Spatio-temporal changes of physicochemical parameters during cheese ripening

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ABSTRACT

During the production process of cheese significant spatio-temporal changes in chemical and physical parameters are induced due to salt and water transfers during brining and water losses during ripening. In this research, the fundamental material parameters describing the visco-elastic behaviour of Gouda cheeses of 4, 8, 11 and 19 weeks were determined throughout the geometry of a cheese block, together with the hardness and dry matter content. Young's modulus, fracture stress and strain and hardness were measured with uniaxial compression tests. 5 term Prony series were deduced from the results of stress-relaxation compression tests to study the visco-elastic properties.

Repeated-measures ANOVA showed that the sample location in a cheese slice, and to a lesser extent the section of the cheese (the middle or the side of a block) have a significant influence on most parameters. Age has a significant effect on all parameters, except hardness and fracture strain. Ripening of the cheese causes a significant increase in dry matter content and decrease in Young's modulus. Significant second order interactions also occur for most parameters, meaning that the age of the cheese influences the spatial gradients.

1 Introduction

Numerous researches have aimed to characterize the structural, chemical and physical properties of a broad variety of cheeses. However, to date there are two major deficiencies in this research area. Firstly, the majority of the existing researches assume the examined cheese to be homogeneous, although this is often not true. Secondly, research of changes in cheese during ripening is mainly focused on chemical and textural properties. Examination of the changes in fundamental material parameters such as Young's modulus and fracture stress or strain during ripening is very limited.

Numerous cheese varieties, including Gouda cheese, are heterogeneous in both chemical and physical properties due to their production process. The spatial variability of chemical parameters is represented in the literature, but it is mostly limited to the variability of sodium chloride and water content (Messens et al., 1999; Pajonk et al., 2003; Simal et al., 2001). Abraham et al. (2007) studied the Eh and pH gradients in Camembert. Gkatzionis et al. (2009) examined the variability of volatile compounds in different zones of Stilton cheese. Pachlova et al. (2012) took the chemical heterogeneity into account when researching the free amino acids and biogenic amines content of Dutch type cheese. Very little can be found on the textural and physical heterogeneity of cheese. Since the spatial variability of cheese has an influence on further processing such as slicing or grating, an insight in this heterogeneity is required.

The effect of ripening on a variety of chemical parameters of cheese has been researched for several cheese types. The effect of cheese ripening on Eh and pH (Abraham et al., 2007), on water and salt content (Simal et al., 2001) and on water activity (Saurel et al., 2004) has been examined. Changes in chemical composition and proteolysis during ripening have been examined for Spanish goat cheese (Franco et al., 2003), for Prato cheese (Cichoscki et al., 2002) and for Picon Bejes-Tresviso blue cheese (Prieto et al., 2000). The effect of ripening on textural parameters such as firmness and cohesiveness has been researched by Fenelon et al. (2000) for Cheddar and by Buffa et al. (2001) for goat cheese. The influence of cheese age on the rheological properties loss modulus and storage modulus has also been described (Karami et al., 2009; Lucey et al., 2005).

Research on the influence of ageing on fundamental cheese parameters is limited to the work of Charalambides & Williams (1995). They investigated the effect of ripening on Young's modulus and fracture toughness of Cheddar cheese.

2 Material and Methods

2.1 Cheese preparation

This research was performed on Gouda type cheeses, produced in an SME situated in Mol (Belgium). Each rectangular block of cheese was produced in the same batch and had standard dimensions of 47x30x10cm (fig. 1). The cheese blocks were stored under ideal ripening conditions and were tested at different ages. At each ripening stage one block was analyzed. The cheese was examined at 4,8, 11 and 19 weeks old.

Every block of Gouda cheese was prepared for measurements following the same procedure. Three slices of cheese with a thickness of 3 cm were taken out of the middle of the block and 3 slices were taken at one side of the block (fig.1). Comparing slices from the middle M with slices from the side S allowed to investigate the heterogeneity of the cheese in the x-direction. To obtain every measurement in 3-fold, the three slices from the middle (M1,M2,M3) were considered to be the same, as well as the three slices at the side (S1, S2, S3). The assumption of equality of the slices was made based on preliminary research.

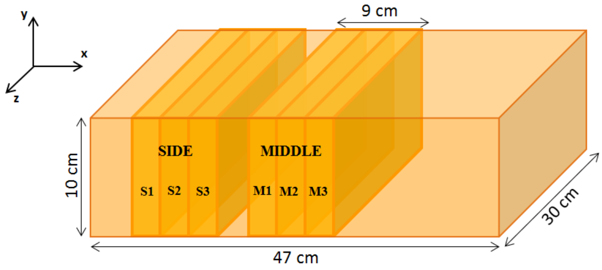
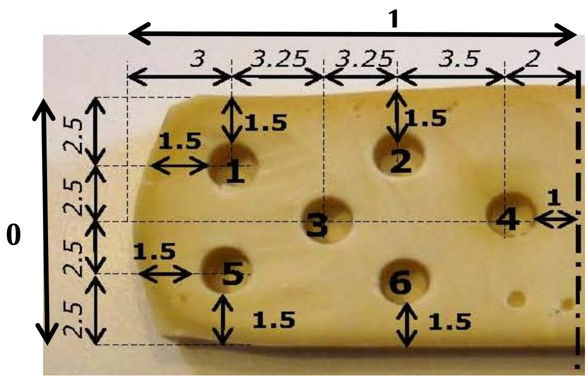
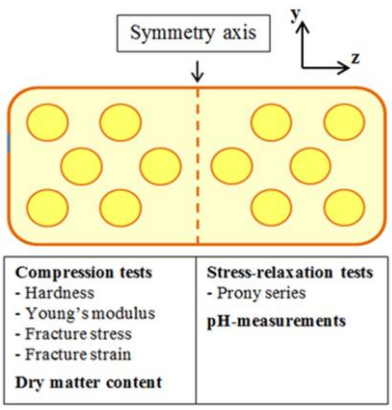


Figure 1: division of a cheese block in groups of slices

Heterogeneity in the z-direction was analysed by taking samples at different places in one slice. Every slice was considered to be symmetric around a central line, based on previous measurements. 6 samples were taken from every side of a slice. Figure 2a shows the different measurement point in each slice half. Figure 2b summarizes the different measurements on one slice.



2a)



2b)

Fig. 2a: Measurement points in the left side of a slice of cheese (measurements are in cm); 2b: Location of measurements in one slice

2.2 Sample collection

The samples used for the compression and stress relaxation tests were cylindrical samples with a diameter of 18mm and a height of 27mm, based on the norm ISO 17996 (2006). The samples were extracted from a block of cheese using a cylindrical tube. The samples were cut at the desired height of 27mm using a wire cutting device.

Every sample was stored at room temperature for 60 minutes before measuring in order to let the material relax after disturbing it by sampling. During this hour the samples were properly protected from the air to prevent drying at the surface.

The samples were measured at room temperature.

2.3 Uniaxial compression tests

All measurements were performed using a Texture Analyser TA.XT2i (Stable Microsystems, UK) with a flat compression plate (diameter 7.5cm). A compression test with a compression speed of 0.83mm/s was performed to determine Young's modulus, fracture stress and strain and hardness (ISO 17996, 2006). The sample was compressed until a strain of 80% was reached.

The peak value (in kg) of every compression curve was considered to be a value for the hardness of the measured sample. To determine the other parameters, the measured force and deformation were transformed to engineering stress and strain values. Young's modulus was calculated as the tangent of the linear stress curve between 5-10% strain. All linear trend lines fitted to the stress-strain curve with an $R^2>0.995$. According to the ISO-norm, fracture stress and fracture strain were measured as the stress and strain in the fracture point on the stress-strain curve (ISO 17996, 2006). This fracture point could be a maximum on the curve (first derivative = 0) or an inflection point on the curve (second derivative = 0). If there was neither a maximum, nor an inflection point, there was no fracture.

2.4 Stress Relaxation tests

Stress relaxation tests were performed to determine the time-dependent behavior of the visco-elastic material. A compression test was performed with a compression speed of 6mm/s for 5mm and this strain was maintained for 180s. The corresponding stress was registered as function of time and Prony series were fitted to the obtained curves.

The fitting of the Prony series was done with a Solver tool of Excel (Microsoft, U.S.). A best fit was searched based on the least square method. A model with 4 exponential terms (G_1, G_2, G_3 and G_4) with relaxation times 0.1, 1, 10 and 100s and a residual term G_∞ at an infinite relaxation time was selected.

2.5 Dry matter content

To determine the dry matter content, the cheese samples were grated. For each position, a homogeneous mixture of the graded cheese of three similar slices was made. From this mixture six samples of 3g were put on pre-dried and weighed glasses with sand and spatulas and mingled with the sand. The samples were dried in an oven (Jouan, St-Herblain, France) at 105°C for 3h. After drying, they were placed in an exsiccator to cool down, after which they were reweighed. Based on the mass difference before and after drying, the water content of the cheese samples is calculated.

2.6 Statistical analysis

SPSS v.20 (SPSS Inc., Chicago, IL) was used for all statistical analyses. Multivariate repeated-measures analysis of variance was used to test the effects of different cheese ages, section of the block (middle or side) and sample locations on hardness, dry matter, Young's modulus and the Prony series coefficients. The differently aged cheese blocks were considered as between-subject factors. The cheese sections and the sample locations were seen as within-subject factors, therefore counting as the repeated factors. Hypotheses concerning the within-subject factors were tested with the Wilk's Lambda test statistic. The differences caused by the between-subject factor age were evaluated with Tukey post-hoc tests.

When measuring fracture stress and strain, often there was no fracture point. Since the multivariate repeated-measures ANOVA is very sensitive for missing values, univariate repeated-measures tests with Huynh-Feldt test statistics were used for these parameters.

3 Results & Discussion

At first, the spatio-temporal variability in a cheese block was examined by studying the effect of all variables (age, location and section) and their first order interactions on the different parameters. The significances of the different effects on the model are shown in table 1. Significant model effects (at a 0.05 significance level) are marked with an asterisk.

Table 1: Significance of the variable effects on the different parameters

Effects	Hardness[a]	Dry matter content[a]	Young's Modulus[a]	G∞[a]	Fracture Stress[b]	Fracture strain[b]
Age (A)	0.136	0.000*	0.010*	0.000*	0.010*	0.174
Section (S)	0.032*	0.000*	0.053	0.000*	0.829	0.275
Sample Location (L)	0.000*	0.000*	0.000*	0.000*	0.061	0.006*
(S)*(A)	0.338	0.000*	0.343	0.004*	0.096	0.764
(L)*(A)	0.060	0.000*	0.003*	0.013*	0.024*	0.867
(S)*(L)	0.611	0.236	0.465	0.034*	0.488	0.437
(S)*(L)*(A)	0.149	0.611	0.263	0.331	0.868	0.342

[a]test statistic: Multivariate approach
[b]test statistic: Univariate approach

Subsequently, the effect of age was studied in more detail. Table 2 shows the results of the Tukey post-Hoc tests. The values at each age are means over the factors location and section. Age groups that are not connected by the same letter are significantly different according to a 5 % significance level.

Table 2: ANOVA results for hardness, dry matter content, Young's modulus and G∞

Age	Hardness (kg)	Dry matter content (%)	Young's modulus (kPa)	G∞
4 weeks	0.6561[a]	57.7506[a]	114,0786[a,b]	0.13639[b]
8 weeks	0.7536[a]	58.0064[b]	124,9222[b]	0.15359[c]
11 weeks	0.6947[a]	58.0464[b]	96,5661[a]	0.12825[a]
19 weeks	0.664[a]	59.6942[c]	94,7556[a]	0.15483[c]

3.1 Hardness and dry matter content

It is clear from table 1 that the section in a cheese block and the sample location had a significant influence on the hardness of the cheese and on the dry matter content. The latter was influenced by the age as well. Age also influenced the effect of section and location on dry matter. Thus ripening of the cheese influences the spatial gradients. Prentice, Langley & Marshall (1993) reported that the hardness in an otherwise uniform cheese can have a variation of about 50 % at different distances from the surface. Similar variation was observed in this research. The dry matter in a cheese block of 8 weeks old ranged from 56.66% at the centre to 59.23% at the outer corner points, while the hardness ranged from 0.51 to 1.03kg. This heterogeneity is caused by the gradual forming of a uniform salt distribution in the cheese and by water losses at the surface due to the dehydration of the cheese.

There was no significant difference in hardness over the ripening period. However, at 8 weeks a small increase could be seen in the results, followed by a decrease in hardness (although not significant). This small increase is caused by proteolysis, but this is balanced by the hardening due to the loss of water. The dry matter content significantly increased during the ripening, due to a continuous loss of water at the cheese surface.

3.2 Young's Modulus

The results of the model effects are shown in table 1. The age of the cheese blocks and the sample locations in one slice had a significant influence on Young's Modulus.

It can also be seen that the cheese age had an influence on the effect of the sample location (L*A), meaning that the difference in Young's modulus between the corner points and the central part of the slices changes with age. Whether the samples were taken out of the middle or the side of a cheese block had no influence on Young's Modulus on a 0.05 significance level, but it can be considered to be weakly significant ($p<0.10$).

Figure 1 shows the mean results of Young's modulus for the middle section of a cheese block at every ripening stage. The heterogeneity in one cheese slice is distinct on this graph. Especially the corner points 1 and 5 clearly had higher Young's moduli than the other points. A decrease in moisture content towards the center of the cheese blocks leads to an increase in the resistance of the cheese to deformation. Hence, the Young's modulus increases (Rohm et al., 1992; Visser, 1991).

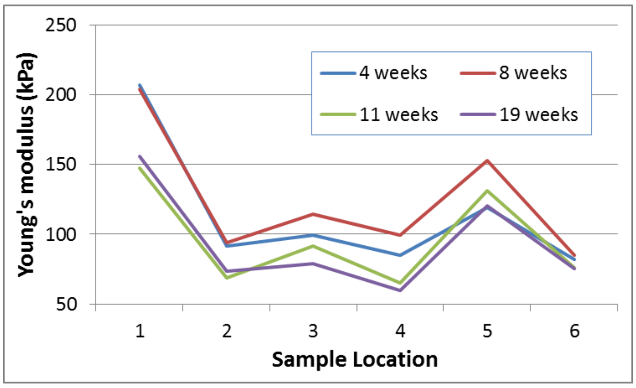


Figure 1: Mean Young's moduli for the middle section of a cheese block

The results of a Tukey post-hoc test (table 2) show a slight increase in Young's modulus at 8 weeks (although not significant) followed by a significant decrease of Young's modulus at 11 weeks.

3.3 Prony series coefficients

Only the results of the residual Prony coefficient G∞ will be discussed as it is the main varying factor. Table 1 shows that all within- and between-subject factors and their first order interactions had a significant influence on the residual coefficient. The distribution of G∞ in a cheese slice was analogue to that of Young's modulus, with higher values at the corner points. As the residual coefficient corresponds to the material behaviour after an infinite relaxation time, it is related to the elastic behaviour of the material. A higher G_∞ corresponds to a more elastic behaviour. The corner points of a cheese slice have a lower water content and therefore the viscous part of their visco-elastic behaviour will be less prominent.

The residual Prony coefficient changed in function of the cheese age (table 2), but this changes are very irregular.

3.4 Fracture stress and strain

According to table 1 age had a significant effect on fracture stress and on the effect of sample location on this stress. Sample location had a significant influence on fracture strain and a weakly significant effect on fracture stress.

The distribution of fracture strain results in one cheese slice was reversed to the Young's modulus results, with lower values at the corner points. According to Visser (1991) and Rohm et al. (1992) the strain at fracture either remains unaffected or increases with the moisture content, depending on the age of the cheese. It can be assumed that a stiffer material, ergo a material with a higher Young's modulus, will break at smaller deformation levels. There were also differences in a cheese slice regarding the fracture stresses, but these differences are not so distinct. This could already be seen in the results for the factor effects ($p=0.061$). Due to the missing values, post-hoc tests could not be performed on the fracture stress and strain results.

4 Conclusions

The repeated-measures ANOVA show that there were distinct spatio-temporal gradients in physicochemical parameters of Gouda cheese. Cheese age, section (middle or side), sample location and their first order interactions significantly affected most physicochemical parameters.

These findings will be used in further research, during the designing of finite element models of cheese. The spatial gradients will need to be incorporated in the material properties to obtain valid models of Gouda cheese.

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