the melting of the fat (e.g. Eberhard, 1985), although no evidence for this has been given. Moreover, a temperature influence on the behaviour of the matrix may also be expected (Roefs, 1986).

The fat content of cheese will only affect the strain at fracture if the stress concentration caused by the fat globules is higher than the stress concentration caused by other defects in the cheese. In sections 3.2.3 and 3.2.4 we calculated a defect size of 0.1-0.3 mm in Gouda cheese, much larger than the mean diameter of fat globules (d_{vs} = 3.5 µm). We therefore do not expect much influence of the fat content on the fracture strain.

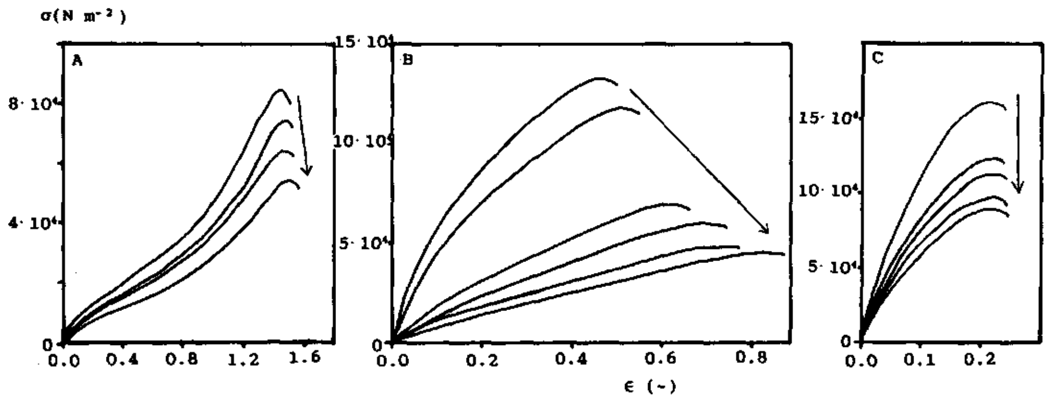
4.3.2 Influence of water content

The effect of water content on the rheological and fracture behaviour of cheese was studied by examining different cheese:

- The water content of pieces of several cheese was increased later on by absorption of different amounts of water at constant pH and NaCl and Ca content (see section 4.2).
- Cheeses of varying water content but with about the same age, pH and salt content were compared. These cheeses were not specially made for studying this relation.

We performed uniaxial compression tests and dynamic experiments in shear (sections 2.3.1 and 2.3.4). Examples of results for cheese with increased water content by absorption are shown in figures 4.3 and 4.4. The influence of strain rate and of the temperature did not (significantly) vary with the water content in the measured range ($\dot{\epsilon}=2.8\cdot10^{-3}-1.4\cdot10^{-1}$ s^{-1}; T = 14–26°C; water content 26–48%). Therefore, results are only shown for a strain rate of

Fig. 4.3 Compression curves of a 1 week (A, pH 5.21), 7½ month (B, pH 5.51) and a 13 month old Gouda cheese (C, pH 5.69) with different water content. The water content was increased by absorption of moisture at constant pH, NaCl and Ca content; A (41.9-42.7-45.6-47.5%), B (32.3-35.6-38.6-41.4-43.9-46.2%), C (25.6-26.1-27.0-30.2-31.6%). T = 20°C; $\dot{\epsilon}_c=2.8\cdot10^{-2}$ s^{-1}



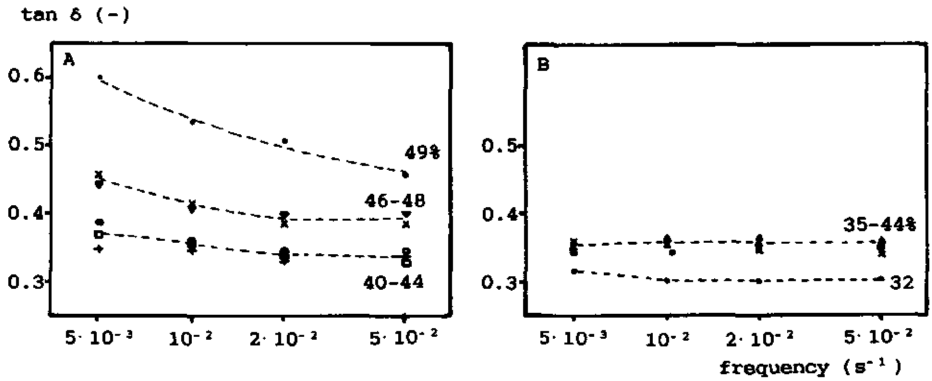


Fig. 4.4 Influence of the water content on the loss angle tan δ in dynamic experiments for 2 different cheeses; a 6 weeks old (A) and a 7½ month old (B) standard cheese. The water content was increased by adsorption of small amounts of moisture at constant pH, NaCl and Ca content. T = 20°C.

$2.8 \cdot 10^{-2}$ s^{-1} and a temperature of 20°C.

From the results it is clear that:

- The modulus E decreased with increasing water content.
- The strain at fracture was mostly independent of the water content, for some cheese it increased with increasing water content.
- The shape of the σ-ε curve seemed to be independent of the water content for most cheese, for some cheese, however, an increasing water content induced more "flow" in the cheese sample.
- The loss angle in dynamic experiments in the time scale measured seemed to be little dependent on the water content for low water contents, and possibly increased at higher water contents.

Results for the compression modulus as a function of water content are summarized in figure 4.5. The water content is expressed as the ratio water to solids non fat (SNF) to facilitate comparison with cheese of a different fat content (see section 4.3.3) and also to cheque (see later) whether we can imagine cheese to be a water-protein matrix with fat particles acting as a filler. With increasing water content the modulus of cheese indeed de-

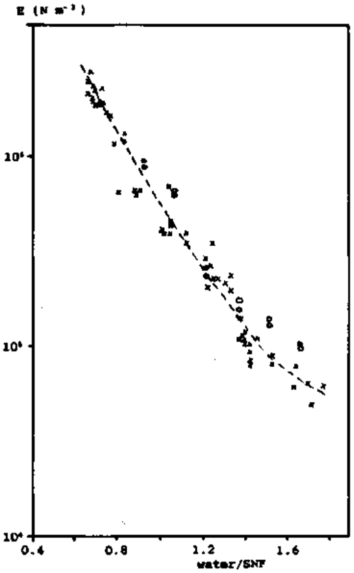


Fig. 4.5 Influence of the water to SNF ratio on the compression modulus of cheese with 48% fat in dry matter. The (X) refer to cheese with a water content changed later on, the (O) refer to different natural cheese. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}; 1 week-13 months old cheese.

creased as was expected (see section 4.3.1). The reasons for this decrease possibly are

1. the decrease in protein (=stress carrying component) content of the matrix material,
2. a more swollen character of the protein particles which causes more freedom for parts of the protein molecules to move or vibrate and a higher deformability of the particles.

The more viscous behaviour can increase the loss angle as well as the strain at fracture. By lowering the water content of a material the transition of a more solid-like to a more viscous-like behaviour shifts to longer time scales. The change in shape and height of the tan δ - frequency curve of cheese with increasing water content points to such a shift.

No influence of the maturation time (protein breakdown) of the cheese on the modulus in the measured water content range could be found. For cheese with a higher water content the modulus will decrease with increasing proteolysis as is known for soft cheese like Meshanger and Camembert (de Jong, 1978; Noomen, 1983). Possibly the changes in flow behaviour with changing water content also depend on the protein breakdown. One may imagine that

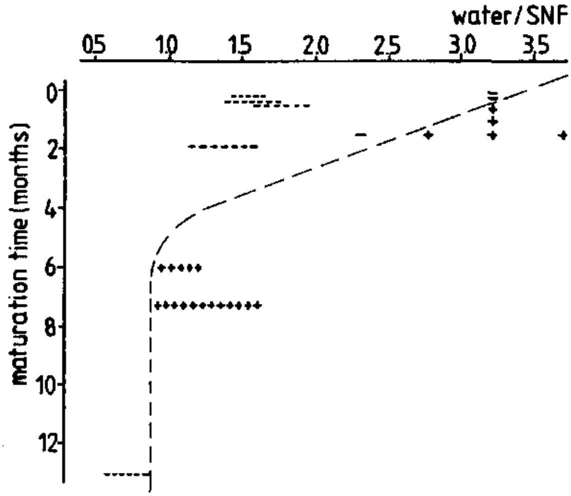


Fig. 4.6 Influence of the ratio water to SNF and the maturation of cheese on the extent of viscous-like character as measured at one strain rate in the range of $2.8 \cdot 10^{-3}$ to $1.4 \cdot 10^{-1}$ s^{-1}.

+ = increase of tan δ or ϵ_f with increasing water content at a certain age or with ripening at a certain constant water content. This implies that the system is relatively more viscous-like.

- = the same, but no increase.

proteolysis shifts the transition from a more solid-like to a more viscous-like behaviour to shorter time scales.

In a standard Gouda cheese with ripening the protein breaks down and the water content decreases (see section 5.4). Both effects have an opposite influence on the viscous behaviour of cheese at a certain time scale. In figure 4.6 the influence of the ratio water to SNF on the viscous behaviour after a certain ripening time as well as the influence of ripening on the viscous behaviour at a certain ratio of water to SNF is shown. A cheese was supposed to behave more viscous-like (see section 3.1.2) if the loss tangent increased or the strain at fracture increased (as measured at a certain time scale) with increasing water content or age. In the literature following supplementary results could be found:

- For several types of cheese (e.g. de Jong, 1978; Noomen, 1983) it is known that cheese with extensive proteolysis and a high enough water content liquifies. This may be translated into a high value of tan δ and a very high fracture strain (Cruysen, 1987). This effect highly depends on pH.

- Creamer and Olson (1982) found no influence of the water content on the strain at fracture for Cheddar cheese of 7 weeks old and with 37.5-45% water, i.e. the ratio of water to SNF is 1.3-2.1.
- Eberhard (1985) found no influence of the water content on the strain at fracture for Emmentaler cheese of 150 days old and with 33.5-37.5% water. The protein breakdown in Emmentaler cheese is less than in, for example, Gouda and Cheddar cheese because of the denaturation of chymosin caused by the high cooking temperature.
- Cruysen (1987) found for cheese with 55% water (water/SNF is about 2.3) a very sudden increase in tan δ with increasing age.

We can conclude from this that the flow behaviour of cheese changes at a certain water/SNF ratio. In a younger cheese this change takes place at higher ratios of water to SNF than in a more mature cheese. The transition does not have to be the same for the different types of behaviour, e.g. for the increase in the loss angle and the increase in the strain at fracture. It is also very likely that the transition depends on time scale, temperature and pH. Supplementary experiments would be very useful.

4.3.3 Influence of fat

To study the influence of fat we made cheese with varying fat content, leaving all other parameters, such as pH and water/SNF ratio, as constant as possible. Because we did not succeed completely, we will often compare only some cheese, not all, when describing an effect.

First we will describe the influence of fat on the rigidity and firmness of cheese (section 4.3.3.1), after that the influence of fat on the fracture behaviour will be described (section 4.3.3.2).

4.3.3.1 *Influence of fat on the rigidity and firmness*

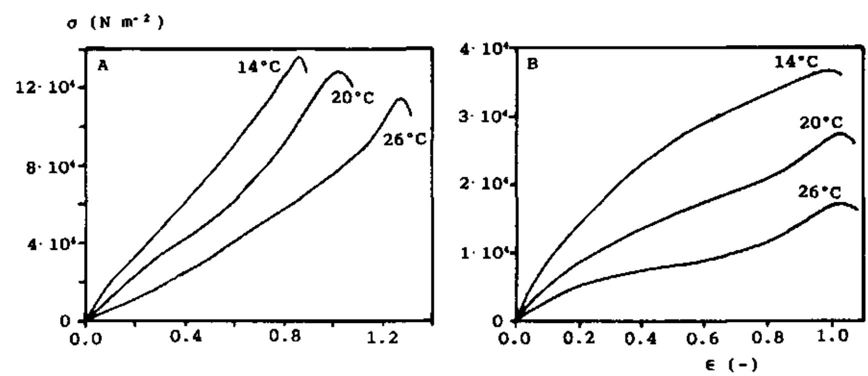
To study the influence of fat on the rigidity and firmness of Gouda cheese, we studied cheese

- with different fat content, namely 10, 48 (=standard) and 60 % fat in the dry matter
- with a different fat globule surface, namely natural fat globules and fat particles covered with casein or with whey proteins
- at different measuring temperatures
- with different types of fat, namely with milk fat and soy oil.

Temperature influence

We studied the effect of measuring temperature on cheese in the range of 14°C to 26°C (14°C = ripening temperature; 20°C = room temperature) in uniaxial compression and in dynamic shear experiments. Some examples of results for compression tests are in figure 4.7. Here we can see that with increasing temperature the modulus and fracture stress decreased and the strain at fracture somewhat increased. The first effect is also shown in figure 4.8. The log(E)-T curve seems to be linear and the slope depends on the fat content of the cheese. We found no significant influence of the pH, salt content or age on this slope. To compare cheese with different fat content, we considered the ratio of the modu-

Fig. 4.7 Influence of the measuring temperature on the compression curves for cheese with 10% fat in dry matter (A) and with 60% fat (B). $\dot{\varepsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.



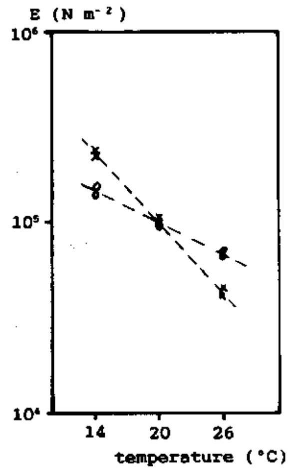


Fig. 4.8 Influence of measuring temperature on the compression modulus for cheese with 10% (O) and with 60% (X) fat in dry matter. Both cheeses had a water to SNF ratio of 1.45. $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

lus E (and σ_f and ϵ_f) found at 14°C to that at 26°C. The results for cheese made from natural milk with 10, 48 and 60% fat in the dry matter and for cheese made from recombined milk with milk fat or from filled milk with soy oil (see further in this section) are shown in table 4.2. From this we can conclude that

- At 20°C the compression modulus of the cheese was independent of the fat content.
- The temperature influence on E and σ_f of cheese made with milk fat decreased with decreasing fat content.

Table 4.2 90% confidence limit of the ratio of compression parameters (E, σ_f or ϵ_f) found at 14°C to 26°C. Values are for cheese with different fat content made from natural milk and for 60+ cheese from recombined milk (with milk fat) and from filled milk (with soya oil).

cheese	E_{14}/E_{26}	$\sigma_{f,14}/\sigma_{f,26}$	$\epsilon_{f,14}/\epsilon_{f,26}$
natural milk			
10+	1.79-2.63	1.13-1.93	0.74-0.84
48+	3.68-4.20	1.49-2.20	0.89-0.97
60+	4.21-4.89	2.33-3.03	0.86-0.92
recombined milk			
60+	3.23-5.11	2.48-2.86	0.69-0.84
filled milk			
60+	1.48-1.88	1.22-1.45	0.70-0.85

- The temperature influence depended on the melting properties of the fat particles in the cheese. Soy oil is completely liquid at all temperatures employed and the rigidity of the fat particles will therefore not change as much with temperature as that of milk fat particles.
- The temperature influence of the cheese made with soy oil was similar to that of the low fat cheese.
- Part of the temperature effect can not be ascribed to the melting of the fat, and must be due to a change in properties of the matrix. This effect is comparable to the temperature influence found for rennet skimmilk of pH 5.2 gels made at 30-35°C (G'(14°C)/G'(26°C) = 1.35-1.40, Roefs,1986).
- With increasing temperature the strain at fracture increased for all cheese. This may cause the temperature influence on σ_f to be less than that on E.

The temperature influence on the elastic modulus G' for the cheeses of table 4.3 (same cheese as in figure 4.12) was markedly higher than that on the modulus E in compression testing, but, again we found the influence for the cream cheese to be higher than for the standard cheese. We can not explain this discrepancy between the shear and the compression modulus. A possible reason could be the different strain at which G' and E were measured, although there was not that much difference.

Summarizing, the effect of the measuring temperature on the rheological and fracture behaviour of cheese is partly due to a temperature dependent behaviour of the casein-water matrix but

Table 4.3 Ratio of elastic shear modulus G' at 10^{-2} s^{-1}, found at 14°C to 26°C. Values are for cheese from natural milk and with different fat content.

cheese	G'(14°C)/G'(26°C)
48+	
7 weeks old	5.55-5.85
10 weeks old	4.28-5.55
60+	
½ year old	8.48-9.91

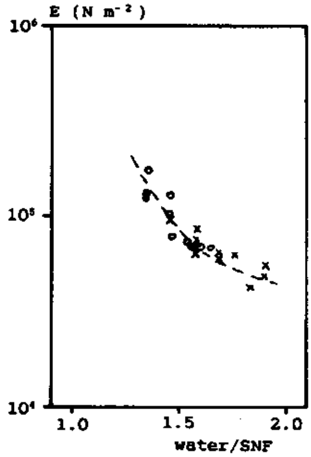


Fig. 4.9 Influence of the ratio water to SNF on the compression modulus E for cheese with 10% (O) and with 60% (X) fat in dry matter. $T = 20°C$; $\dot{\varepsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

for the greater part to a change in rigidity of the fat particles.

Fat acting as a filler in a swollen protein matrix

For compression curves we found that at a water-SNF ratio of about 1.4 the modulus at 20°C is about independent of the fat content (compare figure 4.8 with 4.5). To check this, the water content of a 10+ and a 60+ cheese were changed by adding moisture to it. The results for the modulus as a function of the water to SNF ratio are shown in figure 4.9 and can be compared to figure 4.5. We can explain this behaviour and the fact that at low temperatures the modulus increased with increasing fat content and at high temperatures it decreased, by assuming the cheese to be a composite material with filler particles that deform when deforming the matrix. At 20°C there is no or nearly no influence of the fat content (volume fraction of filler) on the modulus when the water to SNF ratio is about 1.3 or higher, which would imply that at this temperature the rigidity of the filler equals that of the matrix ($E_f = E_m$), thus is about 10^5 N m^{-2}. At higher temperatures the fat then is softer than the protein water matrix and increasing fat content should decrease the modulus of the composite, i.e. the cheese. At lower temperatures the fat is more rigid than the matrix and the modulus should increase with increasing fat content.

Table 4.4 Fat content of different cheese. (water/SNF = 1.4; ρ(milkfat)=915 kg m^{-3}; ρ(cheese)=1100 kg m^{-3})

fat in dry matter (%)	weight % fat	volume % fat
10	4.38	5.27
48	27.8	33.4
60	38.5	46.2

The shear modulus of a natural fat globule which is completely liquid can be estimated to be about 2 10^3 Nm^{-2} (see section 4.3.1). From this, the volume fraction of fat (table 4.4) and the modulus of the casein matrix at 26°C (temperature influence on acid milk gels 20-26°C is 1.18; Roefs,1986) E_c at that temperature can be calculated by using formula 4.2. The results are shown in table 4.5. The calculated values for the decrease in E_c with increasing temperature for the cheese with different fat content were quite good comparable to the found results for compression tests (table 4.2). The discrepancy is highest for the cream cheese.

Table 4.5 Calculated results for the compression modulus at 26°C and the ratio E(20°C) to E(26°C) for cheese with 10, 48 and 60% fat in dry matter. E_c(20°C) is taken to be 10^5 N m^{-2} (see text).

Assumptions:
1. $E_m=10^5$ N m^{-2}; $E_f=2\cdot10^3$ N m^{-2}; $\mu=0.5$
2. $E_m=10^5$ N m^{-2}; $E_f=2\cdot10^3$ N m^{-2}; $\mu=0.45$
3. $E_m=10^5$ N m^{-2}; $E_f=6\cdot10^3$ N m^{-2}; $\mu=0.5$
4. $E_m=10^5$ N m^{-2}; $E_f=6\cdot10^3$ N m^{-2}; $\mu=0.45$
5. $E_m=8.45\cdot10^4$ N m^{-2}; $E_f=6\cdot10^3$ N m^{-2}; $\mu=0.45$

assumptions	E(26°C) in 10^5 N m^{-2}			E(20°C)/E(26°C)		
	10+	48+	60+	10+	48+	60+
1	.917	.557	.426	1.09	1.80	2.35
2	.915	.547	.416	1.09	1.83	2.40
3	.923	.581	.455	1.08	1.72	2.20
4	.920	.573	.447	1.09	1.75	2.24
5	.779	.489	.384	1.28	2.04	2.60

There the temperature influence according to table 4.5 is higher than the one found for cheese (table 4.2). A most likely reason for this is the not completely liquid state of the fat particles at 26°C.

Assuming that the temperature influence on the matrix modulus from 14°C to 20°C is the same as from 20°C to 26°C, we can estimate the matrix modulus at 14°C to be $1.18 \cdot 10^5$ Nm^{-2}. Then it is possible to estimate the modulus of the fat globules at 14°C. The calculated value for E_f is shown in table 4.6 and is $4.6\text{-}8.8 \cdot 10^5$ Nm^{-2}. The compression modulus of butter at 14°C is about 10^5-10^7 Pa (Oortwijn, unpublished results), in milk fat globules it is possibly only 10% of this value. A modulus of the fat globules of about $6 \cdot 10^5$ N m^{-2} thus is not an unlikely result.

Temperature influence was determined at increasing temperature; all cheese samples were prepared at ripening temperature (14°C) and some of them were tested at 14°C, some after warming to 20°C (in 1½ hour) and some after warming to 26°C. After 1½ hour no significant influence of the warming time on the rheological and fracture parameters could be found. (This had also be found by Lee et al., 1978) However, cheese samples (with milk fat) cooled from 26°C to 20°C in 1½ hour still were much softer than the

Table 4.6 Calculation of the modulus of milk fat particles at 14°C from the results of the ratio E_c(20°C) to E_c(26°C) for different fat volumes.
assumption 1: ratio 20°C to 26°C from table 4.5 and assumption 5.
assumption 2: ratio 14°C to 26°C from table 4.2

assumptions	E_f(14°C) in 10^5 N m^{-2}
φ = 0.053	
1	7.37
2	4.89
φ = 0.334	
1	8.00
2	6.80
φ = 0.462	
1	8.79
2	4.59

Table 4.7 Influence of temperature history on the mean fracture stress of two 60+ Gouda cheeses of about 6 months old. $\dot{\varepsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

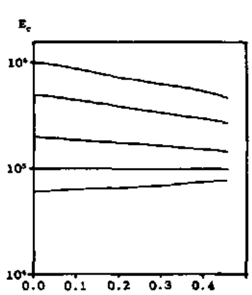
temperature	fracture stress (10^4 N m^{-2})	
	cheese 1	cheese 2
14°C	13.6	11.1
↓ 20°C	9.1	6.9
↓ 26°C	5.5	4.1
↓ 20°C	7.2	5.0

"normally" tested 20°C samples (see table 4.7). This implies less rigidity of the fat globules at 20°C when cooled from 26°C than when warmed from 14°C. A reason for this may be that after cooling, it takes considerable time before fat crystallization is complete and especially before the fat crystals are fully sintered to form a rigid network.

In view of the results on the influence of the water and fat content, theoretically there has to be an effect of the water content on the effect of fat. For different filler volumes, different matrix moduli and a filler modulus of 10^5 Nm^{-2} the calculated composite moduli (using formula 4.2) are shown in figure 4.10. From this it can be concluded that

- There has to be an influence of the fat content on the compression modulus of cheese at 20°C, if the water content of the cheese is higher or lower than corresponding with a water/SNF ratio of about 1.4. Because we performed nearly all

Fig. 4.10 Influence of the matrix modulus and filler volume on the modulus of the composite according to formula 4.1. $E_f = 10^5$ N m^{-2}; $\mu = 0.45$.



experiments at about the same water/SNF ratio and the scatter of the results is considerable (section 2.3.1.5), we did not observe this effect.

- The influence of the water/SNF ratio on the compression modulus shown in section 4.3.2 is not only an influence of the different behaviour of the casein matrix, but it is also influenced by a different filler volume influence due to a change in E_f/E_m with changing water content. This would imply that the slope for a log(E_m)-water/SNF curve is steeper than that of a log(E_c)-water/SNF curve.

To calculate the modulus of cheese from a matrix and a filler rigidity, several assumptions have been made which are not always warranted:

- Due to the size distribution of the fat particles in cheese the rigidity of all particles is not the same. Particles with only liquid fat have a higher rigidity if they are smaller (E is proportional to 1/d). If part of the fat is crystallized, the amount of crystallized fat may depend on the size of the fat particle and possibly the rigidity of the network of the fat crystals as well; if so, larger particles would be more rigid.
- The modulus of the cheese was determined in a (apparently) linear region, at 3-5% deformation. For bulk fat has been found that the behaviour is linearly up to about 1% deformation (Haighton, 1964).
- The behaviour of an intermediate layer between filler and matrix can influence the composite behaviour very much (Maurer, 1983); a layer with a low modulus decreases the composite modulus, a rigid layer increases it. For milk gels with non-interacting fat particles, it has been shown that a water layer between the filler and the protein matrix diminishes the effect of the filler rigidity ($E_f > E_m$) (van Vliet, 1988). We do not expect such a water layer between the fat particles and the protein matrix in cheese, because at the studied water contents the matrix still is able to adsorb more moisture.

Cheese from recombined or filled milk

In table 4.2 we already presented some results for compression tests of cheese made from recombined and filled milk. These experiments were performed to study

- the effect of interaction between the fat particle and the casein micelle.
- the effect of the melting properties of the fat on the behaviour of cheese. We presented those results with the temperature influence.

The cheese was made from "milk" obtained by mixing skimmilk with an emulsion of milk fat or soy oil into skimmilk or whey (see section 4.2 for method). We also tried to make cheese from milk with palm fat, which is at the tested temperature range more rigid than milk fat. But we did not succeed in making a cheese from this milk which we could use for rheological testing, because the resulting cheese contained numerous holes and the curd particles were poorly fused. The reason for this may be a higher rigidity of the curd grains and larger defects, both possibly caused by partial coalescence of the more rigid fat particles during the cheese making process.

The fat or oil which was homogenized into whey resulted in globules with a coat consisting of whey proteins, which do not interact with the casein matrix (Roefs, 1986). The fat homogenized in skimmilk, on the other hand, gave casein coated globules, which thus will take part in the casein matrix. For acid milk gels it was found (van Vliet and Dentener-Kikkert, 1982), that fat particles with casein at their surface increased the modulus of the milk gel, whereas particles without casein somewhat decreased it. Therefore we expected the cheese made with fat, homogenized in skim milk, to be more rigid than the cheese with the fat homogenized in whey, because in the first cheese the fat particles will take part of the matrix (according to the theory of composite materials). However, we already indicated that the temperature behaviour of cheese made from natural milk (with fat globule membranes that certainly do not contain much casein) can be explained very well by the change in rigidity of the particles interacting

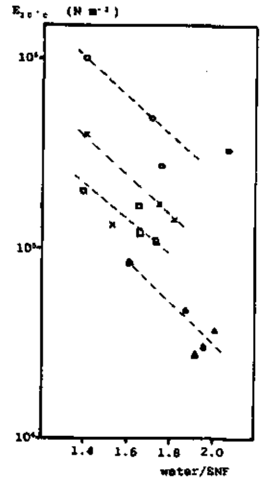


Fig. 4.11 Estimated compression modulus at 20°C (see text) of different cheese from recombined (O whey-low pH, X skimmilk-high pH) and filled (□ whey-low pH, △ whey-higher pH) milk as a function of the ratio water to SNF. $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

with the matrix. Another point is that the casein in cheese is broken down with ripening. This implies that, although the fat globule surface may contain casein, there are no chemical bonds between matrix and filler particle. Eventually interaction only can be caused by friction between the fat globule and the matrix and we can not imagine that this would be much different for the different fat globule surface layers.

In figure 4.11 the results for the moduli of the different cheese made from recombined milk are shown. The interpretation of the results is difficult because of the differences in water/SNF ratio and pH, but we may tentatively conclude that

- for cheese with soy oil, the milk with fat homogenized in skim milk and the milk with fat homogenized in whey did not give a significant different cheese.
- for cheese with milk fat, the milk with fat homogenized in skim milk did not yield a cheese with a significantly higher modulus than the milk with fat homogenized in whey.

A possible explanation of the lack of differences in the modulus between cheese made with fat particles covered with and without casein and of the increase in modulus of cheese made with natural fat globules with decreasing temperature (increasing E_f), may be that deformation of the matrix always is directly passed on to the fat particles, possibly by friction. Their is not a low-viscosity layer between matrix and filler, since the cheese will absorb added moisture, causing the protein mass to swell.

Literature results point to cheese made from homogenized milk being more firm and elastic than normal cheese (Emmons et al.,1980; Green et al., 1983). In these experiments, however, several simultaneous differences with the normal cheese existed:

- The fat globules were smaller and had a higher interfacial tension (due to the acquired protein coat). This implies that the fat particles have a far higher Laplace pressure, i.e. they are more rigid, and thus the cheese is more rigid too.
- Part of the fat surface is covered with casein. Therefore the fat particles will take part of the network.
- The water content of the cheese is higher. This decreases the modulus of the cheese.
- The fat content of the cheese is somewhat higher due to less fat loss in the whey. Dependent on the E_m, this may either increase or decrease the cheese modulus.

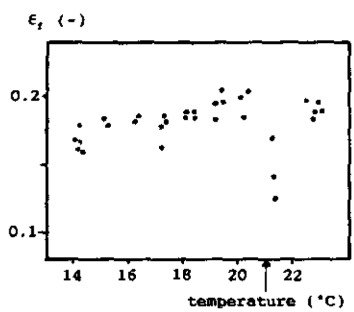
In figure 4.11, estimated values for the compression modulus of cheese from recombined and filled milk at 20°C are shown. We measured the moduli at 14°C and 26°C and assumed a temperature influence similar to figure 4.8. The compression moduli for the cheese from recombined milk were all higher than for a comparable normal cheese (compare figure 4.11 with figure 4.5). At high temperatures this can be explained by the difference in surface layer and in interfacial tension. For recombined milk fat globules the interfacial tension is about 10 times that for natural milk fat globules. Because the size of the fat particles was about the same (with homogenization we took care that the mean (volume/surface) diameter was always about the same and comparable to natural milk), the rigidity of the recombined fat globules was about 10 times that of natural fat globules. This higher filler modulus causes a higher rigidity of the cheese. At lower temperatures, however, the milk fat is partly crystallized and the network of crystals inside the fat particles caused this to be very rigid. Differences in surface layer will affect the rigidity far less. As a consequence the modulus of cheese made from natural milk and from recombined milk should differ at high (the modulus of the recombined cheese should be higher), but not at lower temperatures. The temperature influence, for example the ratio of E(14°C) to E(26°C), would be smaller for the cheese from recombined milk. This however has not be found (table 4.2). Also the moduli of the cheese at 14 and 20°C were not the same. Our results point to a higher increase in the modulus of cheese from recombined milk at the same fat content. Possible reasons (very speculative) may be a higher effective volume fraction of filler caused by aggregation of fat particles (van Vliet and Dentener-Kikkert, 1982) or more rigid fat particles caused by different crystal growth.

Sweating of cheese

When the temperature of the cheese becomes higher, at a certain moment fat droplets appear at the surface. At the same temperature (21-23°C) we once observed a small but clear decrease in the strain at fracture with compression (see figure 4.12). At higher temperatures the strain at fracture was again comparable to the result at 20°C.

The loss angle in dynamic experiments appeared to be almost independent of temperature for low temperatures, but it increased

Fig. 4.12 Influence of the temperature on the strain at fracture for a 1 year old standard cheese. $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}. At ↑ the cheese started to sweat.



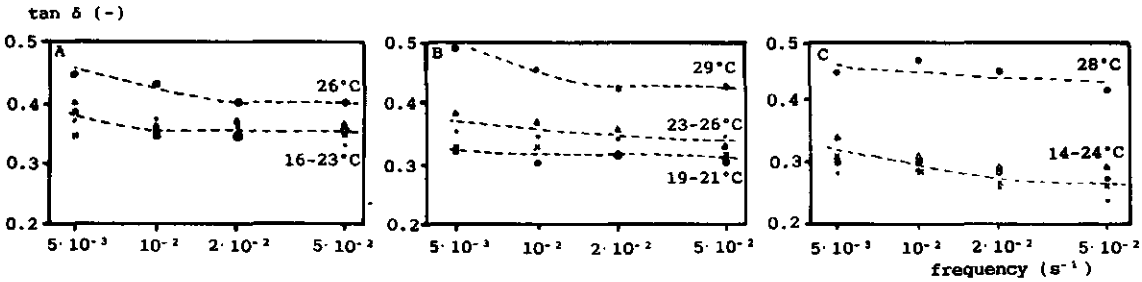


Fig. 4.13 Influence of the measuring temperature on the loss tangent in dynamic experiments for 3 different cheese.
A. 7 weeks old standard cheese.
B. 10 weeks old standard cheese.
C. ½ year old 60+ cheese.

for temperatures higher than about 23°C (figure 4.13), about the same temperature at which the fat droplets appear on the cheese. This possibly implies that the fat does not act as a plasticizer at temperatures below 23°C. Whether it acts as a plasticizer at higher temperatures is not completely clear; at 26°C the moduli are about as calculated for a casein-water matrix with separate liquid fat droplets, but the fat droplets on the outside and the increase in tan δ point to a more or less continuous fat phase.

Taking into account the results for the moduli of matrix and filler in cheese, a possible reason for cheese sweating at high temperatures, and for its occurance at somewhat lower temperatures for more mature cheese can be given. It is well known that in very mature and/or dry cheese the fat phase is continuous: fat can easily be pressed out. A possible reason for this may be that at higher temperatures the fat particles are less rigid than the matrix. With maturation the cheese dries out, the matrix modulus increases and the temperature at which E_m is larger than E_f than becomes lower. For very dry cheese, even at 14°C E_m is higher than E_f (for example $E_m = E_f = 6 \cdot 10^5$ N m^{-2} at 14°C if water/SNF = 1.2 or the water content is 38.5% for a cheese with 48% fat in the dry matter).

The transition from separate fat particles to a continuous fat phase may not happen spontaneously, the fat possibly has to be deformed. But already during maturation and/or small temperature changes deformations inside the cheese occur:

- Due to the drying out of the cheese mass the matrix shrinks and thereby deforms the fat particles.
- Due to (small) temperature changes the volume of the cheese changes. The relative swelling of the fat particles with increasing temperatures is much larger than the swelling of water: by increasing the temperature from for example 15 to 20°C the volume of milk fat particles increases by 2.4%, that of milk plasma, milk serum or water by only 0.1% (Walstra and Jenness, 1984). This swelling of the fat can be locally hindered by the matrix, especially if the latter is more rigid. Then the fat particle may (locally) be deformed, the strands between them can break and fat particles can coalescence.

Small deformation of fat particles can already result in (particial) coalescence of two adjacent particles because the distance between the globules is very small (in average 1.4 µm in a cheese with 48% fat in the dry matter with a d_{vs} of 3.5 µm and .7 µm in a 60% fat cheese, calculated according to Walstra, 1969). Such coalescence may be easier if the fat globule membrane has been attacked by enzymes during maturation.

4.3.3.2 Influence of fat on fracture behaviour

At higher deformations low fat and cream cheese behave differently. The shape of the σ-ϵ curve in compression differs more from a straight line for the 60+ cheese than for the 10+ cheese (see figure 4.7), indicating that for a cheese with a certain modulus less stress is needed at higher deformations if the cheese has a higher fat content. Reasons for this could be that the deformation of the fat particles is easier than that of the matrix material, or that there are also other fracture and yield phenomena in the material due to the presence of the filler particles. In table 4.8 the deviation from a straight line, expressed as the ratio of σ_f to $(E \cdot \epsilon_f)$ is shown for several types of cheese. For the cheeses made from natural milk this factor indeed is lower if the fat content is higher. But the results for the cheeses made

Table 4.8 90% confidence limit for the deviation from linearity of the stress strain curve calculated as X (= $\sigma_f/(E \cdot \epsilon_f)$) for different cheese.

cheese	temperature	X
from natural milk		
10+	20°C	0.56-0.73
48+	20°C	0.41-0.44
60+	20°C	0.31-0.41
from recombined milk (milk fat)		
60+	14°C	0.65-0.71
	26°C	0.59-0.72
from filled milk (soya oil)		
60+	14°C	0.30-0.43
	26°C	0.38-0.45

from recombined or filled milk do not support this. This indicates that the above mentioned possible reasons are not valid for cheese and we can not explain the observed phenomenon.

According to the theory of composite materials (section 4.3 1) the strain at fracture will decrease with increasing filler volume. The reason for this is the strain and stress amplification due to the presence of the filler particles. However, we could not find such an influence for cheese. Figure 4.14 shows that the difference in the strain at fracture for one week old Gouda cheese with a fat content in the dry matter of 10-60% must be ascribed to a difference in pH (the pH influence on the behaviour of cheese will be described in section 4.4.1). The fracture in cheese possibly starts at defects in the cheese causing a stress or strain concentration higher than that caused by the fat particles. The same kind of results were found for the cheeses made from recombined milk. The strain at fracture depended completely on the pH and the age of the cheese (see figure 4.15). An influence of the fat globule layer could not be found. The absolute values for ϵ_f, however, were somewhat lower for the cheeses made from recombined milk than for the cheeses made from natural milk;

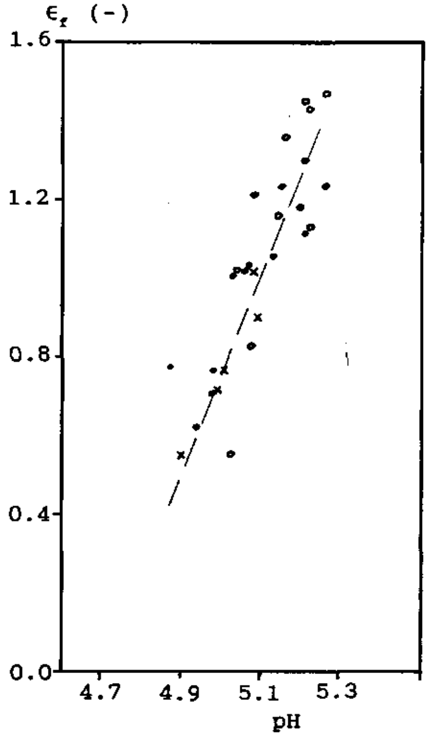


Fig. 4.14 Influence of the pH on the strain at fracture for a 1 week old cheese with 10 (●), 48 (○) and 60% (X) fat in dry matter. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

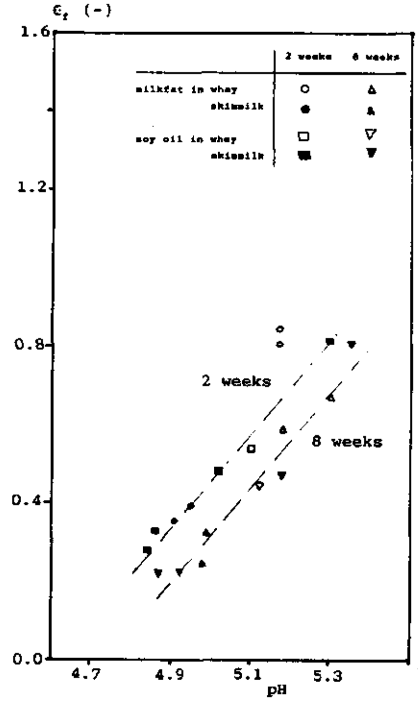
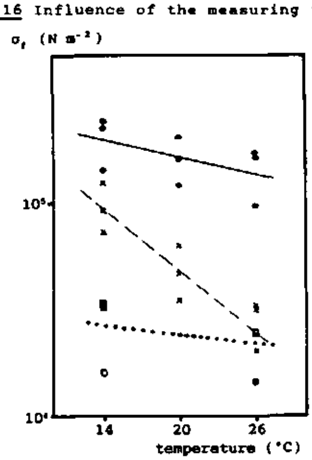


Fig. 4.15 Influence of the pH on the strain at fracture for 2 weeks and 8 weeks old cheese from recombined and filled milk. T = 20°C: $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

the cheese made from recombined milk was always shorter. A possible reason may be larger defects in the first cheeses.

The stress at fracture depends on the value for E, ϵ_f and X.

Fig. 4.16 Influence of the measuring temperature on the strain at fracture σ_f. $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.



line	cheese	age	water / SNF	pH
solid	10+	4 weeks	1.08	5.25
		2	1.25	5.12
		1	1.34	5.13
broken	60+	4	1.26	4.88
		6	1.28	5.05
		8	1.29	5.10
dotted	60+(soy)	8	1.39	4.87
		2	1.96	5.30
		2	1.62	5.10

Because the fat content does not influence ϵ_f, only E and X influence the fracture stress. The influence of the temperature on the fracture stress is shown in figure 4.16 for several cheese with about the same water-SNF ratio and pH but with different fat contents. From this it is very clear that cheese with liquid fat particles behaves different from cheese with more rigid fat particles.

The behaviour of 10+ and 60+ cheese in tension is different from that in compression. For compression we saw that the stress at fracture is lower for the 60+ cheese. In tension testing this is not so, as can be seen in figure 4.17. The stress at fracture as well as the strain at fracture were higher for the cream cheese than for the low fat cheese, although the ratio water/SNF and the pH and age of the cheese were similar. The difference between crack initiation and propagation was also the same for both cheeses. The values found for the stress at fracture in tension and in compression at about the same strain rate were similar for standard cheese (see section 2.4.1.3). This can also be found for cream cheese, but not for the low fat cheese (table 4.9). For the latter the fracture stress in tension is much lower than in compression. A reason for this may be the larger inhomogeneities estimated in low fat cheese. As can be seen in figure 4.17 the

Fig. 4.17 Overall stress at fracture σ_o in tension experiments as a function of the notch length l. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-3} s^{-1}.
(x) 60+ cheese: water/SNF = 1.99; pH 4.90
(o) 10+ cheese: water/SNF = 1.58; pH 4.89

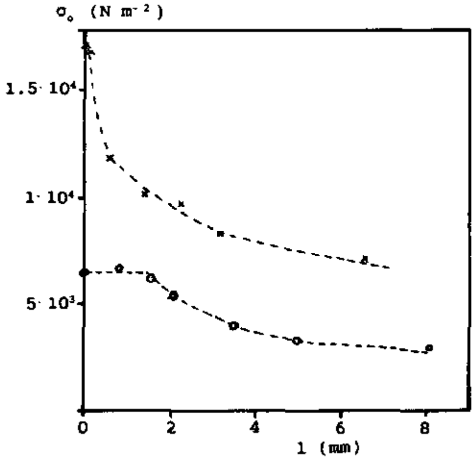


Table 4.9 Fracture stress in compression and in tension for different samples of cheese with 10 or 60% fat in dry matter. $T = 20^\circ C$; $\dot{\epsilon}_c = 2.8 \cdot 10^{-3}\ s^{-1}$.

cheese + age		fracture stress ($10^4\ N\ m^{-2}$)	
		compression	tension
10+	1 week	8.2	2.6
	1 week	5.2	0.65
	1 week	2.7	0.65
	5 weeks	4.4	1.0
60+	1 week	3.0	1.5
	6 weeks	2.4	2.4
	2 months	6.1	5.2
	2½ month	8.3	5.2
	5 months	3.0	5.5

stress and strain at fracture were independent of the notch length for this 10+ cheese at small notch lengths. For these notch lengths the fracture of the samples always started at other points in the test piece and not at the notch. This implies that the defects in the 10+ cheese caused a higher stress and strain amplification than the notch and also that these defects are much larger than those in standard and cream cheese. Large visually inhomogeneities in low fat cheese were also mentioned by Emmons et al. (1980). A reason for the large size of the defects may be poor fusion of the curd particles due to still extensive syneresis in low-fat cheese. It is not clear why these defects did not clearly decrease the stress and strain at fracture in compression. For other cheese with poorly fused curd particles (for example cheese of 0-3 days old, see section 5.3) a smaller fracture strain in compression had been found. Possibly the defects in standard cheese of 0 to 3 days old have a greater effect on the fracture behaviour than the defects in low fat cheese.

As a consequence of this the calculated apparent fracture energy R_s (not corrected for energy dissipation) was somewhat higher for the 60+ cheese than for 10+ as is shown in table 4.10. One would expect a lower value for the higher-fat cheese, because to frac-

Table 4.10 Range of values found for the fracture energy R_s for different cheese with 10 and 60% fat in dry matter.
T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-3}\ s^{-1}$.

age of cheese	R_s (J m^{-2})			
	natural milk		filled/recombined milk	
	10+	60+	60+(soya)	60+(milkfat)
1 week	1.3-3.5 2.1-3.8 1.5-2.0	1.8-3.8		
2 weeks			1.2-1.5 2.0-2.1 2.9-4.5 1.5-2.9	4.3-5.8 1.9-7.0
5 weeks	1.8-2.2			
6 weeks		2.0-6.1		
8 weeks			0.9-1.2 1.1-2.1 1.0-1.8	3.9-6.6
2 months	4.0-5.3			
2½ month		3.7-5.7		
5 months		1.5-4.1		

ture this less matrix material has to be broken per unit of fracture surface. This dependance was indeed found with cutting experiments on Cheddar cheese by Green et al. (1986). At the other hand, a higher fat content may increase the actual fracture area because the fracture path has to go around the particles and because the friction between the matrix and the filler particles can cause extra energy dissipation. The found value for R_s for the 10+ and the 60+ cheese were both somewhat lower than found for the standard cheese.It is possible that both factors mentioned cause a maximum toughness at a certain filler content, but too little experiments were performed to prove this.

There is some influence of the fat content on the notch-sensitivity of cheese. Unfortunately, we did not perform experiments with zero notch length for all the cheese tested, so we can only compare the results for higher notch lengths.

Table 4.11 Notch-sensitivity of two 10+ and 60+ cheese, calculated as the ratio σ_f for l=1 mm to l=5 mm.

cheese and age	$\sigma_f(l = 1\ mm)/\sigma_f(l = 5\ mm)$
10+ 1 week	2.30
60+ 1 week	1.49
10+ 5 weeks	2.07
60+ 6 weeks	1.86

In table 4.11 the decrease for the fracture initiation stress from l = 1 mm to l = 5 mm is given for different cheese. It appears that cream cheese is somewhat less notch-sensitive than low fat cheese. A possibly reason for this behaviour may be that fat particles in the notch tip blunt the notch and thereby decrease the stress concentration, possibly in the same way as when a tension experiment is done at slower deformations (see section 3.2.2).

4.4 Influence of pH, calcium and sodium chloride

As is shown in the previous section, cheese can be considered as a composite material. The casein network is the matrix; the fat particles are acting as a filler. Some compositional factors influence the behaviour of the filler, such as the amount and kind of fat (see section 4.3.3). Other variables determined the behaviour of the matrix. Examples of these are the water, the calcium and the NaCl content and the pH, which were studied in a range that is normal for Gouda cheese. The (possible) effects of other compositional factors have not been studied here.

The network in cheese consists of protein. This protein in swollen due to the water present. The water content therefore has a large influence on the matrix behaviour, as was discussed in section 4.3.2. In this section we will consider the influence of the pH (section 4.4.1), the calcium content (section 4.4.2) and

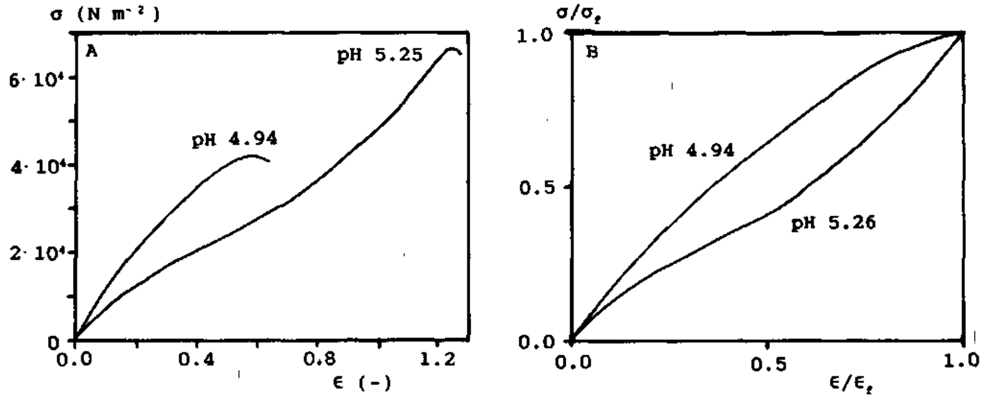


Fig. 4.18 A. Stress-strain curves in compression for 2 one week old cheese. (pH 4.94; 49.7% water, pH 5.26; 43.3% water) T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}.
B. The same results represented as the stress and strain relative to their values at fracture.

the NaCl content (section 4.4.3). Ca and NaCl influence are only studied in a limited concentration and pH range. Effects outside this range are probably very different, as is for example known for the Ca effect in high-moisture, high pH cheese (Noomen, to be published).

4.4.1 pH

To study the influence of the pH, we made cheese with different pH but with all other compositional factors constant (see section 4.2.1 for methods) and we changed the pH of test-pieces of standard cheese later on by absorption of HCl or NH_3 vapour (section 4.2.3). Examples of compression curves are in figures 4.18 and 4.19 for cheese of different pH but of the same age, ratio of water to solids-not-fat (SNF) and Ca and NaCl content. In figure 4.20 compression curves of test-pieces of which the pH was changed later on are shown. Results for compression experiments at different strain rates were shown in section 3.2.1. From these results it can be concluded that:

- The compression modulus decreased with increasing pH (pH 4.8 to 5.2), above this pH the modulus maybe increased again.
- The strain at fracture increased with increasing pH up to a

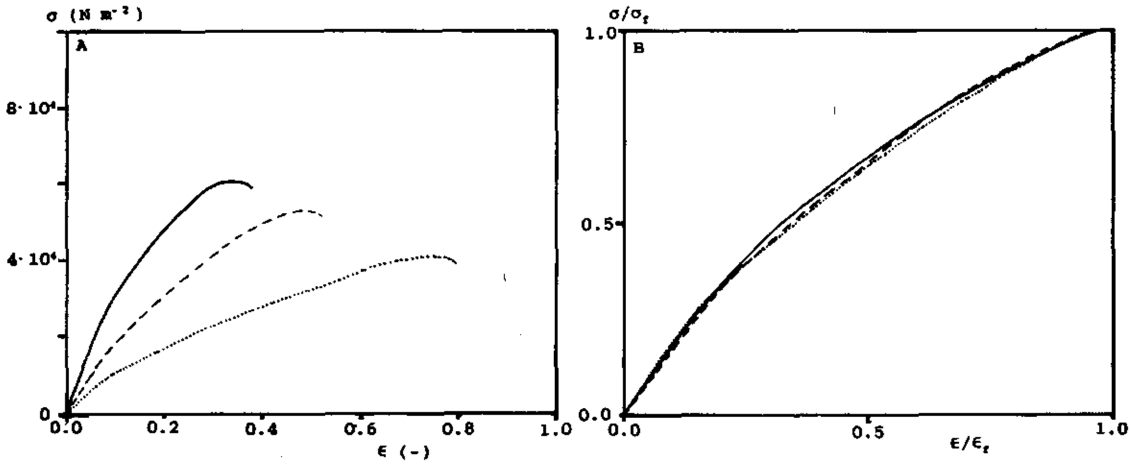
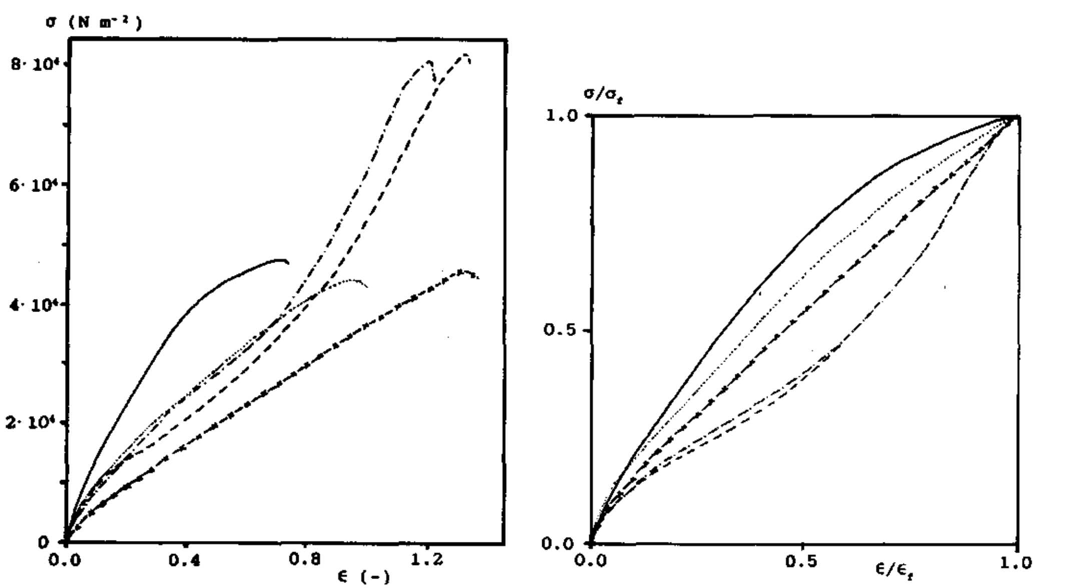


Fig. 4.19 Same as fig. 4.18 but 1 month old cheese
pH 5.01: 43.9% water (——), pH 5.12: 44.0% water (- - -), pH 5.18: 44.8% water (·····)

pH of roughly 5.3. Above this pH, ϵ_f decreased again. This is also shown in figure 4.21. The influence of the age of the cheese on this relation will be discussed in chapter 5.

Fig. 4.20 A. Stress-strain curves in compression of a one week old Gouda cheese. The pH was changed later on. pH 5.02 (——); 5.10 (·····); 5.20 (-x-); 5.43 (- - -); 5.58 (-·-·); T=20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.
B. The same results represented as the stress and strain relative to their values at fracture.



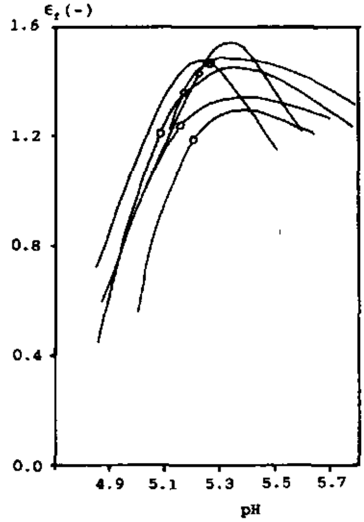


Fig. 4.21 Influence of the pH on the fracture strain of 6 different 1 week old Gouda cheese. The pH was changed later on. The original pH is given as O . T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.

- The shape of the compression curve depended on the pH and the age of the cheese. At a low pH the shape of the compression curve was convex over the whole range, at pH 5.2 and higher part of the curve was concave (only for young cheese).
- The influence of the strain rate on the fracture behaviour depended on the pH. At low pH the strain at fracture seemed to be constant; at a pH around 5.2 ϵ_f increased with decreasing strain rate. This has already been discussed in section 3.2.2. The results for the cheese manufactured with varying pH and for samples of cheese changed later on were not significantly different.

It was also found that the temperature influence did not vary with the pH of the cheese (results not shown). In the latter section we showed that the temperature influence could for the greater part be ascribed to the melting of the fat with increasing temperature. Therefore we did not expect the temperature influence to vary significantly with the pH, although this has been found for rennet skimmilk gels (Roefs, 1986). The results found for E and ϵ_f were consistent with the literature, although there the pH was not the only variable.

All these results point to a change in cheese behaviour around pH 5.2-5.35, possibly comparable with the change in casein micelles and the character of milk gels around the same pH (Roefs, 1986; Luyten et al., 1987).

At pH 6.7, most of the calcium and anorganic phosphate are part of the casein micelles, but they become soluble when the pH is decreased. At pH 5.3 all phosphate is transferred to the serum, but still about 14% of the calcium is in the micelles (van Hooydonk et al., 1986A). The remainder dissolves at still lower pH. The solubilization will diminish the interaction between the proteins, and this may cause swelling and dissociation of the casein. On the other hand, electrostatic repulsion between the casein molecules will diminish, due to a decrease in negative charge within the protein (the IEP of casein in milk is about pH 4.6; Walstra and Jenness, 1984) and near the IEP considerable electrostatic attraction between oppositely charged groups will occur. Jointly, these effects cause a maximum in the solubility of the proteins and in the voluminosity of the protein particles around pH 5.4-5.6 (Roefs et al., 1985; van Hooydonk et al., 1986A; Roefs, 1986).

This pH range is about the same as where changes in the behaviour of milk gels have been found:

- For rennet milk gels with pH 4.4 to 5.9, Roefs (1986) has found that around pH 5.2-5.3 a minimum in the storage modulus occurs. At both higher and lower pH G' increases, but this increase is steeper for decreasing pH. Van Hooydonk et al.(1986B) found a minimum in the elasticity modulus of a rennet milk gel around pH 5.3.
- Rennet milk gels showed a maximum in viscous character around pH 5.2 (Roefs, 1986): the loss tangent in dynamic measurements was at a maximum. At lower and higher pH the gel was more solid like, tan δ being lower. The decrease in tan δ is steeper for decreasing than for increasing pH.

These results for rennet milk gels fit in nicely with our results for the compression curves. The clear pH effect on the modulus of the more acid cheese (pH 4.8-5.2) and the far smaller pH effect at pH above 5.2 is very similar to the results for G' of rennet milk gels as found by Roefs (1986). The maximum fracture strain was found at pH 5.2-5.35, but especially the change in shape of the compression curve and the increase in ϵ_f with decreasing ϵ for very young cheese pointed to a more viscous-like character of cheese at pH 5.2-5.35 than at lower pH. However, this could not be confirmed by measurements of the loss tangent in dynamic experiments. In figure 4.22, tan δ of several cheese manufactured with varying pH and of samples of cheese changed later on is shown as a function of the pH. The distinct maximum at pH 5.2 found by Roefs (1986) was not observed for cheese. The loss tangent is about constant; maybe it decreased somewhat for very high pH. In contrast to this, a pH effect on the loss tangent has been found in dynamic experiments on high-moisture cheese. Cruysen (1987) found a higher tan δ for a cheese with pH 5.8 (water content≈55%; 7-50 days old) than for the same cheese with pH 5.3. Noomen (1983) found that a high-moisture cheese of pH 4.7 liquified when exposed to NH_3 vapour. For a 10 days old Gouda cheese with a water content of at least 50%, we also found a slight pH influence; the cheese with a pH of about 5.2 was more viscous-like than a cheese with a pH of about 4.9 (figure 4.23).

Fig. 4.22 Influence of the pH on the tan δ for different cheese of 4-8 weeks old, measured at a frequency of 10^{-2} s^{-1}.
X pH decreased from 5.48 with HCl.
● pH increased from 5.22 with NH_3.
○ natural pH of the cheese.
— results for rennet milk gels of 1 day old (Roefs, 1986).

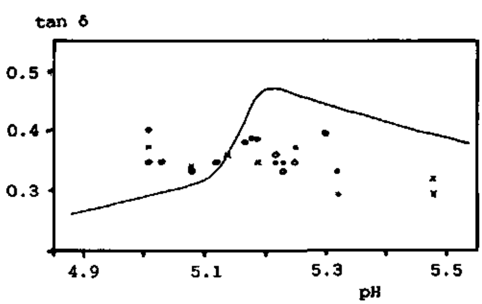
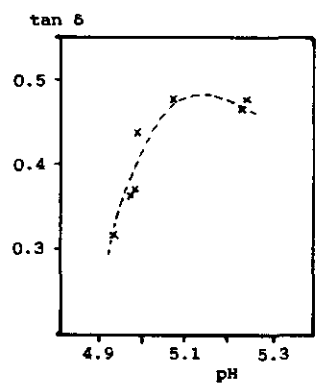
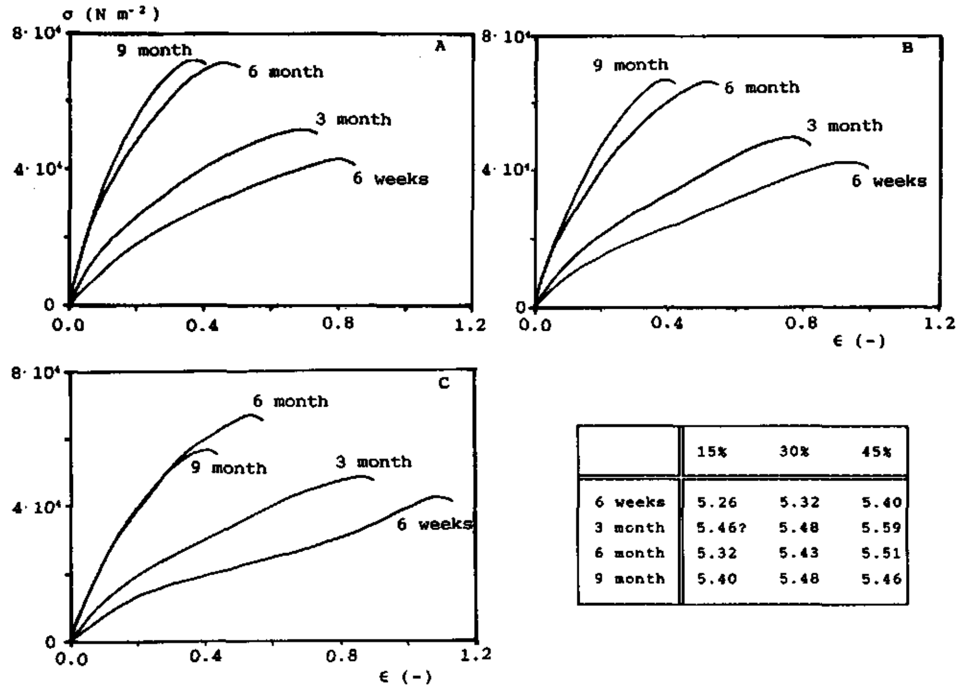


Fig. 4.23 Influence of the pH on the tan δ at 10^{-2} s^{-1} for a 10 days old cheese. The water content was at least 50%.





	15%	30%	45%
6 weeks	5.26	5.32	5.40
3 month	5.46?	5.48	5.59
6 month	5.32	5.43	5.51
9 month	5.40	5.48	5.46

Fig. 4.24 Stress-strain curves in compression for 3 different cheese at different age. The cheese was manufactured by applying different amounts of curd wash water: 15% (A), 30% (B), 45% (C). T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}. The pH is given in the table.

This difference in behaviour may possibly be caused by the different water content in respect to the transition point (section 4.3.2); the pH effect on the loss angle for lower water contents then would have been detectible at longer time-scales (lower frequencies). For eye formation, for example, (see section 6.3) it was found that the cheese flows at low stresses during long time scales (1 day$\approx 10^5$ s; $\dot{\epsilon} \approx 10^{-5}$ s^{-1}).

The effect of the pH on the behaviour of cheese (ϵ_f, shape of the compression curve) does also depend on the maturation of the cheese. In figure 4.24 compressive stress-strain curves at different maturation time for 3 cheese manufactured with different amounts of curd wash water are shown. The pH of the cheese was different, all other compositional factors were about constant. From this it is clear that for all maturation times, cheese with pH 5.2-5.4 has a higher strain at fracture than cheese with a

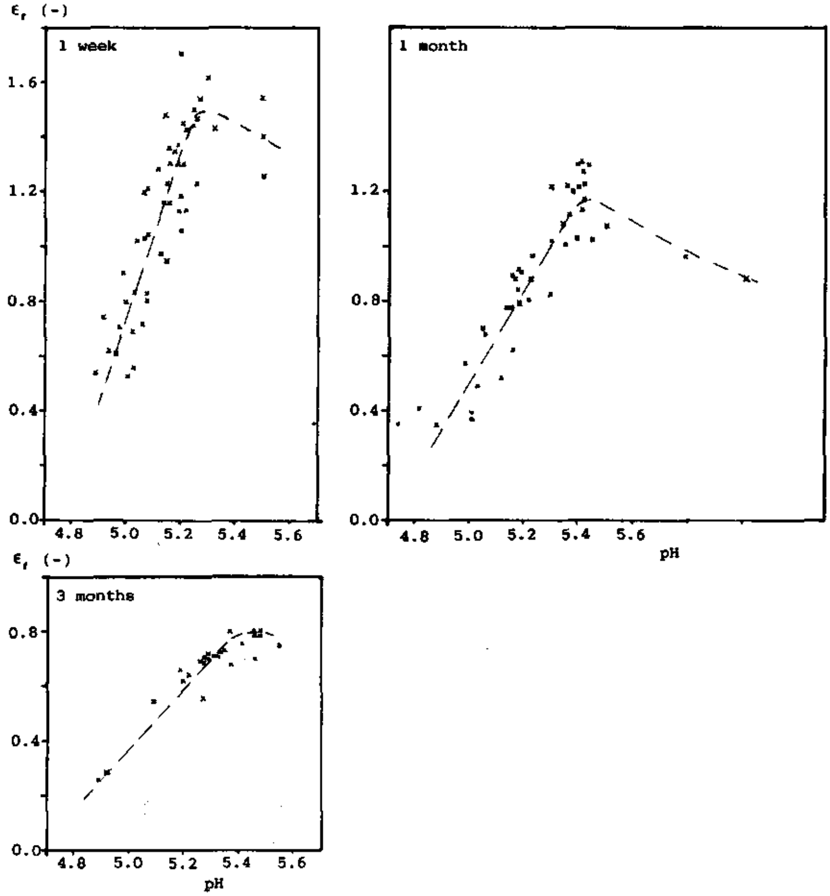


Fig. 4.25 Influence of the pH on the fracture strain for different maturation times. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.

lower pH, but differences become smaller for more mature cheese. This is shown for all measured cheese in figure 4.25. We will discuss this further in chapter 5.

Some of the cheese manufactured with varying pH has also been tested in tension. Results for the σ_f and ϵ_f were very similar to those found with compression tests (see table 2.6). Young cheese with a low pH seemed to be somewhat less notch-sensitive and had a smaller R_s than a young cheese with a higher pH (see figure 4.26A and table 4.12). The differences disappeared more or less when the cheese was more mature (figure 4.26B; table 4.12).

Table 4.12 Fracture energy (R_s in J m^{-2}) for 1 and 4 weeks old cheese with different pH, measured at $\dot{\varepsilon}_c$=2.8·10^{-3}s^{-1}.

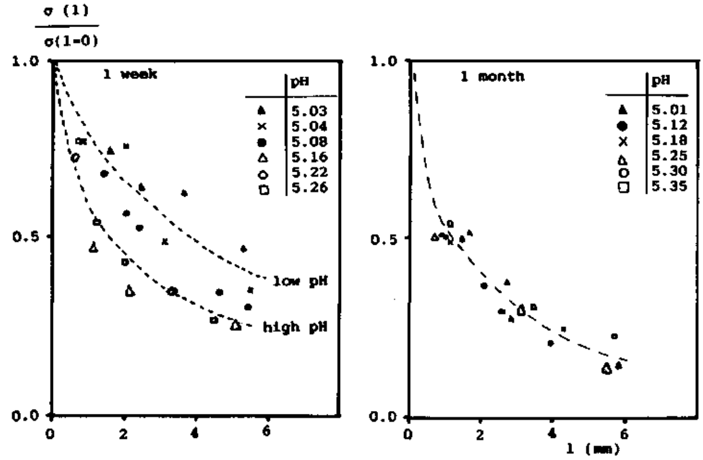
1 week		4 weeks	
pH	R_s	pH	R_s
5.03	1.6-2.3	5.01	1.3-2.4
5.04	4.0-6.4	5.12	2.3-3.0
5.08	2.1-4.4	5.17	4.6-10
5.22	10-20	5.18	3.0-3.6
5.26	10-18	5.30	5.2-9.6
		5.35	4.9-7.5

A possible reason for this behaviour may be the different behaviour of the casein matrix at different pH. At pH 5.2 the protein particles are more deformable than at lower pH and a greater part of the energy can be dissipated. Then less energy is stored and available for fracture, which then occurs at larger deformations. This will be discussed further in section 4.5.

4.4.2 Calcium

To study the influence of calcium, we made cheese with a varying calcium content but with all other compositional factors constant

Fig. 4.26 Overall stress at fracture relative to overall fracture stress for zero notch length in tension experiments as a function of the notch length l, for 1 week and 4 weeks old cheese of different pH. T = 20°C; $\dot{\varepsilon}_c$=2.8·10^{-3} s^{-1}.



(see section 4.2.1 for methods) and we changed the calcium content of test-pieces of standard cheese later on by absorption of small amounts of solution with varying $CaCl_2$ content (see section 4.2.3). In the pH range 4.9 to 5.3 and for a calcium content of 0.65 to 0.95% no influence of the calcium content on the compression curve and the loss angle could be observed (results not shown).

Very low or no influence was expected over the tested pH range because nearly all calcium and phosphate is dissolved. Influence of the calcium content at higher pH has been found for Camembert cheese. This cheese only liquifies if the calcium content is very low (Karahadian and Lindsay, 1987); otherwise calcium phosphate acts as a cross-linker between protein chains and prevents flow of the cheese mass. At lower pH the Ca is not bonded to the protein and no linking effect can be expected. The only influence may be that a higher concentrations of calcium increases the ionic strength of the aqueous phase, which could change the repulsion and attraction between ionic groups of the protein. This, however, is very small because of the high NaCl content (4% in water).

4.4.3 NaCl

To study the influence of the salt content, we changed it by absorption of constant amounts of different salt solutions by small samples of cheese (see section 4.2.3). The salt content thus was the only compositional difference.

In figure 4.27 compression curves of samples of the same cheese but with different salt content are shown. From this it is clear that:

- The modulus increased with increasing salt content. This is shown again in figure 4.28. The results agree very well with those of cheese brined in the usual way (compare 4% NaCl in water with results in figure 4.5, water/SNF of these cheese were 1.96 and 1.78, respectively).
- The strain at fracture decreased with increasing salt content.

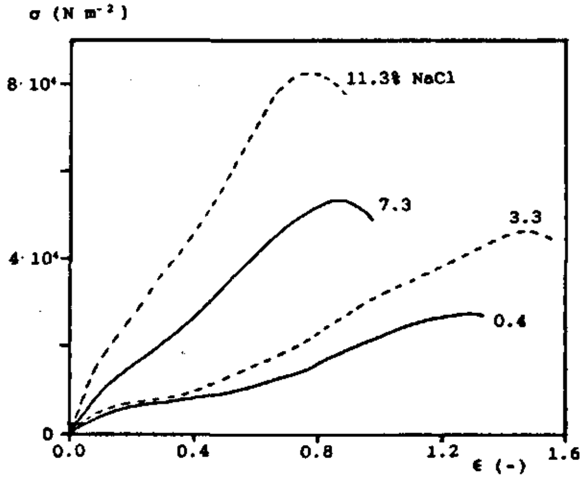


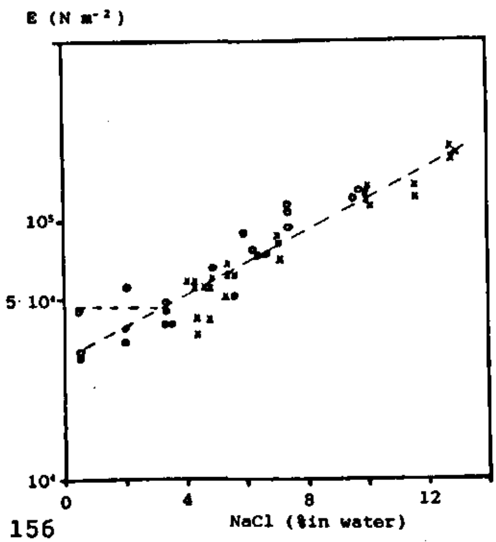
Fig. 4.27 Influence of the NaCl concentration (weight % in water) on the compressive stress-strain curves. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.

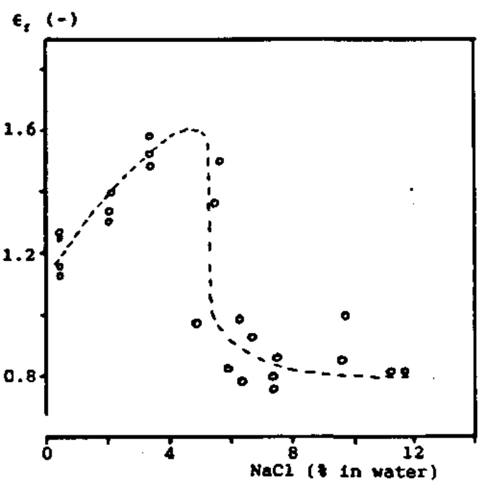
This is shown again in figure 4.29. From this it appears that the strain at fracture decreased suddenly at about 5% salt in water.

- The shape of the curve depended on the salt content. Cheese with less than about 5% salt in water seemed to have a more viscous-like behaviour.

Fig. 4.28 Influence of the NaCl concentration (weight % in water) on the compressive modulus. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.

Fig. 4.29 Influence of the NaCl concentration on the strain at fracture. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.





These results correlate with the chalky and brittle appearance of a high salt cheese and the more smooth appearance of a low-salt cheese. Geurts (1972) found that cheese directly after brining had a hard and brittle rind and a more soft and smooth centre. The transition was very clear and the salt content at this point was 7-12% in water. The pH very much affected this; at a pH lower than 5.0 there was almost no visible difference between the salt rind and the centre, both were brittle, hard and white.

The observations of Geurts and the decrease in ϵ_f with increasing salt content point to a salting out of the protein by the NaCl. This salting out effect is less pronounced at lower pH, where the casein is closer to its iso-electric point. We therefore expect a different influence of the salt content at different pH.

A possible explanation for the lower E and the more viscous-like behaviour of cheese (shape of the σ-ϵ curve) at lower salt contents is the extent of unfolding of the casein mass. Geurts (1972) found that cheese strips (pH 5.11) swelled when put in salt solutions containing 0.6% Ca and less than 8% NaCl. The cheese strips shrinked when the NaCl concentration was higher. One now may imagine that the protein molecules in a casein mass that has a higher extent of unfolding have more kinetic freedom. Because of this the compression modulus of the cheese will be lower and the shape of the compression curve different. We will discuss this further in section 4.5.

Our results compare well with those found in the literature.

- Creamer and Olson (1982) found for Cheddar cheese with 3.1-3.5% NaCl in moisture that adding a further 0.5% salt had no marked effect on the force-time curve. Figures 4.28 and 4.29 indicate that the difference in E and ϵ_f between, for example, 3.5 and 4.0% salt in water are within experimental error.
- Eberhard (1985) found for Appenzeller with a water to SNF ratio of about 1.2 and a salt content of 1.4 up to 5.8% that an increasing salt content gives a higher force at 20% compression and a lower fracture strain. The salt content was varied by brining.

- MPagana and Hardy (1986) varied the salt content of Mozzarella by brining and found the longer brined cheese to be harder (higher E) and more brittle (lower ϵ_f). It is not clear whether the water content was kept constant in these experiments.

With maturation, a cheese loses water due to protein breakdown and evaporation. The salt content in the moisture therefore increases. This certainly affects the behaviour of the cheese; E will increase and ϵ_f decrease. We will discuss this further in section 5.4.

4.5 General discussion and summary

In this chapter the influence of composition on the rheological and fracture behaviour of Gouda cheese has been discussed. Only variations in the range found normally for Gouda cheese were studied.

Cheese may be considered as a casein matrix filled with fat particles. The properties of the matrix and of the filler, as well as the interaction between them, are important for the behaviour of cheese.

The matrix of cheese consists of a swollen protein network. The protein can be found in small particles with a diameter of 10-15 nm in Gouda cheese (e.g. Hall and Creamer, 1972). The volume fraction of the protein particles in the cheese matrix must be very high; for casein in renneted skimmilk a solvation of about 1.5 g H_2O per g paracasein has been found (van Hooydonk, 1987B), in a standard Gouda cheese with 42% water in it the ratio water to SNF is about 1.4. This implies that the mechanical properties of the particles strongly affect the rheological and fracture behaviour of the matrix. Geurts (1972) found that cheese strips can swell or shrink when put in a salt solution (the amount of salt determined the extent of swelling or shrinking). Swelling can occur without really dissolving the cheese, although when an excess of a weak salt solution is added the cheese really can dissolve (Geurts, 1972). This implies that the protein particles can absorb water and thereby change their volume and that the protein particles are not covalently bonded. Because it is possible to add moisture (with the same composition as cheese moisture) to a Gouda cheese and this moisture is absorbed (see section 4.2), the protein particles themselves have a tendency to swell (the entropy increase due to 'dilution' of the particles probably is negligible). The extent of this will depend on conditions, for example the composition of the cheese.

The matrix properties of a cheese now depend on:

- the volume fraction of protein particles, which depends on the protein concentration (thus also on the water content) and on the voluminosity of the particles, thus on the extent of swelling.
- the viscosity of the liquid between the particles. Because it will not vary greatly among various cheeses, little influence is expected.
- the mechanical behaviour of the protein particles, i.e. their elastic and viscous deformability.
- friction between the particles.

In general we may assume that an increase in the state of swelling (or of the potential state of swelling if not enough moisture is present) or in the tendency of the proteinaceous molecules to unfold, will increase the elastic deformability of the protein particles and increase the viscous-like properties (this is the ratio of the amount of energy dissipation by the deformed particle to the amount of energy stored in the particle during a certain period of time (see section 2.3.4.1), thus a kind of tan δ of the particle). The first effect will decrease the modulus of the matrix, the latter effect will increase tan δ and probably ϵ_f. The effect of the extent of swelling of the particles on the friction between them is unclear: the possible increase in contact area (including more interpenetration of the protein molecules and particles) may increase the friction, but the higher deformability may decrease it.

Several factors may have an effect on the behaviour of the matrix (an outline is given in figure 4.30):

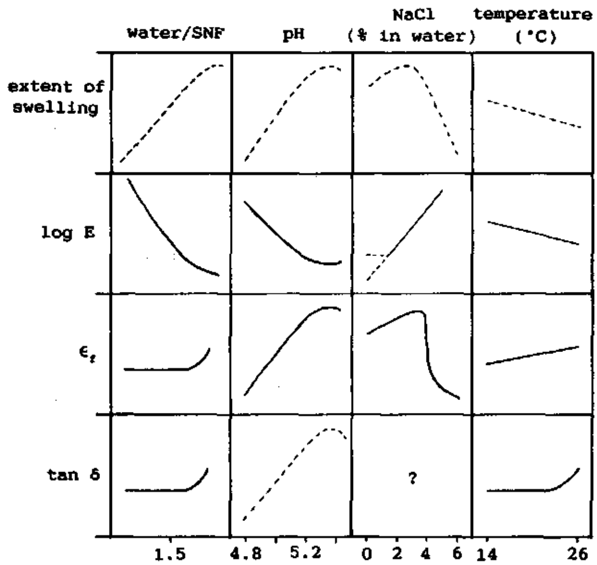


Fig. 4.30 Influence of water and NaCl content, pH and temperature on the behaviour of the matrix in cheese. See text for further explanation.

- The water content has two major effects on cheese behaviour:
  1. At a higher water content, the protein concentration in the matrix is lower. Because protein is the real stress carrying component of the network, a decrease in the protein concentration will decrease the modulus.
  2. At a higher water content the protein particles will be more swollen. Water can act as a kind of plasticizer and increase the freedom to move of (parts of) the proteinaceous molecules with respect to each other. This effect can increase the viscous-like properties of the cheese. This increases the deformability and the viscous-like properties of the particles, and thus possibly also of the cheese.

  In section 4.3.2 we found a decrease in the modulus with increasing water content. At very high water content we also found an increase in ϵ_f and tan δ, and we suppose these effects also to occur for a lower water contents (like in Gouda cheese), if we could measure over longer time scales.

A high-moisture cheese (for instance Meshanger cheese; de Jong, 1976) behaves very viscous-like at a time scale of seconds; it also looks more like a liquid.

- The voluminosity of casein or paracasein in milk is at maximum around pH 5.4-5.6 (Roefs et al., 1985; van Hooydonk, 1987B; Roefs, 1986). For rennet milk gels a minimum in the modulus and a maximum in the viscous-like character (tan δ) have been found around pH 5.2. Hall and Creamer (1972) observed that the protein particles in a more acid (and less Ca containing) cheese (Cheshire cheese) are smaller (i.e. about 5 nm) than in a Gouda cheese (i.e.10-15 nm).
Due to the greater voluminosity of the protein particles around pH 5.4-5.6, we would thus expect a higher modulus of the cheese in this pH region, but due to the higher deformability we would expect a lower modulus. For cheese we found a minimum rigidity and a maximum ϵ_f around pH 5.2-5.4, this implies that the latter effect probably is preponderant. The change in the properties of the proteins in milk, in milk gels and in young cheese with pH are probably similar. The influence of protein breakdown on these properties will be discussed in chapter 5.
An effect on tan δ was less clear in cheese. For young Gouda cheese with a high moisture content an increase in tan δ with increasing pH (from 4.8 to 5.3) was found (see figure 4.23).
In cheese with a lower water content we expect this effect to occur at longer time scales than we could apply.
- At high salt contents an increase in the NaCl concentration will decrease the volume of the protein particles (Geurts, 1972) and decrease their deformability. The first effect will result in a lower modulus, the latter effect in a higher one. The cheese matrix becomes more rigid and short (see section 4.3.3), indicating the effect on the elastic and viscous deformability to be preponderant. At low salt contents (0-4% in the moisture), the viscous character possibly increases with increasing salt content, since the cheese tends to swell in such conditions (Geurts, 1972). For cheese we found a small increase in fracture strain when increasing the salt concentration from

0 to 4 % (figure 4.29). A change in the rigidity in this range is less clear: the modulus may be either constant or somewhat increasing with increasing salt concentration (figure 4.28). The influence of the salt content on tan δ was not determined.

- With increasing temperature, the extent of swelling (unfolding) of the protein decreases (due to an increase in hydrophobic interactions; Roefs, 1986; Zoon, 1988), but the viscous properties markedly increase, especially at pH 5.2 (Roefs, 1986). Probably, the number of physical crosslinks (Zoon, 1988) and/or the friction between the protein particles and molecules decrease with increasing temperature. For cheese we found a small increase in fracture strain and tan δ. The modulus also decreases, but this was mainly due to the smaller rigidity of the fat particles.

Summarizing these effects, we conclude that increasing the extent of swelling (unfolding) of the protein, increases the deformability and viscous properties of the protein particles. This implies a decrease in the modulus and an increase in the fracture strain and tan δ of the cheese. These latter changes are not always noticeable, because measurements were only performed over a narrow range of time scales and changes may occur outside this range. It is therefore better to explain the changes in the behaviour of the cheese matrix with changing composition by a shift of the transition from a more solid-like to a more viscous-like behaviour to shorter time scales if the protein is more swollen (unfolded). This is schematically indicated in figure 4.31.

The type of fat used, its melting properties, the temperature, the strength of the crystal network and - at high temperatures- the size and the interfacial tension of the fat globules, determine the rigidity of the fat particles and this and the amount of fat present make up the influence of the fat on the cheese. We found no influence of the amount of fat on the fracture strain, probably because fracture started at defects causing a greater stress concentration than the fat particles.

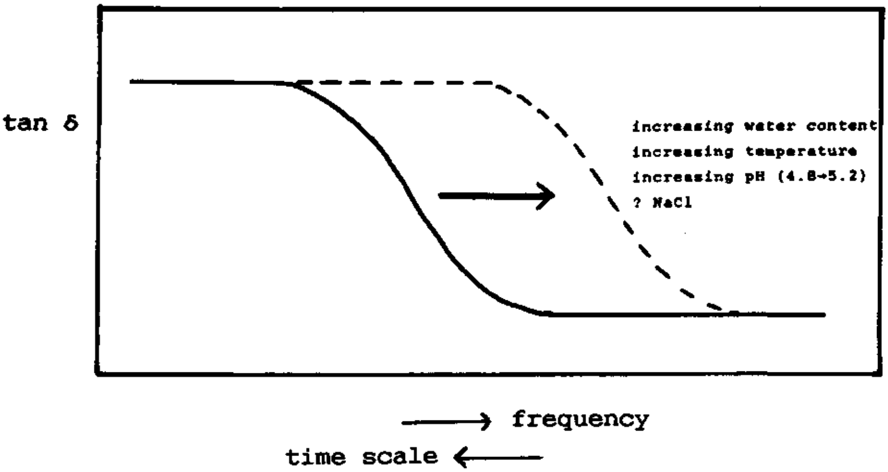


Fig. 4.31 Shift of the transition from a more solid-like to a more viscous-like behaviour to shorter time scales with changing composition (and temperature) of the cheese matrix.

Changing the interaction between the casein matrix and the filler, for example by using fat particles covered with and without casein, did not markedly affect the properties of the cheese. An explanation for this may be that in a ripened Gouda cheese, the protein is broken down and chemical bonds between the filler and the matrix do not exist in any case. Friction between matrix and filler, however, causes any deformation of the network to be directly passed on to the filler.

5. INFLUENCE OF MATURATION ON THE RHEOLOGICAL AND FRACTURE PROPERTIES OF GOUDA CHEESE

5.1 Introduction

Changes in cheese consistency with aging have been studied before (e.g., Mulder, 1946; Raadsveld and Mulder, 1949A; Creamer and Olson, 1982; Eberhard, 1985). For hard and semi-hard cheese it is mostly found that the cheese becomes harder and shorter during ripening. Interpretation of results is not easy because several changes occur simultaneous: water evaporation and enzyme reactions, in particular proteolysis. This results for Gouda cheese in:

- a lower water content
- a higher ion concentration
- protein breakdown
- a pH decrease during the first time (due to starter activity), after this an increase in pH (due to proteolysis)

The precise changes depend on cheese parameters (manufacturing procedure, size, composition), and ripening conditions (for example the temperature).

For hard and semi-hard cheese much attention has been paid to the influence of protein breakdown on the changes during ripening. Creamer and Olson (1982) found a high correlation between the breakdown of α_{s1}-casein and the shortness of Cheddar cheese. According to them α_{s1}-casein acted as a link in the protein network because it can interact with two or more other protein molecules (either α_{s1}- or β-casein). Consequently if the α_{s1}-casein molecule is cleaved so that it loses its ability to act as a link in the protein network, then the network would lose much of its strength. For soft high-moisture cheese it has been shown that the α_{s1}-casein breakdown regulates the softening of the cheese, independent of age (de Jong, 1977). For cheeses with a lower water content the observed result of α_{s1}-casein breakdown (as due to ripening) is different (see section 4.3.2).

In this chapter we will discuss the influence of maturation on the rheological and fracture properties of Gouda cheese. This cheese is made of curd particles (diameter = a few mm) which are pressed into one cheese block of a few kg. Hereby the curd particles have to fuse for the cheese to become one homogeneous mass. This fusion process will be discussed in section 5.3. The overall influence of maturation will be discussed in section 5.4 and the influence of proteolysis separately in section 5.5.

5.2 Materials and methods

The cheese making process is described in section 4.2.1. Samples were made according to section 2.2.1 and measured with the methods described in section 2.3. The composition and protein breakdown of the cheese were determined according to table 2.1.

5.3 Fusion of curd particles

5.3.1 Introduction

Cheese is made by renneting milk, cutting the gel, collecting the curd particles and pressing them together. This process causes several inhomogeneities to occur in the cheese:

- inside the curd particles there is an uneven protein network, which has also been found in the rennet gel (Roefs, 1985; Walstra and van Vliet, 1986; Zoon, 1988)
- due to syneresis, there are differences between the protein content in the rind and the centre of the curd grains (van Dijk, 1982; van Dijk and Walstra, 1986).
- an uneven fat distribution causes a difference between the central part and the outside of a curd particle. This is caused

by a mechanical removal of the fat globules during the curd making process (Mulder et al., 1966; Rüegg and Moor, 1987).

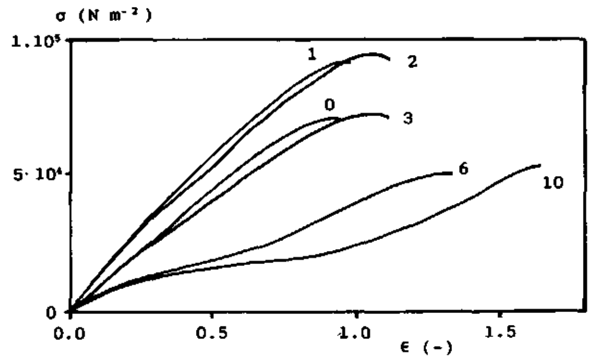
- the fusing of the curd grains can be incomplete.

It is not know how important the fusion of the curd particles is for the properties (esp. the fracture properties) of the cheese. One may imagine that insufficient fusion of curd particles causes fairly large defects in the cheese (of the order of the size of the curd particles, that is a few mm), and this causes the overall fracture stress and strain to be low. Poor fusion possibly may be caused by (considerable) syneresis of the curd particles continuing during pressing (for example in the 10+ cheese of section 4.3.3) or by a low deformability of the curd during pressing (high viscosity, for example, when the pH or the temperature is low) (Walstra and van Vliet, 1986). If the fusion of the curd particles is poor, it may be expected that fracture occurs around the original particles. If the fusion is good, it may be expected that the fracture path goes through the curd particles. Inside the curd grains the fat content is higher and therefore the fracture stress lower (see section 4.3.3). This was found in preliminary experiments: in just pressed cheese fracture occurred around the curd particles, while the fracture surfaces in cheese of 1 week old were smooth, i.e., the fracture path went through the curd grains.

5.3.2 Results and discussion

To determine the influence of the fusion of the curd grains on standard Gouda cheese, we studied the fracture behaviour of this cheese during the first 10 days. Also the influence of pH and ripening temperature were studied. Besides, the fracture surfaces were usually examined by stereo microscopy (amplification 10-40 times).

To avoid differences in behaviour between the samples due to a different salt content, the cheese was not brined. One percent NaCl was added to the cheese milk to avoid rapid spoilage. This



age	pH	water
0 days	6.60	51.8%
2	5.26	50.0
6	5.21	49.7
10	5.18	50.2

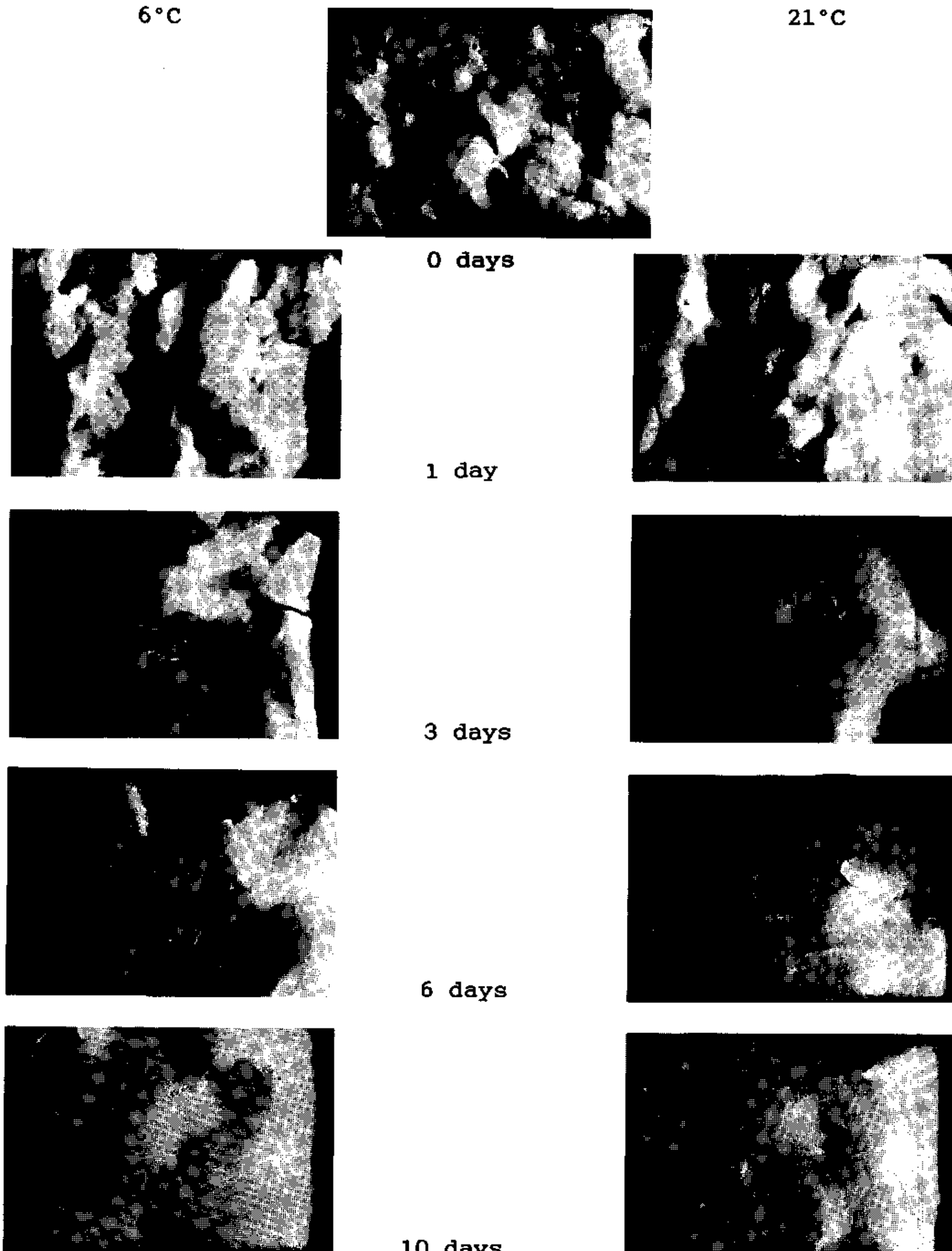
Fig. 5.1 Compressive stress-strain curves for a 0 up to 10 days old Gouda cheese. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}. Parameter is the age of the cheese in days.

had no effect on the rheological and fracture behaviour (results not shown). This was expected; in section 4.4.3 it was shown that increasing the salt in moisture content from 0 to 1% gave a constant strain at fracture, while the modulus increased somewhat, but not significantly.

Standard cheese

Examples for compression curves for a young standard Gouda cheese of 0 (directly after pressing the curd) up to 10 days old are shown in figure 5.1. It is seen that the modulus first increased somewhat, and decreased after 1-2 days. The strain at fracture increased after 3 days. The fracture surface of the 6 days old cheese looked different from that of younger cheese. For cheese samples up to 3 days old, the fracture surface was uneven (see figure 5.2, the temperature influence showed here will be discussed below) and fracture occurred around the original curd particles. Also the appearance of the surface depended on the direction of fracture. A horizontal fracture surface (see figure 5.3) looked more smooth and the curd grains were more flat, as compared to a vertical fracture surface. The reason for this is the deformation of the curd grains during pressing (Rüegg and Moor, 1987). For 6 days old or older cheese the fracture surfaces looked smooth (see figure 5.2) and the fracture path was through the curd grains.

Fig. 5.2 Fracture surface of a young Gouda cheese. Ripening temperature was 6°C (A) and 21°C (B). Parameter is the age of the cheese in days.



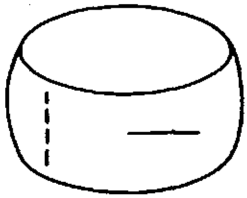


Fig. 5.3 Direction of a horizontal (——) and a vertical (---) fracture surface in cheese.

The fusion of curd particles probably consists of two processes:

1. flow of curd particles resulting in a larger contact area between the particles
2. formation of bonds between the network of curd particles in contact

As mentioned above, during pressing, the curd particles are deformed and the contact area between the curd grains is enlarged; most of the whey between the particles is removed. However, small whey pockets still remain after pressing and they can retard the formation of bonds between the network of curd particles. This whey first has to move away and the resultant space has to be filled with curd; these processes probably occur by diffusion, since the pressure gradients probably are very small. Assuming the size of these whey pockets to be about 0.1 mm, and diffusion of the protein to occur within a few days, the effective diffusion coefficient would have to be about 10^{-13} m^2 s^{-1}, which is not an unlikely figure, taking into account that a casein network in the presence of enough water has a rather viscous-like character (Roefs, 1986; Zoon, 1988).

If syneresis still is considerable, as, for instance, in low-fat cheese, whey pockets between the curd grains may not fully disappear and the curd may fuse incompletely (see section 4.3.3).
After the formation of a contact area between the curd grains, new bonds must be made. The speed of this process will also be determined by diffusion.

Which of both processes determines the time needed for fusion is unknown. Before new bonds can form, a large contact area must be formed. This implies that the speed of this process determines the maximum speed of the fusion. The effect of both processes hardly can be distinguished. For instance, a low pH causes the curd particles to be less deformable during pressing, the syneresis to be higher (Walstra and van Vliet, 1986) the network material to be less viscous-like (Roefs, 1986) and the effective diffusion coefficient to be smaller.

Anyway, the curd particles in a standard Gouda cheese appear to be fully fused after 6 days. The deformability of the cheese clearly changed between about day 2 and 6 (E decreased strongly). Also the shape of the stress-strain curve changed: up to 3 days it was convex, at 6 to 10 days part of the curve had a concave shape. The latter points to a more viscous-like character of the cheese mass after 6 days than up to 3 days old. The loss angle increased somewhat during the first week (measured at 50% water, results not shown). Possibly, this increase in viscous-like character, increases the speed of formation of new bonds, thereby enhancing fusion.

The reason for the decrease in the modulus is uncertain. A possible reason is the breakdown of the protein. In section 4.3.2, however, we found no influence of the maturation period (proteolysis) on the modulus, but this concerned with cheese of 1 week and older where a large part of the casein (in Gouda cheese about 40% of α_{s1}- and β-casein; Visser, 1977) is already hydrolysed. Proteolysis may also be the reason for the increase in viscous-like behaviour (observed as an increase in tan δ) during the first days of ripening.

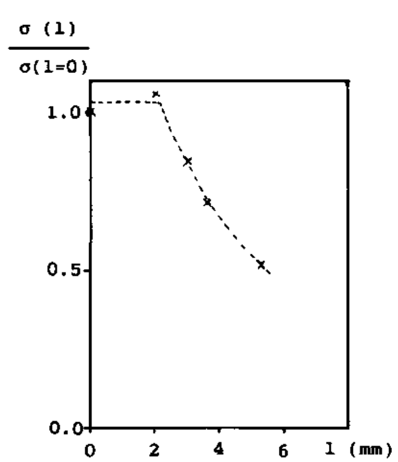
Another possible reason for the decrease in the modulus perhaps could be the change in homogeneity in the curd particles during the first days after cheese manufacturing. Directly after cheese manufacturing, the outer layer of the curd particles has a lower water content and a higher protein content than the central part of the curd grains. This outer layer therefore will be more rigid than the central part and can cause the cheese matrix to be more rigid as well. To obtain a more homogeneous curd particle, protein and water have to diffuse. Assuming a diffusion coefficient of 10^{-13} m^2 s^{-1}, diffusion occurs over about 0.2 mm within 5 days, which implies that the increase of homogeneity within the curd particles could be a possible reason for the decrease of the modulus. However, the diffusion of the water may be somewhat faster, would imply this process to occur faster.

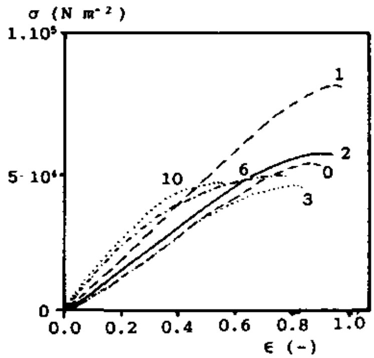
To determine the size of the defects in the cheese at different age, we also did tension experiments with a notch in the sample. The performance of these experiments was difficult; fracture quite often started near the grips and onset of breaking was difficult to determine, because the fracturing was slow in the young cheese (see section 3.2.3). We therefore were not able to support the results of the compression tests and the change in appearance of the fracture surface by tension experiments. The deviation in results was much too large to calculate the size of the defects, as was possible for the 10+ cheese in figure 4.15. An example of some (rare) good results we found is shown in figure 5.4. From this we may estimate a defect size of about 2 mm in the very young cheese. This size compares well with the size of curd particles.

Influence of pH

The behaviour of cheese of one week and older was found to be pH dependent (section 4.4.1). The strain at fracture increased with

Fig. 5.4 Overall stress-notch length curve for a 3 days old cheese. The stress is given relative to the overall stress at zero notch length. T = 20°C; $\dot{\varepsilon}_c = 2.8 \cdot 10^{-3}$ s^{-1}; pH 5.33; water 50.0%.





age	pH	water
0 days	6.16	53.7%
1	5.06	48.5
3	5.02	49.6
6	4.92	48.3
10	4.89	48.1

Fig. 5.5 Compressive stress-strain curves for a 0 up to 10 days old Gouda cheese with a low pH. $T = 20^{\circ}C$; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$. Parameter is the age of the cheese in days.

increasing pH up to a maximum around pH 5.2-5.35. In this range the modulus decreased with increasing pH. The cheese is possibly less deformable and less viscous-like at lower pH. We therefore expected the fusion in a cheese with a lower pH to be less than that in a standard cheese.

In figure 5.5 compression curves for a low pH cheese of 0-10 days old are shown. After 3 days the strain at fracture did not increase and the modulus did not decrease, in contrast with standard cheese. Fusion was less than in standard cheese; in some low pH cheese there were more small openings, but most cheese was well fused and the fracture path went through the curd grains. Maybe the decrease in pH was not enough or not fast enough to slow down the fusion of the curd grains. The pH during the first 3 days (when the fusion is not complete, but possibly already advanced) never was below 5.0.

In figure 5.6 the strain at fracture is shown as a function of the pH for different ripening times. The fracture strain seemed to be independent of the pH if the curd was not fully fused, this is up to 3 days. After this the same pH dependence as observed for standard, brined cheese of one week old (figure 4.25) was found.

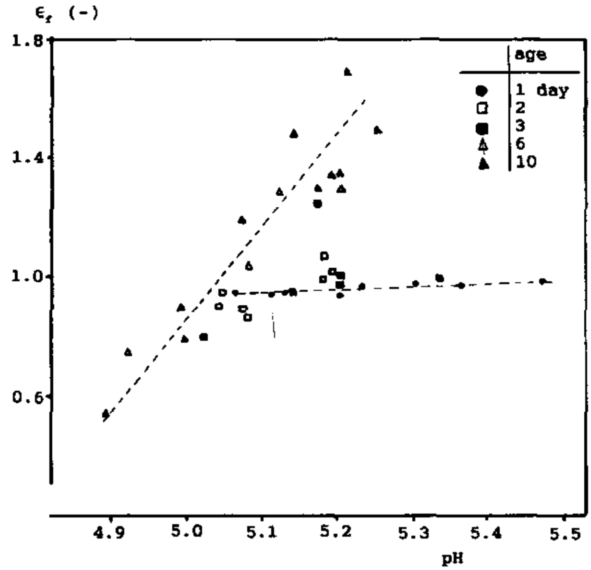


Fig. 5.6 Influence of the pH on the fracture strain for different maturation times. T = 20°C; $\dot{\epsilon}_c=2.8\cdot10^{-2}\ s^{-1}$.

Influence of the ripening temperature

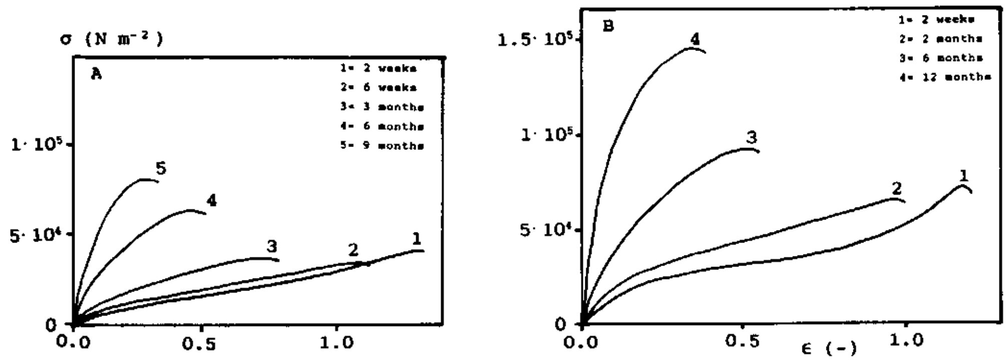
At lower temperatures cheese is much more rigid (section 4.3.3). We therefore expected the ripening temperature to influence the fusion of the curd; this would be better at higher temperatures. To examine this, cheeses from one batch were kept at 6°C and 21°C after pressing and the fracture behaviour was compared. At 6°C the water content of the cheese decreased less and the pH was somewhat higher. But these differences were within the range studied above.

In figure 5.2 fracture surfaces of the different cheese at different age is shown. The fracture surface of a 3 days old cheese kept at 21°C is somewhat smoother and the curd grains are more difficult to distinguish than when the cheese was ripened at lower temperatures. All cheese fractured through the curd particles when 6 days old. Differences in the experimental results for the stress-strain curves (measured at 20°C, results not shown) could be completely ascribed to the small differences in pH and water content.

Discussion

From the experiments described above can be concluded that:

- complete or nearly complete fusion of the curd particles in standard Gouda cheese takes place within a week.
- before the curd is enough fused, the fracture path goes around the curd particles. The appearance of the fracture surface is rough and depends on the direction of breaking, the strain at fracture is pH independent. The defect size probably has the same order of magnitude as the curd grains: a few millimeters.
- after more or less complete fusion of the curd particles the fracture path goes through the curd grains. Fracture strain then is determined by the internal curd structure and is pH dependent. The cheese is isotropic regarding its fracture behaviour. The defect size is 0.1-0.3 mm (see section 3.2.3). This is smaller than the curd grains and larger than irregularities in the cheese like fat globules and the unevenness of the network (table 3.7). A cause of the defects in Gouda cheese may be imperfections in the fusion of the curd grains. The fracture path, however, goes through the curd grains because the fracture strength there is lower because of the higher fat content. In the junction zones the fracture stress is higher due to the high protein content (low fat content and low water content, the latter due to syneresis of the curd particles).
- Fusion may be somewhat slower at 6°C than at higher temperatures (14 and 21°C).
- The fusion process possibly is determined by two different processes: 1/ the formation of a (large) contact area between the particles and 2/ the formation of new bonds between adjacent curd particles. The effect of both processes could not be distinguished by means of the experiments performed.
- Between day 2 and 6 after cheese manufacturing, the deformability and the viscous-like behaviour of the cheese increased. Possible reasons could be the curd grains to become more homogeneous and/or the protein breakdown.



age	figure A water	figure A pH	figure B water	figure B pH
2 weeks	43.1%	5.24	41.1%	5.20
6 weeks	42.3	5.50?		
2 months			39.0	5.25
3 months	41.3	5.35		
6 months	38.2	5.39	29.4	5.54
9 months	36.7	5.42		
12 months			26.8	5.51

Fig. 5.7 Stress-strain curves in compression for Gouda cheese of different age. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$. A. a 12 kg cheese. B. a 2 kg cheese.

5.4 Influence of maturation

Maturation of cheese greatly affects its rheological and fracture behaviour. In figure 5.7 compression curves of two different standard cheeses, tested at different age are shown, a 12 kg (5.7A) and a 2 kg cheese (5.7B). In section 3.2.3 and 3.2.4 also some differences between young and more mature cheese were described. From these results it may be concluded that:

- The compression modulus increased with ripening time. The value for E is higher for the smaller cheese, the water content in this cheese is distinctly lower. In section 4.3.2 it was found that variation in the compression modulus can (almost) exclu-

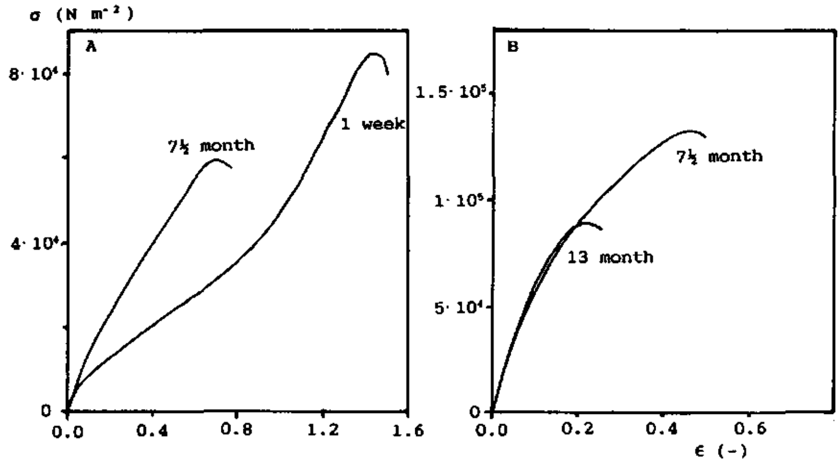


Fig. 5.8 Stress-strain curves in compression for cheese with different maturation times but with the same water content. Same cheese as in figure 4.3. $T = 20°C$; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}\ s^{-1}$.
A. 1 week old: 41.9% water, 7½ month old: 41.4% water
B. 7½ month old: 32.3% water, 13 months old: 31.6% water

sively be ascribed to variation in the water content. The influence of the water to SNF ratio on E was given for cheese of different age in figure 4.5. Because of this dependence we think that the increase of E with age is caused by the decreasing water content (and possibly somewhat by the increasing salt concentration). The experimental results for E for the different sized cheese (different water content at the same age) fitted exactly in figure 4.5. Wodecki et al. (1984) already found that the firmness of cheese can be regulated by controlling the evaporation of water. Their results agree with ours. In figure 5.8 compression curves for different cheese with the same water content (changed later on) but with different age are shown. This also indicates that the modulus does not depend on the age, but (almost) only on the water content.

- The strain at fracture decreased with increasing ripening time. This is shown in figure 5.9A. From this it is clear that there is no unequivocal relation between the strain at fracture and the age of a cheese. For cheese of 1 to 4 weeks old the fracture strain may range from 0.35 to 1.7, for cheese of 1 year old from 0.18 to 0.27. A fracture strain of, for instance, 0.35 can be found for a cheese of 9 months old, but also for an acid cheese of 1 month old. It therefore is not possible to predict the age of a cheese by measuring the shortness alone.

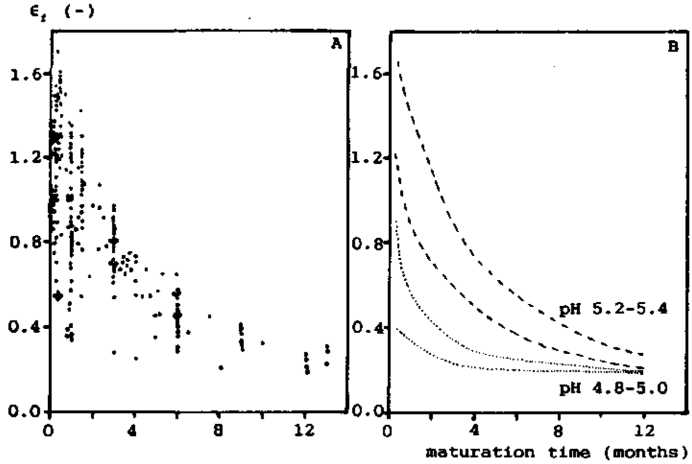


Fig. 5.9 A. Strain at fracture as a function of ripening time for different Gouda cheese. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.
B. Range of fracture strain as a function of ripening time for different Gouda cheese with pH 5.2-5.4 and with pH 4.8-5.0. T = 20°C; $\dot{\epsilon}_c$=2.8·10^{-2} s^{-1}.

In section 4.4.1 (figure 4.25) we already showed that the pH of a cheese influenced the fracture strain very much. The large difference in ϵ_f for young cheese can be ascribed to differences in pH (figure 5.9B). The fracture strain is determined largely by the ripening time and the pH.

The precise reason for the decrease in fracture strain with increasing ripening time is not clear. The decrease in water content as such can not be the reason, because a mature cheese with the same water content as a younger cheese also has a lower fracture strain (see figure 5.8). The increasing ionic strength due to the decrease in water content can have a small effect (section 4.4.3) but the largest influence possibly have to be ascribed to the protein breakdown. We will discuss this further in the next section.

- In section 3.2.3 it has been shown that the notch-sensitivity of a cheese decreased with increasing maturation. Experiments independent of water content have not been done. During maturation the protein is broken down, which causes fewer protein-protein contact points, and the water content decreases, which causes an increase in friction within the material. The overall effect possibly is caused by a decrease in total strength of the shear connections between rows of material (see section 3.1.1).

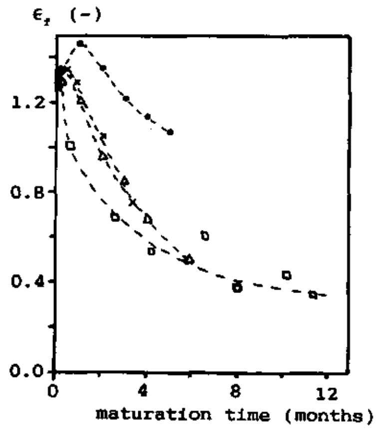
- Flow properties of the cheese change with maturation (section 3.2.1 and 3.2.2). For a young Gouda cheese with pH 5.2-5.4 an influence of the strain rate on the strain at fracture was found. This influence disappeared with maturation, at least within the time scale of the experiments. The fracture energy of a Gouda cheese decreased with maturation (section 3.2.4). In section 6.1 we will explain that these effects may be caused by protein breakdown and loss of water.

5.5 Influence of protein breakdown

During maturation cheese becomes harder and shorter. The first effect is due to the decreasing water content. The reason for the second is not yet clear. In literature the shortness is ascribed to protein breakdown (e.g. Creamer and Olson, 1982), but for hard cheese this has not been proved independent on maturation time (i.e. independent of variations in water and salt content). Figure 5.8 indicates that maturation as such indeed decreases the strain at fracture. We therefore expand on the influence of proteolysis in this section.

5.5.1 Introduction

A recent review of the acting of proteolytic enzymes in hard cheese has been given by Visser (1981).The principal pathway of proteolytic breakdown during the ripening process is thought to be the one by which rennet causes a primary, limited, degradation of the caseins after which the starter bacteria produce smaller peptide fragments and free amino acids. In first instance rennet cleaves α_{s1}-and β-casein to produce α_{s1}-I and β-I casein, still large fragments. This step determines the extent of the proteolysis in cheese. The depth of proteolysis is principally determined by the action of the bacterial enzymes.



symbol	type of cheese	literature reference
•	Emmentaler	Eberhard (1985)
Δ	Greyère	Eberhard (1985)
x	Appenzeller	Eberhard (1985)
◻	Cheddar	Creamer and Olson (1982)

Fig. 5.10 Strain at fracture as a function of ripening time for different cheese.

De Jong (1977) has found a direct relation between the α_{s1}-casein breakdown and the liquification of a high-moisture cheese (Meshanger). According to Creamer and Olson (1982) the first cleavage of α_{s1}-casein determines the shortness of hard cheese. This conclusion can, in principle, explain the difference in shortness between Emmentaler and, for instance, Cheddar cheese (see figure 5.10). During the manufacturing of Emmentaler cheese, rennet enzymes have been inactivated and the breakdown of α_{s1}-casein would be much slower. The fracture strain of this cheese at a certain age therefore is higher. It is tempting to conclude from this that the extent of proteolysis regulates the shortness of hard and semi-hard cheese, but one must be aware that there are more differences between these cheese.

Differences in protein breakdown can be caused by:

- different maturation periods. This has been described in the latter section.
- different rennet concentration in the cheese, for instance by varying the amount added to the cheese milk. De Jong (1977) has used this method for studying the influence of the α_{s1}-casein breakdown in Meshanger cheese. With a higher rennet concentration the extent of proteolysis is increased, the depth of proteolysis is almost unchanged. The amount of rennet present in a standard cheese is affected by manufacturing conditions; a lower pH of the curd, for instance, increases the amount of rennet associated with the paracasein (Walstra et al., 1987).

- varying the ripening temperature. At higher ripening temperatures proteolysis is increased. Roefs (1985) found for rennet milk gels at pH 4.6 and with no starter bacteria present, an clear increase in α_{s1}-casein (and a small increase in β-casein) breakdown with increasing temperature (5-15-25°C) for 1 to 6 days of 'ripening'. In a model cheese (pH 5.2; 4% NaCl in moisture), where only rennet and plasmin were present, Noomen (personal communication) could find no influence of the temperature (4-14-24°C) on the extent of proteolysis. In cheese an increasing amount of soluble nitrogen (indicating increasing proteolysis) with increasing ripening temperature has been found by several workers (e.g.Raadsveld and Mulder, 1949; Fedrick and Dulley, 1984; Eberhard, 1985). Eberhard (1985) found for Emmentaler cheese that an increase of the ripening temperature from 5°C to 20°C increased the extent of proteolysis somewhat less than the depth of proteolysis. These results indicate that the action of the bacterial enzymes certainly is enhanced by increasing the ripening temperature, a change in the proteolytic action of the rennet enzymes is less certain.
- the type and amount of starter. The depth of proteolysis is determined by the action of the bacterial enzymes. Eberhard (1985) found higher amounts of NPN and a lower strain at fracture for cheese when using a more proteolytic type of starter.
- adding enzymes to the cheese or using other enzymes instead of calf rennet. Sood and Kosikowski (1979) added microbial enzymes to cheese and found an increased casein breakdown. According to them the fracture strain also decreased, but looking at their compression curves we are not so sure about their conclusion. Law and Wigmore (1982) added neutrase or proteinase R to Cheddar cheese milk. In the cheese they found an increased α_{s1}- and β-casein breakdown as well as an increased amount of soluble N and amino acid N. In sensory testing, the cheese with added enzymes was less firm and more crumbly. The compression curves gave about the same informa-

tion; the stress at fracture (and possibly also the compression modulus) were smaller for the cheese with added microbial enzymes. The authors also found a relation between the protein breakdown and the fracture strain of the cheese, regarding the results given in their publication we think this conclusion to be doubtful.

- the composition of the cheese. Proteolytic action depends, for instance, on the pH or the salt concentration (Noomen, 1978); but changing the composition causes many other changes in consistency than those originating from protein breakdown.

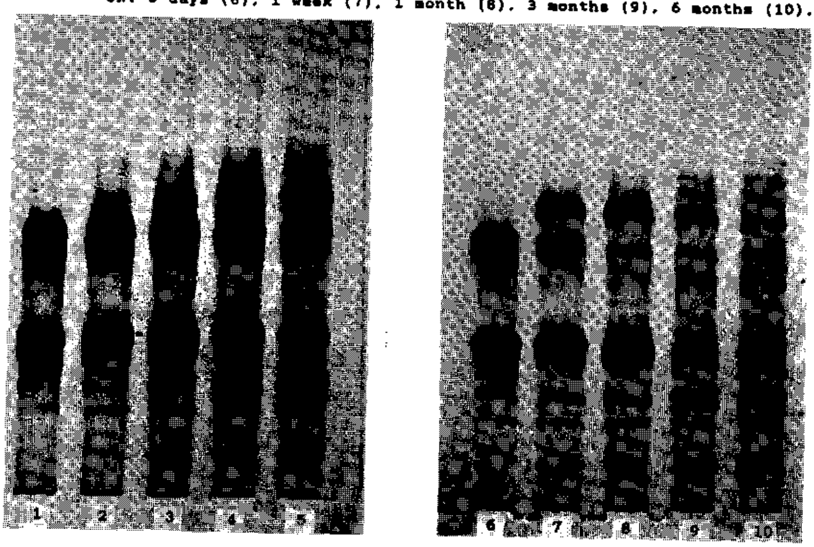
In this study we only investigated the influence of rennet concentration and ripening temperature on the rheological and fracture behaviour of Gouda cheese. Further experiments, for example with added enzymes, would be very useful.

5.5.2 Results and discussion

Influence of rennet concentration

Cheese with different amounts of rennet (the normal amount (=N),

Fig. 5.11 The PAE patterns of Gouda cheese with ¼N and 3N amount of rennet after different periods of time. ¼N: 0 days (1), 1 week (2), 1 month (3), 3 months (4), 6 months (5).
3N: 0 days (6), 1 week (7), 1 month (8), 3 months (9), 6 months (10).



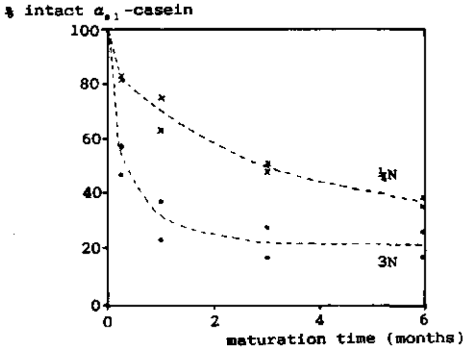
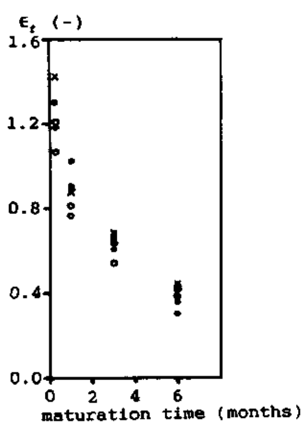


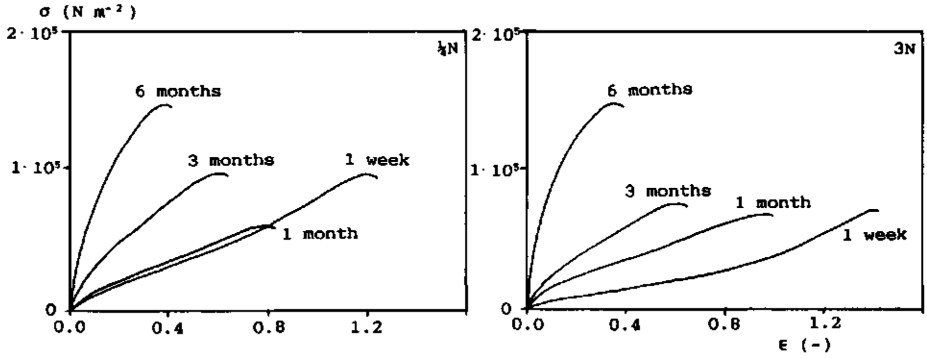
Fig. 5.12 The breakdown of α_{s1}-casein in cheese with ¼N (×) and 3N (●) amount of rennet.

¼N, ½N and 3N) but with about the same composition, was made according to the description in section 4.2.1. Differences in rennet concentration indeed caused differences in protein breakdown as is shown in figure 5.11 and 5.12. Especially the α_{s1}-casein breakdown increased with increasing rennet concentration. Also Visser (1977) found that higher rennet concentration increase the α_{s1}-casein breakdown. There was essential no effect on the depth of proteolysis, that is on the starter enzyme activity.

Compression and dynamic shear experiments were performed with samples of these cheese. Examples of compression curves are in figure 5.14. Comparison of figures 5.14A and 5.14B shows that there is only a small influence of the rennet concentration on the compression curves. In figure 5.13 the fracture strain during maturation is shown for cheese with different rennet concentra-

Fig. 5.13 Strain at fracture as a function of ripening time for Gouda cheese manufactured with different amounts of rennet. ½N(●); ¼N(×); 3N(○). T= 20°C; $\dot{\varepsilon}_c$=2.8·10^{-2} s^{-1}.





age	¼N		3N	
	water	pH	water	pH
1 week	44.0%	5.18	42.7%	5.16
1 month	40.1	5.30	40.8	5.23
3 months	36.5	5.22	35.5	5.19
6 months	30.4	5.32	28.1	5.27

Fig. 5.14 Stress-strain curves in compression for Gouda cheese manufactured with ¼N and 3N amount of rennet. Parameter is the age of the cheese. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}.

tions. This decrease of ϵ_f with maturation is for each rennet concentration the same as found for standard Gouda cheese. Differences in ϵ_f could be completely ascribed to differences in pH (results not shown). A higher α_{s1}-casein breakdown did not cause the cheese to be shorter (lower fracture strain). There may be a small difference in the rigidity of the cheese caused by the different protein breakdown. In figure 5.15 the compression modulus of cheese with different amounts of rennet is shown as a function of the water to SNF ratio. All results of the cheese with ¼N rennet are somewhat higher than those of other cheese, indicating a more rigid cheese when the α_{s1}-casein is less broken down. However, the differences are not significant and the results for ½N rennet are not supporting the relation. In figure 4.5, it was already shown that the modulus of a cheese depends on the water content and is independent of ripening time. The results of figure 5.15 imply that, there is at most a small influence of the extent of proteolysis on the rigidity.

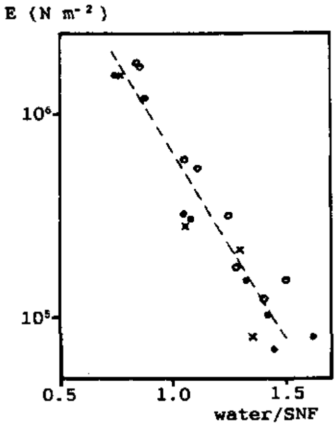


Fig. 5.15 Compression modulus E as a function of the water to SNF ratio for Gouda cheese manufactured with different amounts of rennet, ¼N(●); ½N(×); 3N(○). T = 20°C; $\dot{\varepsilon}_c$=2.8·10^{-2} s^{-1}.

In figure 5.16 the results for the loss tangent in dynamic experiments for cheese of different rennet content are shown. The values found for tan δ for the cheese with 3N rennet (figure 5.16) were about independent of ripening time and similar to the results for standard cheese (figure 3.13). However, the value for tan δ measured for cheese with ¼N rennet decreased with maturation. In section 4.3.2 we showed that an increasing water content can increase the viscous properties of the cheese and for example increase the tan δ. With maturation the water content of a cheese decreases and the protein is broken down. Our hypothesis is that a decreasing water content decreases the loss tangent and that proteolysis increases this value. The simultaneous change of both causes the tan δ to be roughly constant during ripening of stan-

Fig. 5.16 Tan δ as a function of the frequency of dynamic measurements for cheese manufactured with 3N (A) and ¼N (B) amount of rennet, measured at different ripening times:
1 week(×); 1 month(○); 3 months(Δ).

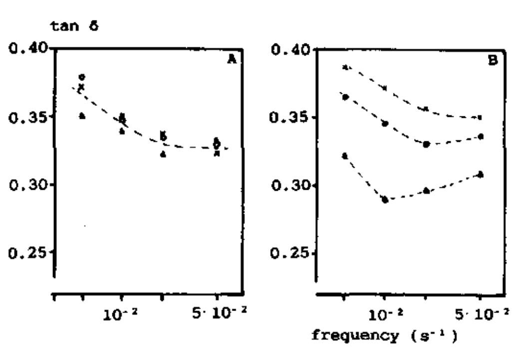


Table 5.1 The composition of cheese ripened at different temperatures. Example of results after 6 months ripening.

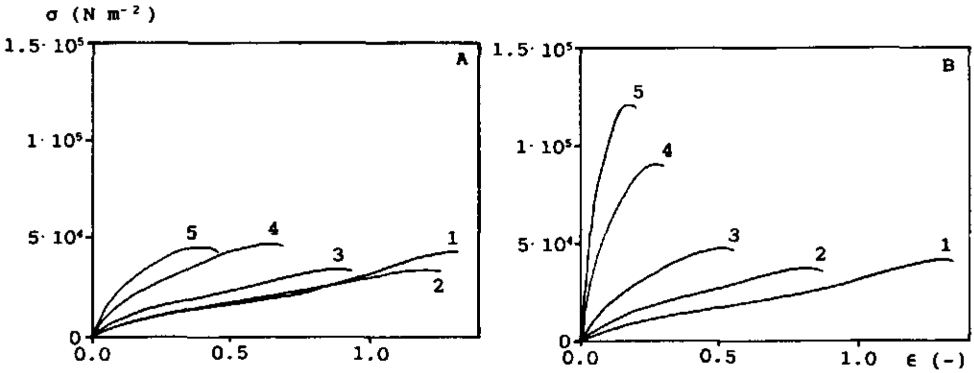
	ripening temperature			increase 8 to 18°C
	8°C	13°C	18°C	
water (%)	39.0	37.7	36.5	
pH	5.52	5.49	5.51	
SN/TN (%)	29.2	32.7	39.7	+ 36%
AN/TN (%)	5.8	7.1	9.7	+ 67%

dard cheese. This implies that when the extent of proteolysis is less, and the water evaporation is not different, tan δ decreased. Energy dissipating properties of Gouda cheese are thus somewhat influenced by the extent of proteolysis, but not to that extent that the fracture strain is altered.

Influence of ripening temperature

To study the influence of the temperature during maturation, cheeses from one batch were ripened at different temperatures, i.e. 8, 13 and 18°C. This was done twice. With increasing temperature the water content decreased faster and the protein breakdown increased faster (table 5.1). Soluble nitrogen (SN) as well as amino acid nitrogen (AN) increased. However, the increase in the extent of proteolysis (% SN in TN) was less than the increase in depth of proteolysis (%AN in TN).

Examples of compression curves are shown in figure 5.17. Cheese ripened at higher temperatures was more rigid (higher compression modulus) and shorter (lower fracture strain). The higher compression modulus can completely be ascribed to the different water content; all data fitted exactly in the curve shown in figure 4.5. The influence on the fracture strain is shown again in figure 5.18. From this it is clear that ϵ_f is lower for cheese ripened at higher temperature. This lower value for ϵ_f may have been caused by the lower water content (see section 4.3.2), the higher NaCl content (section 4.4.3) or the more extensive protein

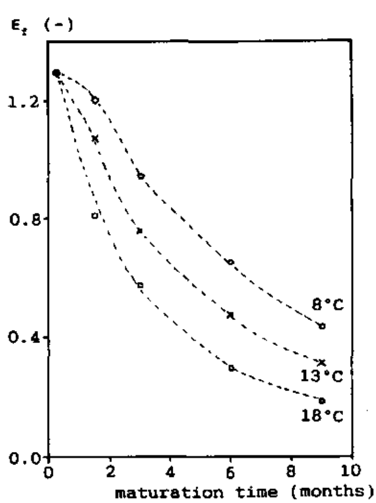


age	8°C (A)		18°C (B)	
	water	pH	water	pH
1 = 2 weeks	43.1%	5.24	43.1%	5.24
2 = 6 weeks	43.2	5.43	41.4	5.44
3 = 3 months	42.4	5.32	39.7	5.33
4 = 6 months	39.7	5.44	37.4	5.40
5 = 9 months	38.4	5.45	35.3	5.44

Fig. 5.17 Examples of stress-strain curves in compression for Gouda cheese ripened at 8°C (A) and 18°C (B). Parameter is the age of the cheese. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}.

breakdown. Differences in fracture strain with different ripening temperatures were, however, quite large and the differences in

Fig. 5.18 Strain at fracture as a function of ripening time for Gouda cheese ripened at different temperatures. Same cheese as in figure 5.17. T = 20°C; $\dot{\epsilon}_c = 2.8 \cdot 10^{-2}$ s^{-1}.



water content (and thus also in salt content) relatively small. Therefore, increased protein breakdown as caused by a higher ripening temperature, have to influence the fracture strain.

Discussion

From these preliminary experiments on the influence of proteolysis on the consistency of Gouda cheese it may be concluded that:

- the breakdown of α_{s1}-casein into large fragments is probably not a sufficient cause for a Gouda cheese to become short (smaller fracture strain).
- shortness is increased by increasing proteolysis in depth, i.e. the splitting of proteins into small peptides and amino acids.
- protein breakdown does not (significantly) influence the rigidity of a Gouda cheese. The modulus E (at a certain pH) is determined by the water content and the ionic strength.

These results are not in contradiction with results found in literature. Most workers studied the effect of proteolysis by comparing cheese of different age. Then the extent as well as the depth of proteolysis were varied, and the cheese indeed was shorter. Eberhard (1985) studied proteolysis and cheese consistency of varying cheese types. He concluded that the extent of proteolysis caused a cheese to become softer and that the depth of proteolysis caused a shorter and firmer cheese. We do agree with his conclusions about the cause of shortness, although we doubt whether this was a right conclusion from his results. However we do not agree with his conclusion on the effect of proteolysis on the firmness on cheese. Possibly, the change of firmness found by Eberhard is due to his definition of firmness (force at 33.3 % compression or at fracture) and to differences in water content.
The exact reason for a cheese to become short during ripening still is unknown. The explanation often given in the literature (the cheese becomes shorter if α_{s1}-casein, that acts as a link in the protein network, is cleaved) could not be confirmed. Possibly, the large fragments that are formed with the first breakdown of the casein, are so large that the network in the particles still

can be deformed quite far. The high fracture strain of young cheese can be due to the ability of the large protein molecules and fragments to deform and stretch. This is much less so for smaller fragments, thus in cheese which is more ripened.

Due to proteolysis the viscous-like character of the protein mass in cheese increased. This is very clear at a high water content. A Meshanger cheese, for instance, will liquify due to ripening. In Gouda cheese, however, this could not be found, presumably because of the lower water content.

For a very young Gouda cheese we did find that the fracture strain increased with decreasing strain rate. This points to a more viscous-like behaviour of the cheese mass in the considered time scale. For more mature cheese, ϵ_f did not depend on the strain rate in the time scale considered. The transition to a more viscous-like behaviour possibly has been shifted to longer time scales, because of the lower water content (see section 4.5). It is thus likely that a young Gouda cheese with a very low water content will neither show a strain rate dependent fracture strain, but experiments to confirm this have not been performed.

6. GENERAL DISCUSSION

6.1 The rheological and fracture behaviour of Gouda cheese

In section 4.3 cheese was regarded as a swollen protein matrix filled with fat globules. The fat globules act as a filler: the particles influence the rigidity of the cheese, according to their modulus and volume fraction. No influence of the fat on fracture strain was found (section 4.3.3).

Gouda cheese is a visco-elastic material (section 3.2.1). The flow and fracture behaviour for the most part depend on the properties of the matrix, i.e. the swollen protein particles. Similarities between the extent of unfolding of these proteins, the viscous-like character and the fracture strain do exist, as was discussed in section 4.5 (see also figure 4.30). These properties determine the energy dissipating processes in the protein matrix. Outside the latter energy is also dissipated due to fracture and due to friction between components: by motion of the protein matrix with respect to the fat globules or by liquid moving through the protein matrix. In accordance with formula 3.9, the next equation may be written:

$$W = W' + W_m'' + W_f'' + W_f \tag{6.1}$$

W = total energy input
W' = stored energy
W_m'' = dissipated energy due to network flow
W_f'' = dissipated energy due to friction between components
W_f = energy used for fracture

It is not quite sure whether both energy dissipating processes (besides fracture) play an essential role in the viscous and fracture behaviour of Gouda cheese, but it offers us an opportunity to give a (qualitatively) explanation for some influences found. For a young cheese with a not too low pH, it has been found that the fracture strain increased with decreasing strain rate (see section 3.2.2), possibly due to flow of the casein matrix. This implies that the term W_m" must be important. The importance of W_f" is less clear. Deformation of the cheese matrix is passed on to the fat particles, due to friction between these two structural elements (see section 4.3.3). The friction causes energy to be dissipated. This effect then would increase the deformation energy needed for a certain strain, the more so for a higher fat content. However, we found the stress to decrease with increasing fat content (see table 4.8). This possibly can be explained by the large differences in deformation between the different components, causing extra stress concentration, which effect will be larger than the friction.

In a very young cheese (just pressed) movement of moisture with respect to the cheese mass may clearly occur. When pressing a finger on such a piece of cheese, one can see moisture coming out of the cheese. This moisture probably is the whey that can be found between the curd particles in a just pressed cheese. This indicates movement of liquid relative to the curd particles. For such a few hours old Gouda cheese, values for σ_f and ϵ_f of about 10^5 N m^{-2} and 1.0, respectively, can be found (see figure 5.1). The total energy input up to fracture (W) then is about $5 \cdot 10^4$ J per m^3 cheese. During compression quite some liquid is pressed out of the cheese. The energy needed for this flow can be very roughly estimated by assuming:

- the moisture content of the cheese to be 50%. 10% of this moisture can be found in the spaces between the curd particles and about half of this amount actually flows. This is not an unlikely figure: when compressing a sample of 20 mm height and 15 mm diameter, this would imply that 0.1 ml moisture flows, which is roughly equal to what can be seen.
- a Poiseuille flow to occur through capillaries with a radius (r) of about 5 to 50 µm (≈ the radius of the pores between the curd particles).
- the cause of this flow being a stress difference (ΔP) of $5 \cdot 10^4$ N m^{-2} over the radius of the sample, i.e. over 7.5 mm (=L).

- the viscosity of the cheese moisture being twice that of water ($\eta^* \approx 2 \cdot 10^{-3}$ N s m^{-2}).

The strain rate of the moisture ($\dot{\gamma}_1$) now can be calculated according to

$$\dot{\gamma}_l = \frac{r \, \Delta P}{2 \, \eta^* L} \qquad (6.2)$$

and the energy dissipated per unit volume of liquid moving relative to the curd particles and per second:

$$W_f'' = \eta^* \cdot \dot{\gamma}^2 \qquad (6.3)$$

From this, and the amount of liquid moving per unit volume of cheese, the energy dissipation per unit of volume of cheese can be estimated. Calculated results for different pore radii are shown in table 6.1. The total energy input up to fracture, however, is not more than $5 \cdot 10^4$ J m^{-3}. This means that even if a smaller proportion of the moisture in cheese actually flows during deforming of the cheese or if the other assumptions made are not completely right, the flow would nevertheless cause a considerable

Table 6.1 Calculated values for the strain rate of the liquid phase and the energy dissipation due to movement of liquid in respect to the curd particles in a few hours old Gouda cheese. See text for further explanations.

r (µm)	$\dot{\gamma}_1$ (s^{-1})	W''_{fl} per m^3 cheese ($J \ m^{-3}$)
5	$8.3 \cdot 10^3$	$7.7 \cdot 10^4$
10	$1.7 \cdot 10^4$	$3.1 \cdot 10^5$
50	$8.3 \cdot 10^4$	$7.7 \cdot 10^6$

amount of energy dissipation in proportion to the total energy input W.

This energy dissipation due to movement of liquid in respect to the cheese mass, must be far less important in more mature cheese. Certainly no moisture comes out when pressing on a piece with stresses smaller than σ_f. The pores within the matrix are (much) smaller. Due to protein breakdown, the viscosity of the moisture in the protein matrix has increased. With further ripening, there is not any more a distinct low viscosity liquid within the matrix and eventually it is even questionable whether we may distinguish between a matrix and a liquid.

The discussion above is only qualitative. Up till now no good calculations can be made, because too many parameters have to be guessed. It would therefore be useful to study model systems for which the two different energy dissipating processes can be distinguished and measured separately. However, some tentative qualitative conclusions can be drawn:

1. Viscous properties of the protein matrix certainly are important (see section 4.5) for the rheological and fracture behaviour of Gouda cheese, and in several conditions probably the most important mechanism.
2. The flow of liquid through the matrix possibly may be an important process during deformation of very young Gouda cheese.
3. Because both mechanism probably are less important in more mature Gouda cheese, friction between fat particles and the protein matrix may than play a larger part.

6.2 Comparison between the behaviour of cheese and of milk gels

Gouda cheese is made of a renneted milk gel. The matrix material of both is the same, namely para-casein. Milk gels have been studied extensively (e.g. van Dijk, 1982; Roefs, 1986; Zoon, 1988). A recent review is given by Walstra and van Vliet (1986). The study of (renneted as well as acid) milk gels is important for:

- understanding and controlling the renneting and curd making process.
- understanding the structure and the behaviour of casein networks in such food materials as yogurt, quark and cheese.

The rheological behaviour of skim milk gels depends on the number of effective bonds within the network (homogeneity and concentration) and the type of bonds. Comparisons between the behaviour of cheese and milk gels are difficult to make because:

- the concentration of network material is very different. In unconcentrated milk gels the protein in the network makes up about 2.5% of the total material and about 25% of that in the strands (Roefs, 1986). In a young Gouda cheese about one third of the network (= cheese without fat) is matrix protein and in an older cheese it is more.
- The protein breakdown is much higher in cheese; most milk gels were tested within one day after renneting, cheese was studied up to more then one year old.

Because of these differences, it is not meaningful to compare the absolute values of rheological parameters (e.g. G', G'', σ_f) of cheese and skimmilk gels, because their values strongly depend on the number of effective bonds per unit volume. However, some corrections for the difference in concentration can be made. From the results of the dynamic moduli of a rennet skim milk gel of pH 5.2 (Roefs, 1986) a shear modulus of about 60 $N\cdot m^{-2}$ can be calculated (Ferry, 1970; Zoon, 1988). This is the modulus for the milk gel with about 2.5% protein. By assuming 10% of the strands to be effective and the protein concentration in the strands to be about 25%, the shear modulus of the strands can be calculated (according to Roefs, 1986), it would be about $1.2\cdot 10^4$ N m^{-2}. One now may assume that cheese consists of strands of swollen protein interspersed with fat globules. The protein concentration in the network is about 30%, thus higher than in the strands in a milk gel. This increase in protein concentration ($=c_{protein}$), increases the modulus. For milk gels $G \sim (c_{protein})^{2.5}$ has been found (factor 2.6 by Roefs (1986) and 2.4-2.5 by Zoon (1988)) which would imply a shear modulus of about $1.9\cdot 10^4$ N m^{-2} for the strands in cheese and a compression modulus E (=3G) of $5.7 \cdot 10^4$ N m^{-2}. This, however, is a too low an estimate, because the protein concentration in a milk gel is much lower than in cheese. The freedom of the protein molecules to move in cheese is much lower, which causes the modulus to increase more (see section 4.5). From figure 4.5 (where E is shown as a function of the water content in the non-fat cheese) the relation $E \sim (c_{protein})^{10}$ can be deduced. By using this relation and a shear modulus of $1.2 \cdot 10^4$ N m^{-2} of strands containing 25% protein, a shear modulus of the cheese network of $7.4 \cdot 10^4$ N m^{-2} may be calculated and a compression modulus of $2.2 \cdot 10^5$ N m^{-2}. Experimentally we found (section 4.3.3) a compression modulus of 10^5 N m^{-2} for the network in a young standard Gouda cheese (water/SNF≈1.4; pH≈5.2), which agrees well with the calculated modulus from the results of milk gels. This would imply that syneresis and pressing do not essentially change the network in cheese.

For effects that are primarily determined by the type of bonds, the behaviour of milk gels and of young cheese can also be compared, as for example with the pH effect (section 4.4.1): the flow properties of Gouda cheese as well as those of rennet milk gels are most predominantly around pH 5.2.

For milk gels it has been concluded that the loss tangent in dynamic experiments primarily depends on the type of bonds, not on the number (Roefs,1986). For cheese it has been found that the value for tan δ increases with increasing water content (section 4.3.2) and with proteolysis (section 5.5.2). Its value therefore is probably more dependent on the freedom of the network molecules to move than on the type of bonds. No clear effect of the pH on tan δ was found. The value for tan δ for cheese and for milk gels are, however, about the same (section 3.2.1), but this may possibly be due to two opposite changes that have, by chance, an effect of the same magnitude on tan δ: during ripening the decreasing water content would lower tan δ, while proteolysis would increase tan δ, resulting in a negligible net change (see figure 3.13).

The fracture behaviour of milk gels has hardly been studied. Zoon (1988) found for rennet milk gels of pH 5.75 to 6.75 that the shear strain at fracture (in creep measurements) increased with increasing time-scale. This is in accordance with our measurements of ϵ_f of a young cheese with pH over 5.2; ϵ_f increased with decreasing strain rate. Creep experiments at pH 4.6 in milk gels were performed by Roefs (1986). Then the fracture strain is about independent of the time scale.

With increasing fat content (natural milk fat globules), the modulus of a milk gel decreased, although the rigidity of the fat particles is higher than that of the milk gel (van Vliet and Dentener-Kikkert, 1982). The reason for this behaviour is the existence of a low-viscosity layer around all fat particles (van Vliet, 1988). Due to this, deformations of the matrix can not directly be passed on to the fat globule. The effect of the fat content on the behaviour of cheese is different due to the lower water content and the absence of a low viscosity layer around the fat globules (section 4.3.3).

From the discussion above, it may be concluded that for those properties of cheese for which the behaviour of the network proteins is important, there are clear similarities between the properties of cheese and of milk gels. Because in milk gels compositional differences can be more exactly adjusted, it is useful to study the behaviour of milk gels for a better understanding of some aspects of the behaviour of cheese. Studying milk gels is, of course, also important to broaden the knowledge of the renneting, cutting and syneresis process.

6.3 Application of several results of this study

The results of this study offer us several possibilities of applying them. Some will be discussed in this section.

1. In chapter 2, several methods for examining rheological and fracture properties of a material were described. In chapter 3

was shown how to interpret the results, especially those on fracture behaviour. In the literature on fracture mechanics, most attention is paid to elastic materials and materials that approximately behave like elastic materials. Cheese, however, is a visco-elastic material with no detectable yield stress. This implies that the flow properties are (very) important for the behaviour, and interpretation and measurement of the fracture properties is difficult. A way of thinking is offered in chapter 3. This is, of course, not only applicable to Gouda cheese, but also to several other materials, esp. other food materials. At the moment examples of this are worked out at our laboratory (e.g. Boode, 1985; Verhoeven, 1988).

2. The ideas about the influence of composition on the rheological and fracture behaviour of cheese, as described in chapter 4 and 5, give us the opportunity to make cheese that complies better to the desired properties. Flow and fracture behaviour of a cheese of a certain age, is much influenced by the pH. For eye formation, for example, cheese has to flow. If it does not or too sluggishly, slits can be formed instead of round holes. The influence of the pH on slit or eye formation will be worked out in section 6.3.1.
3. The usage properties of cheese are greatly determined by the rheological and fracture properties. For example, cutting a cheese into pieces can be done with a knife or a wire. The thickness of this determines the volume of material that is deformed and thus also the energy needed to cut (see section 3.2.4 and formula 3.15). When cutting with a knife instead of with a wire, more energy is needed because of the friction between the knife and the cheese. When the cheese is sticky, it even is very difficult to cut a piece of the cheese.
   The deformation of the cheese mass around a wire or knife is considerable (see section 2.3.4). In a cheese of short consistency, fracture may occur around the complete wire, resulting in the formation of side-cracks. It therefore is very difficult or about impossible to cut off thin slices from an old Gouda cheese. When cutting off thick slices, the slices have to curl

away from the knife or wire as it is cut, in order to diminish friction. This requires additional energy, which increases in proportion to the thickness of the slice.

Differences between fracture initiation and propagation are also important usage properties. As was discussed in section 3.2.3, in a more mature Gouda cheese fracture already can propagate at small deformations: when cutting or biting this cheese, the knife, wire or teeth have to penetrate just a bit into a piece of cheese to divide it into smaller pieces. A young Gouda cheese, on the contrary, has to be cut or bitten nearly completely. Fracture does not or much less propagate. This implies that:

- the eating properties of a young and a more mature Gouda cheese are different. The latter is judged to be more brittle (possibly also because ϵ_f is smaller).
- one has to take care when handling a mature cheese, because it fractures much easier than younger cheese.

4. Consistency (rheological and fracture behaviour) as perceived by consumers during eating, probably can be judged semi-quantitatively with the methods described in section 2.3. In traditional grading of cheese consistency, for instance, the shortness is judged by how far a long cylinder of cheese can be bend until it fractures. This can be easily imitated with a bending experiment as described in section 2.3.3. The results for the strain at fracture in bending agree quite well with those of other experiments (see section 2.4.1.3). Cheese firmness is probably related to the modulus E.
5. Fracture stress and strain are very dependent of the defects in the material (see section 3.1). The size and shape of the defects determines the stress concentration. The exact effect of this on the overall fracture stress and strain also depends on the type of deformation. For a low fat cheese, for instance, has been shown (see section 4.3.3.1) that the fracture strain in tension is lower than found for cream cheese, while the fracture strains in compression are the same. This implies

that one has to choose the right type of experiment, adjusted to the property studied.

From these examples of how the results of the study can be used, only the flow and fracture behaviour during eye or slit formation is worked out (see next section).

6.3.1 Application of fracture and flow behaviour of cheese to eye and slit formation

6.3.1.1 Introduction

In several cheese types, including Gouda, the existence of some round holes (eyes) is demanded. The formation of these holes is caused by the production of gas by bacteria. Due to the gas pressure a hole grows and round eyes can be formed. When the gas production is too fast, or when the mechanical properties of the cheese are not good, slits or cracks are formed instead of eyes (Flückiger et al., 1978). This implies that the cheese mass fractures instead of flowing.

A hole is formed because the pressure of the gas causes the cheese mass to deform. If the flow properties of the cheese exceed the elastic (energy storing) properties at the relevant time-scale of days, the material flows and does not fracture: an eye is formed. As shown before, ϵ_f depends on the pH, the ripening time and the rate of deformation. From X-ray pictures of a young cheese with growing eyes, a relative rate of deformation during eye formation of 10^{-6}-10^{-5} s^{-1} was derived (Akkerman et al., to be published). In this strain rate range, young cheese with a pH of about 5.2 does indeed show predominantly viscous properties; it can be greatly deformed without fracturing. We therefore expected an influence of, for example, the pH of the cheese on the formation of slits or eyes. In section 4.4.1 we reported that in the pH range from 5.2 up to 5.4 the flow properties of a Gouda cheese are most predominant: the modulus and the apparent viscosity are low, fracture strain is high and there is an influence of the strain rate on ϵ_f. Therefore we expected that the probability of the formation of slits instead of eyes is lowest around pH 5.2-5.4.

To examine whether the expected similarities between the formation of eyes or slits and the rheological and fracture behaviour as determined with the tests described in section 2.3, do exist, we measured these properties for one week old Gouda cheese of different pH and investigated the eye or slit formation by blowing holes in the same cheese.

6.3.1.2 Methods

Cheese was made with 1% NaCl in the cheese milk to avoid differences in the salt content within a cheese. As mentioned in section 5.3.2, this did not affect the rheological and fracture properties. A non gas producing starter was used to avoid hole formation due to starter activity. Cheese was used after 1 week of ripening, because then the curd particles are fused (section 5.3.2). For each pH 2 cheeses of 2 kg were made, one was used for the rheological and fracture tests and the other for artificial hole formation.

For blowing holes in a cheese, 8 needles with an outer radius of 1.1 mm were put in a Gouda cheese and were glued with Bison-tix. Through these needles air was blown for 48 hours at a constant pressure of $2 \cdot 10^3$ N m^{-2}. It was checked that no leaking of gas occurred. In preliminary experiments (Akkerman et al., to be published) it was found that a higher pressure gave too fast a hole formation (much faster than $\dot{\epsilon} \approx 10^{-5}$ s^{-1}) and therefore more easily slit formation. In the eyes of Emmentaler cheese an over-pressure of $1.5\text{-}2.5 \cdot 10^3$ N m^{-2} has been measured during the first days of eye growth (Flückiger and Walser, 1977). The temperature of the cheese and of the air were 21°C. After 48 hours the cheese was cut and the shape and size of the holes were judged.

6.3.2.3 Results and discussion

The tests described in 6.3.2 were performed on cheese of 1 week old and with varying pH. Results for the rheological and fracture behaviour were similar to those of normal Gouda cheeses, as given in sections 3.2.2 and 4.4.1.

From the increase in circumference of the holes, a (biaxial) tension rate could be calculated. This was, for all tested cheese about 10^{-6}-$3 \cdot 10^{-5}$ s^{-1}, rather similar to the deformation rate during formation of real eyes in Gouda cheese. As was shown in section 2.4.2.1, biaxial viscosities calculated from the artificial hole formation agree well with those from compression tests. Different types of holes were found, depending on the pH of the cheese. This is shown in table 6.2. Sometimes no openings could be found. This was due to leak of air or to stoppage of the needle.

In cheese with a pH of roughly 5.2 to 5.4 only round eyes were formed. An example is shown in figure 6.1A. The holes were large

Table 6.2 The influence of the pH on the appearance of artificial openings in one week old Gouda cheese at 20°C. A gas pressure of $2 \cdot 10^3$ N m^{-2} was applied for 48 hours.

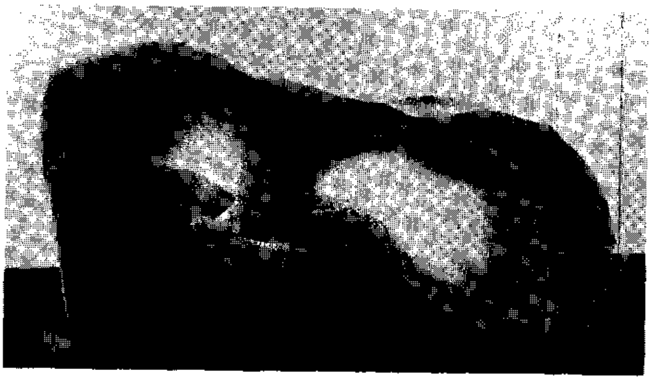
pH	water	openings			
		nothing	slit (1)	slit (2)	round eye
4.94	43.5%	1	7	0	0
4.97	47.1	0	6	0	2
5.03	43.2	3	4	0	1
5.07	43.8	6	1	0	1
5.08	42.2	0	4	0	4
5.13	43.4	1	1	0	6
5.15	45.3	2	1	0	5
5.21	42.4	0	0	0	8
5.24	42.8	0	0	0	8
5.27	42.9	2	0	0	6
5.30	44.1	1	0	0	7
5.33	46.4	0	0	0	8
5.50	43.6	0	0	8	0
5.52	45.4	0	0	8	0

Fig. 6.1 Example of the appearance of artificial openings in one week old Gouda cheese with different pH. A. pH 5.24

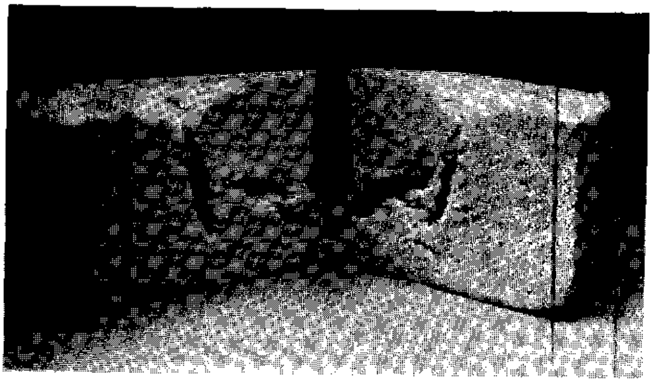
B. pH 5.09 (Lefier, unpublished)

C. pH 5.50

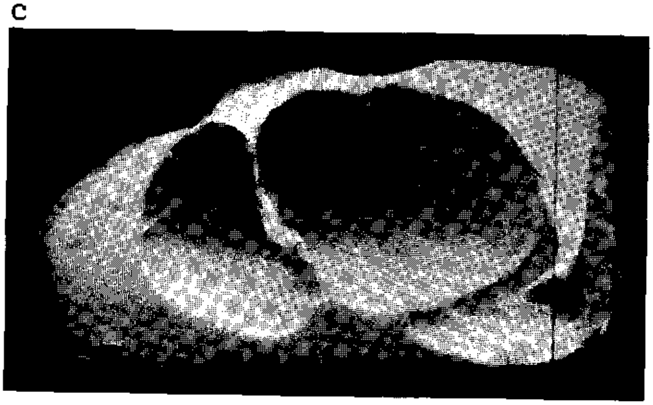
A



B



C



and smooth and clearly formed by flow of the cheese mass. No fracture had occurred. Between two adjacent holes even very thin and transparent sheets could be formed.

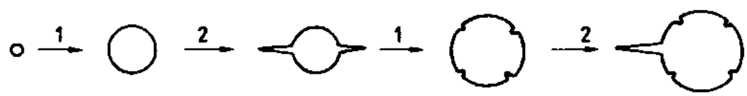
In cheese with a lower pH mainly slits were formed. An example is shown in figure 6.1B. Around the tip of the needle the cheese has fractured completely. No or only very small openings had been formed, which implies that the cheese had no or hardly exhibited flow.

In cheese with a high pH the artificial holes looked like those in figure 6.1C. Openings were formed, which implies flow of the cheese mass. This flow, however, was not enough to completely prevent fracture. On the surface of the openings some ribs could be seen. One may imagine that after sudden fracture of the circumference of an opening, this breaking stopped, either due to energy dissipation caused by fracture or (in real eyes) due to a decrease in gas pressure caused by the growth of the volume of the opening, and flow of the cheese mass continue until fracture started again, etc. An outline of this, still hypothetical, process is given in figure 6.2.

From the results above it may be concluded that:

- The optimum conditions for eye formation are at pH 5.15 to 5.35. This is the same pH range as were the strain at fracture and the flow properties of Gouda cheese were at maximum.
- Values for the apparent viscosity as measured with compression tests were the same as those found for artificial eye forma-

Fig. 6.2 Outline for possible flow/fracture process at high pH. 1 = flow, 2 = fracture.



tion. This implies that compression tests as described in section 2.3.1 indeed, give information about material properties relevant to eye formation.

- Changes in material properties, as measured by the rheological and fracture tests used in this study, with varying pH of Gouda cheese, agree well with changes in the appearance of openings in this type of cheese.

Up to know we only performed this kind of experiments at 21°C and only the pH was varied. Experiments at different temperatures (especially ripening temperature 14°C) and with different gas pressures would be very useful to perform, as would, experiments with different salt content or proteolysis.

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LIST OF SYMBOLS

A	area	m^2
d	diameter	m
D	diffusion coefficient	$m^2\ s^{-1}$
E	compression modulus	$N\ m^{-2}$
E_c	composite compression modulus	$N\ m^{-2}$
E_f	filler compression modulus	$N\ m^{-2}$
E_m	matrix compression modulus	$N\ m^{-2}$
F	force	N
G	shear modulus	$N\ m^{-2}$
G'	storage shear modulus	$N\ m^{-2}$
G''	loss shear modulus	$N\ m^{-2}$
G_c	composite shear modulus	$N\ m^{-2}$
G_f	filler shear modulus	$N\ m^{-2}$
G_m	matrix shear modulus	$N\ m^{-2}$
h	height	m
h_0	initial height	m
h_t	height at time t	m
Δh	change in height	m
l	crack length	m
r	radius	m
R	toughness	$J\ m^{-2}$
R_s	fracture energy	$J\ m^{-2}$
t	time	s
T	temperature	°C
Tr	Trouton ratio	-
v	speed	$m\ s^{-1}$
W	total energy input	$J\ m^{-3}$
W'	stored energy	$J\ m^{-3}$
W''	dissipated energy not due to fracture	$J\ m^{-3}$
W''_n	dissipated energy due to network flow	$J\ m^{-3}$
W''_f	dissipated energy due to friction between components	$J\ m^{-3}$
W_f	energy used for fracture	$J\ m^{-3}$
γ	shear deformation	-
$\dot{\gamma}$	shear rate	s^{-1}

$\dot{\gamma}_l$	shear rate of moisture	s^{-1}
δ	loss angle	-
ϵ	compressive strain	-
ϵ_c	Cauchy strain	-
ϵ_f	fracture strain (expressed as a Hencky strain)	-
ϵ_h	Hencky strain	-
ϵ_t	tension strain (expressed as a Hencky strain)	-
$\dot{\epsilon}$	compressive strain rate	s^{-1}
$\dot{\epsilon}_c$	Cauchy strain rate	s^{-1}
$\dot{\epsilon}_h$	Hencky strain rate	s^{-1}
$\dot{\epsilon}_t$	tension strain rate (expressed as a Hencky strain rate)	s^{-1}
η^*	apparent shear viscosity	Pa s
η^*_E	apparent elongational viscosity	Pa s
μ	Poisson ratio	-
φ	volume fraction	-
σ	stress	$N\ m^{-2}$
σ_o	overall stress	$N\ m^{-2}$
σ_f	fracture stress	$N\ m^{-2}$

SUMMARY

The rheological and fracture properties of Gouda cheese.

The purpose of this study was to obtain a better understanding of the flow and fracture properties of Gouda cheese. To obtain this, several Gouda cheeses of different composition and after different periods of maturation, were examined with several rheological techniques. When studying the influence of composition, care was taken that only one compositional factor was varied, which guarantees that found correlations are causative.

In chapter 2, the methods that were used to study the rheological and fracture behaviour of Gouda cheese are described. The rheological behaviour at large deformations and the fracture behaviour were examined in compression, tension and bending experiments, the rheological behaviour at small deformations in dynamic shear experiments. In this way several parameters could be measured:

- the modulus of the material (in compression: E or in shear: G, depending on the type of deformation) is a measure of the rigidity of the material
- the relative deformation at which a sample of cheese fractures when it is loaded (ϵ_f). The shortness of a material best can be described by the inverse of ϵ_f.
- the fracture stress (σ_f), which value depends on E and ϵ_f. However, $\sigma_f/(E \cdot \epsilon_f)$ is not a constant but depends (among other things) on the fat content.

After correction for differences in measuring conditions, in particular for variation in the extent of stress concentration, the parameters measured were found to be independent of the method used and the size and shape of the test piece. This implies these parameters to represent real material properties.

A description of the rheological and fracture behaviour of visco-elastic materials, and especially that of Gouda cheese, is given in chapter 3. When deforming a visco-elastic material, part

of the deformation energy is dissipated and this causes the behaviour of the material to be rate dependent. The cause of this for Gouda cheese is friction of structural elements with respect to one another; namely protein molecules with respect to each other, protein particles with respect to each other, protein particles with respect to fat globules and flow of liquid through the protein matrix. This is discussed in section 6.1. Gouda cheese has no (perceptible) yield stress, which implies that viscous properties are important at all deformations and stresses.

The energy that is not dissipated can be used for fracturing. This implies that flow (energy dissipation) and fracture properties are related. Fracture begins when defects (inhomogeneities that cause weak spots) in the material start to grow. The size of these inhomogeneities in Gouda cheese is 0.1 to 0.3 mm. In cheese of less than 6 days old, with not yet completely fused curd particles, the defect size is a few millimeters (see section 5.3). The stress needed to initiate fracture in cheese is 30 to 150 kN m^{-2}, according to composition and maturation. Fracture propagates if the (elastic) deformation energy released by progress of a crack is at least equal to the energy needed to create new crack surfaces. The fracture energy of Gouda cheese ranged from 1 to 10 J m^{-2}.

Flow and fracture behaviour of Gouda cheese are rate dependent. In the range of time scales studied (about 1 to 10 000 seconds), we found two different types of rate dependent behaviour. Type 1 cheese (any more mature cheese and young, acid cheese, pH < 5.15) showed a small rate influence on the stress, independent of the strain. The strain at fracture was constant. Type 2 cheese (being both young and not acid), on the other hand, showed an increasing rate influence on the stress with increasing strain. The strain at fracture of such cheese increased with decreasing deformation rate and at very low deformation rates it did not fracture at all.

The influence of composition on the rheological and fracture properties of Gouda cheese is described in chapter 4. Cheese may be considered as a composite material: fat globules act as filler particles in an aqueous matrix of swollen protein particles. The fat content and the rigidity of the fat particles (kind of fat, temperature) affect the rigidity of the cheese. At low temperatures the rigidity of the cheese increased with increasing fat content, at high temperatures it decreased with fat content. No influence of the fat content on the shortness of cheese could be found.

The matrix of cheese consists of proteinaceous particles, their volume fraction being very high. The rheological and fracture properties of these particles determine the behaviour of cheese. In this way the influence of pH, temperature, water and salt content could be explained, at least qualitatively (an outline is given in figure 4.30). The trends are similar to those found for acid and rennet skimmilk gels (see section 6.2).

A more mature cheese is more rigid and shorter (see chapter 5). This is due to water loss (more rigid) and proteolysis (shorter). The increase in shortness appears to be caused by proteolysis in depth, i.e. breakdown of protein fragments into small peptides and amino acids. A certain "extent" of proteolysis is needed, i.e. most protein molecules should be cleaved at least once, but it is not a sufficient cause for a cheese to become short. Proteolysis is not the only cause for getting a short consistency. A low pH or a high salt content also causes the fracture strain to be low. Therefore fracture strain alone is not a good measure of the extent of ripening of a cheese.

In section 6.3 applications of several results of this study are described. The relation between rheological and fracture properties of cheese and the formation of eyes or slits in cheese is worked out. The optimum conditions for eye formation are at pH 5.15-5.35; at lower and higher pH slits are easily formed. Flow and fracture properties of young Gouda cheese in this pH range differ from the behaviour at lower or higher pH; the deformation at fracture and the viscous-like behaviour are at maximum around pH 5.2-5.4. Rigidity then is at a minimum.

SAMENVATTING

De reologische- en breukeigenschappen van Goudse kaas.

Het doel van het beschreven onderzoek is meer inzicht te krijgen in de vloei- en breukeigenschappen van Goudse kaas. Daarvoor werden deze eigenschappen onderzocht aan kaas van verschillende leeftijd en samenstelling met behulp van verschillende reologische methoden. Bij de verandering in samenstelling werd er zorgvuldig op gelet dat slechts één variabele tegelijk werd gevariëerd, om zo oorzakelijke verbanden te kunnen bepalen.

In hoofdstuk 2 zijn methoden beschreven die gebruikt werden om reologische- en breukeigenschappen van Goudse kaas te bepalen. Compressie-, rek- en buigproeven werden gebruikt om reologische- en breukeigenschappen bij grote vervormingen te bepalen. Om reologische eigenschappen bij kleine vervormingen te bestuderen werden oscillerende afschuifmetingen gebruikt. Er werd aangetoond dat de meeste met deze verschillende methoden gemeten parameters (zoals de breukspanning), na correctie voor verschillen in meetomstandigheden, nauwelijks afhankelijk waren van de soort meting en de vorm en grootte van het proefstuk. Ze mogen daarom als materiaaleigenschappen aangemerkt worden.

In hoofdstuk 3 staat een algemene beschrijving van het reologisch- en breukgedrag van visco-elastische materialen, in het bijzonder van Goudse kaas. Bij vervorming van zulke materialen dissipeert een gedeelte van de benodigde vervormingsenergie. Deze energiedissipatie veroorzaakt een snelheidsafhankelijk gedrag. De oorzaak hiervan is, voor Goudse kaas, wrijving van componenten van de kaas ten opzichte van elkaar: eiwitmoleculen en -deeltjes t.o.v. elkaar, eiwitdeeltjes t.o.v. vetbolletjes en vloeistofstroming t.o.v. het eiwit. Deze aspecten worden in hoofdstuk 6.1 verder bediscussieerd.

De energie die niet dissipeert, kan eventueel gebruikt worden voor breuk van het materiaal. Dit geeft meteen aan dat er een verband bestaat tussen breuk- en vloeieigenschappen. Breuk begint

wanneer in het materiaal aanwezige defecten uitgroeien. De grootte van deze defecten in Goudse kaas bleek 0,1 tot 0,3 mm te zijn. In heel jonge kaas, waarin de wrongeldeeltjes nog niet volledig aan elkaar zijn gegroeid (dit duurt ongeveer 3-6 dagen), zijn deze onregelmatigheden groter, namelijk enkele millimeters (hoofdstuk 5.3). De spanning die minimaal nodig is om breuk te veroorzaken (= de defecten te laten groeien) is $3\text{-}15 \cdot 10^4$ N m^{-2}, afhankelijk van de samenstelling en de leeftijd van de kaas. Breuk schrijdt spontaan voort, indien er in de buurt van de breuk voldoende opgeslagen (elastische) energie vrijkomt om nieuwe breukvlakken te kunnen vormen. De breukenergie van Goudse kaas is ongeveer 1-10 J m^{-2}.

Het vloeigedrag van Goudse kaas veroorzaakt dat het gedrag snelheidsafhankelijk is. Ruwweg kunnen we 2 typen snelheidsafhankelijk gedrag onderscheiden. Bij type 1 kaas (alle rijpere kaas en alle jong maar zure kaas) nemen de energie en de spanning nodig om een stukje kaas te vervormen, af met afnemende vervormingssnelheid. De vervorming bij breuk is echter constant. Bij type 2 kaas (jonge kaas die niet te zuur is, pH > 5.15), daarentegen, neemt de vervorming bij breuk toe met afnemende snelheid. Bij heel langzame vervormingen breekt deze kaas zelfs helemaal niet. Dit is o.a. belangrijk voor de ogenvorming in kaas: de kaas om een groeiend oog heen moet ver uitgerekt kunnen worden zonder te breken, want dan zouden er scheuren ontstaan in plaats van ronde ogen.

In hoofdstuk 4 wordt de invloed van de samenstelling op de reologische- en breukeigenschappen van Goudse kaas beschreven. Kaas kan beschouwd worden als een matrix van eiwitdeeltjes in vocht, met vetbolletjes als vulstof (een soort composietmateriaal). De hoeveelheid vet en de stevigheid van de vetbolletjes (soort vet, temperatuur) beïnvloeden de stevigheid van de kaas. Bij lage temperatuur maakt melkvet een kaas steviger, bij hoge temperatuur juist minder stevig. Vet heeft geen effect op de kortheid van de kaas, doordat de onregelmatigheden waar breuk begint, veel groter zijn dan de vetbolletjes. Kortheid is b.v. te definiëren als de reciproke van de relatieve vervorming bij breuk.

De matrix van kaas bestaat uit dicht tegen elkaar gepakte eiwitdeeltjes. De eigenschappen hiervan bepalen voor een groot gedeelte het gedrag van de kaas. Dit gedrag wordt o.a. beïnvloed door de pH, de zoutconcentratie, de temperatuur en het watergehalte. Een overzicht hiervan staat in figuur 4.30. De invloeden komen goed overeen met wat gevonden is voor melkgelen (zie 6.2).

Een oudere (rijpere) kaas is steviger en korter (hoofdstuk 5). De oorzaak hiervan is het uitdrogen van de kaas (steviger) en de eiwitafbraak (korter). Het korter worden van Goudse kaas wordt waarschijnlijk vooral veroorzaakt door eiwitafbraak "in de diepte". Afbraak "in de breedte" is noodzakelijk, maar waarschijnlijk niet voldoende om een uitgesproken korte kaas te verkrijgen. De kortheid van een kaas is echter niet alleen afhankelijk van de eiwitafbraak. Ook een lage pH of een hoge zoutconcentratie maken een kaas korter. Dit is de reden dat de zogenaamde rijpingsgraad van kaas niet bepaald kan worden door alleen de vervorming bij breuk te meten.

In hoofdstuk 6.3 worden toepassingen beschreven voor het gebruik van de gevonden resultaten. Als voorbeeld is het verband tussen de vorming van ogen of scheuren en het reologisch- en breukgedrag, zoals dat m.b.v. de methoden uit hoofdstuk 2 bepaald kan worden, uitgewerkt. Het blijkt dat er voor ogenvorming in kaas een optimale pH van 5,15-5,35 bestaat. Bij hogere of lagere pH ontstaan er gemakkelijker scheurtjes. Ook zijn de vloei- en breukeigenschappen van Goudse kaas in het gebied pH 5,2 tot 5,4 anders dan bij hogere of lagere pH: bij pH 5,2-5,4 zijn de vervorming bij breuk en de vloeieigenschappen het grootst en is de stevigheid minimaal.

CURRICULUM VITAE

De auteur werd op 19 januari 1960 in Roermond geboren. In 1978 haalde zij haar diploma gymnasium β aan de scholengemeenschap St. Ursula te Roermond. In hetzelfde jaar begon zij haar studie levensmiddelentechnologie aan de toenmalige Landbouwhogeschool te Wageningen. In januari 1984 slaagde ze met lof voor het doctoraal examen, met als hoofdvakken zuiveltechnologie en levensmiddelenchemie en als bijvak levensmiddelennatuurkunde. Van 1 januari 1984 tot en met 15 november 1987 was zij in dienst als wetenschappelijk assistente bij de sectie zuivel en levensmiddelennatuurkunde van de Landbouwhogeschool (later Landbouwuniversiteit). In deze periode werd het in dit proefschrift beschreven onderzoek uitgevoerd. Van 1 december 1984 tot 1 maart 1986 was zij tevens (part-time) werkzaam als toegevoegd docente levensmiddelennatuurkunde. Vanaf 1 maart 1988 werkt zij als toegevoegd docente en onderzoekster bij de sectie zuivel en levensmiddelennatuurkunde. Dit laatste in het kader van het innovatie gericht onderzoekprogramma koolhydraten aan de eigenschappen van polysacharide gelen, in het bijzonder bij grote vervormingen.

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