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RESEARCH ARTICLE

Changes in the Rheological Properties of Cheddar Cheese at Different Storage Temperatures

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Abstract Changes in the stress relaxation behavior of Cheddar cheese was measured at different storage temperatures (5-25°C). A 3-element Maxwell model was used for calculation of instantaneous elastic, elastic, and viscous constants. As the storage temperature increased from 5 to 25°C, rheological properties of instantaneous and equilibrium stresses, and instantaneous elastic, elastic, and viscous constants decreased. A master curve was constructed based on moving each stress relaxation curve horizontally on the basis of reference temperature (15°C) with shift factors. The master curve of Cheddar cheese had a linear temperature dependency. The modulus of elasticity decreased as the storage temperature increased. The predicted shelf life and activation energy of Cheddar cheese at different storage temperatures were calculated using the Williams-Landel-Ferry equation. The activation energy was 50.25 kcal/mol, and the expected shelf life was 15 times longer when stored at 5°C than at 15°C.

Keywords: Cheddar cheese, 3-element Maxwell model, stress relaxation, master curve, Williams-Landel-Ferry equation

Introduction

Cheese is produced worldwide and many cheeses are produced in Korea as a result of westernized dietary habits (1). Cheese is a fermented food made by heating, pressurizing, and maturing casein with enzyme addition that curdles cow and sheep milk proteins (2). Nearly 70% calcium, 75% protein, 90% fat, and most of the vitamins in milk are contained in cheese. Thus, cheese plays a critical role in the growth of children and people who are allergic to milk (3).

Cheese type and texture are determined by factors such as the origin, starter, coagulating agent, curding temperature, moisture content, and degree of maturation. In Korea, cheese is classified as hard, semi-hard, soft, and raw depending on the moisture and fat content (1). In light of the current tendency for emphasis of a stable texture of high-quality cheese, an equation can be used to predict changes in physical properties during manufacturing and storage.

Cheese is a protein-rich food with viscoelastic behavior (4-6). Storage temperature is of great importance for influencing mechanical properties of rupture (7) and viscoelastic behavior. Herum *et al.* (8) produced a single master curve that represented the relaxation modulus of whole soy bean based on temperature and moisture content. Pappas and Rao (9) constructed a single master curve for cow peas using the temperature shift factor. Also, research on viscoelastic behavior has been performed for many food systems, such as rice-whole soybeans (10), barley starch (11), ovalbumin gel (12), and whey protein gel (13). However, research on viscoelastic properties related to shelf life at different storage temperatures is limited.

The purpose of this study was measurement of the rheological properties of Cheddar cheese at different storage temperatures and calculation of a master curve to show the time-temperature effect using stress-relaxation data and a shift factor.

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Materials and Methods

Materials Natural Cheddar cheese was provided by the Seoul Dairy Cooperative (Ansan, Korea) in June of 2012 and stored at 5, 8, 15, and 25°C.

Proximate analysis Proximate analysis of Cheddar cheese was performed following the AOAC method (14). The moisture content was measured at 105°C using a dry oven (9HB-502M; Hanbaek Scientific Co., Bucheon, Korea), and the crude protein content was determined using the semi-micro Kjeldahl method (14). The crude fat content was analyzed following the Rose-Gottlieb (RG) method (15).

Measurement and analysis of a stress relaxation curve The stress relaxation of Cheddar cheese (diameter=2 cm and height=2 cm) stored at temperatures between 5 and 25°C was measured at a 150 mm/min crosshead speed and a 0.4 strain level. Stress relaxation values of cheese were recorded over 420 s.

A 3-element Maxwell model composed of 2 elastic springs and a viscous dashpot was used for analysis of the viscoelastic properties obtained from stress-relaxation measurements. The general equation is shown in Eq. 1.

$$\frac{1}{E_1}\cdot\frac{d\sigma}{dt}+\frac{\sigma}{\eta}\left(1+\frac{E_1}{E_2}\right)=\frac{d\varepsilon}{dt}+\frac{E_2}{\eta}\cdot\varepsilon \quad (1)$$

where E=the elastic constant, η=the viscous constant, σ= stress, and ε=strain.

As $\frac{d\varepsilon}{dt}=0$, $\frac{1}{\tau_b}=\frac{E_1+E_2}{\eta}$ is stress relaxation, therefore $\frac{d^2\sigma}{dt^2}+\frac{1}{\tau_b}\cdot\frac{d\sigma}{dt}=0$, shown in Eq. 2.

$$\sigma=\sigma_e+(\sigma_0-\sigma_e)\cdot e^{\frac{\tau_b\cdot(E_1+E_2)}{\eta}} \quad (2)$$

where σ=stress at time t, σ_e=equilibrium stress at time, σ_0 =instantaneous stress, e=Napierian logarithm base=2.72, E_1=instantaneous elastic constant, E_2=elastic constant, η= viscous constant, and τ_b=relaxation time, the time for decay to reach 1/e of (σ_0–σ_e).

The instantaneous elastic constant (E_1), elastic constant (E_2), and viscous constant (η) were obtained from Eq. 3, 4, and 5, respectively.

$$\frac{\sigma_0}{\varepsilon_0}=E_1 \quad (3)$$

$$\frac{\sigma_e}{\varepsilon_0}=\frac{E_1\cdot E_2}{(E_1+E_2)} \quad (4)$$

$$\tau_b=\frac{\eta}{(E_1+E_2)} \quad (5)$$

Master curve creation using the shift factor The dependency of the viscoelastic behavior of Cheddar cheese on storage temperature was analyzed based on the time-temperature superposition principle from elastic modulus data collected at different storage temperatures (16). The elastic modulus value at each storage temperature was obtained from stress-relaxation data. A specific stress-relaxation value was moved left or right horizontally at a reference temperature of 15°C, and the shift factor (a_t) was calculated at that point as:

$$a_t=\frac{t}{t_{ref}} \quad (6)$$

where t_{ref} indicates the change in time after movement, and t indicates time at a randomly set temperature.

Prediction of shelf life and calculation of the activation energy The shelf life and activation energy of Cheddar cheese were obtained from Eq. 7, which was used to predict changes in quality at different storage temperatures using the Williams-Landel-Ferry (WLF) equation (17) which is based on the shift factor and storage temperature.

$$\text{Log}a_T=\frac{C_1\cdot(T-T_r)}{C_2+(T-T_r)} \quad (7)$$

where a_T=shift factor, C_1 and C_2=coefficients, T= temperature, and T_r=the reference temperature.

The relationship between log a_T and temperature can be expressed as:

$$\text{Log}a_T=\frac{\Delta H}{2.303R}\left(\frac{1}{T}-\frac{1}{T_r}\right) \quad (8)$$

where ΔH is the activation energy and R is the gas constant. The activation energy in the correlation between log a_T and temperature was calculated using Eq. 9.

$$\Delta H=2.303R\frac{d\log a_T}{d\frac{1}{T}} \quad (9)$$

The following equation was obtained based on modification of Eq. 7.

$$-\frac{(T-T_r)}{d\log a_T}=\frac{C_1}{C_2}+\frac{(T-T_r)}{C_1} \quad (10)$$

where $(T-T_r)/\log a_T$ for $T-T_r$ here is a nearly straight line. In the WLF equation, C_1 and C_2 were obtained from the relationship between $T-T_r$ and $-(T-T_r)/\log a_T$ using Eq. 10.

Results and Discussion

Stress-relaxation of Cheddar cheese The Cheddar cheese used in this study contained 33.9% moisture, 24.2% crude protein, and 35.3% crude fat. Previous reports showed that the moisture, protein, and fat contents of Cheddar cheese were in ranges of 34-38%, 22-25%, and -38%, respectively (18,19).

Changes in stress relaxation of Cheddar cheese at different storage temperatures are shown in Fig. 1. The instantaneous stress of Cheddar cheese and the equilibrium stress after 420 s changed from 224.71 to 32.77 kPa at 5°C, from 199.75 to 26.53 kPa at 8°C, from 26.40 to 16.54 kPa at 15°C, and from 49.94 kPa to 5.15 kPa at 25°C. The instantaneous stress and equilibrium stress values increased as the storage temperature decreased.

As with other protein gels, such as skim milk gel (20) and mozzarella cheese (21), a lower storage temperature produced a stronger gel with higher failure stress. Relaxation time, the instantaneous elastic constant, elastic constant, and viscous constant were calculated using stress-relaxation data based on application of a 3-element Maxwell model and equations 1 to 5 (Table 1). As the storage temperature increased from 5 to 25°C, the instantaneous elastic constant decreased from 561.79 to 124.48 kPa, the elastic constant decreased from 95.91 to 14.35 kPa, and the viscous constant decreased from 11,036.28 to 1,507.48 kPa·s, indicating that as the storage temperature increased, all 3 rheological constants decreased.

Del Nobile *et al.* (22) determined each constant in a generalized Maxwell model after stress relaxation testing and demonstrated that a higher relaxation time resulted in a higher viscous constant. In addition, relaxation time decreased as storage time increased, indicating that elastic components were more predominant at lower temperatures.

Creation of master curve On the basis of stress-relaxation curves of Cheddar cheese stored at different temperatures, 15°C was selected as a reference temperature for construction of the final master curve shown in Fig. 2. Stress-relaxation at temperatures lower than 15°C was shifted to the left, and

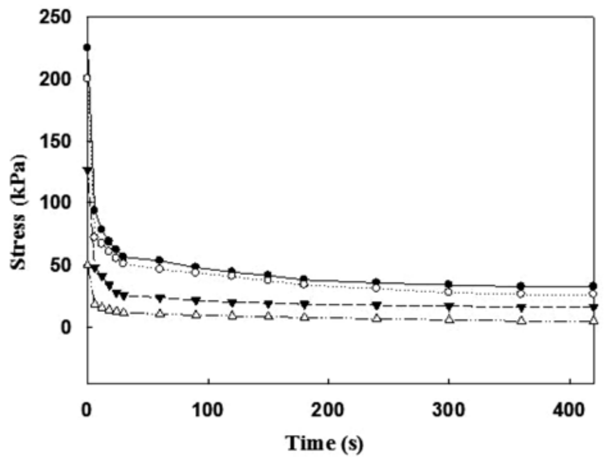

Fig. 1. Stress relaxation curves of Cheddar cheese at different storage temperatures (● 5°C, ○ 8°C, ▼ 15°C, △ 25°C).

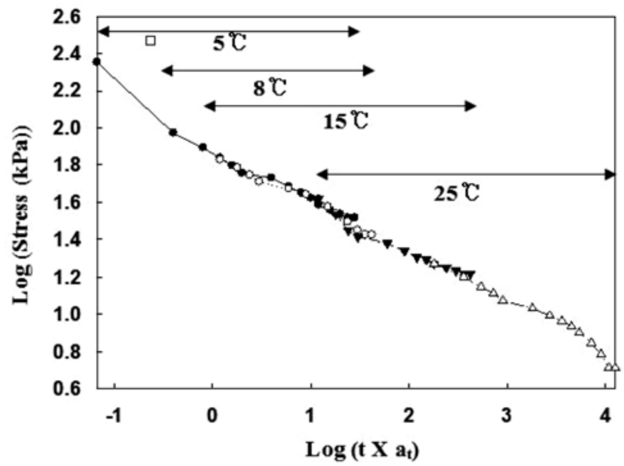

Fig. 2. Master curves of Cheddar cheese superimposed on the reference temperature curve at 15°C from data shown in Fig. 1 (● 5°C, ○ 8°C, ▼ 15°C, △ 25°C).

Table 1. Relaxation time, instantaneous and elastic constants, and viscous constant of Cheddar cheeses at different storage temperatures[1)]

Storage temperature (°C)	T_b (s)[2)]	E_1 (kPa)	E_2 (kPa)	η (kPa·s)
5	16.78±0.51[a3)]	561.79±20.21[a]	95.91±5.78[a]	11036.28±85.97[a]
8	15.29±0.34[b]	499.36±16.18[b]	76.48±2.33[b]	8804.58±88.30[b]
15	12.94±0.55[c]	316.00±21.74[c]	47.58±3.60[c]	4704.73±54.97[c]
25	10.83±0.27[d]	124.84±10.25[d]	14.35±2.11[d]	1507.48±43.14[d]

[1)] Values are mean±standard deviation for n=3.
[2)] T_b=relaxation time, E_1=instantaneous elastic constant, E_2=elastic constant, η=viscous constant
[3)a-b] Mean values within each column with no common superscripts are significantly different (p<0.05).

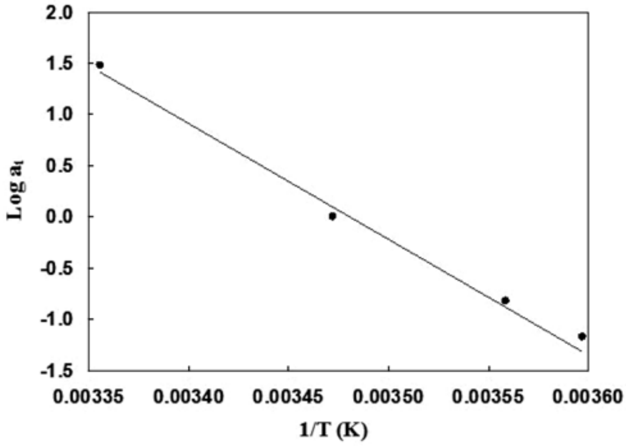

Fig. 3. Relationship between the shift factor (a_t) and the absolute temperature of Cheddar cheese (Correlation coeff.= 0.9938).

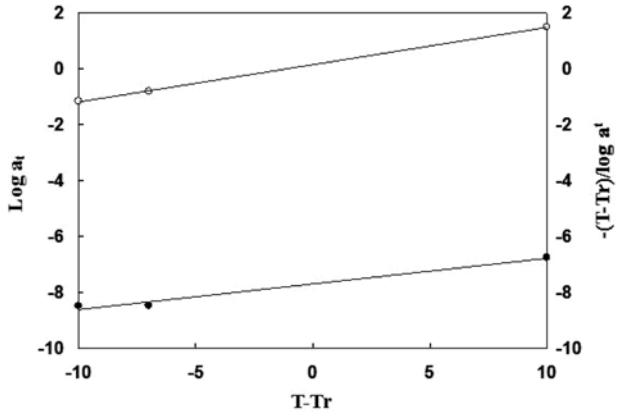

Fig. 4. Effects of temperature on the shift factor (a_t) of Cheddar cheese (Based on a modified WLF equation, ● –(T–T_r)/log a_t, ○ log a_t).

Table 2. Effects of temperature on apparent activation energies of Cheddar cheese

Temperature (°C)	Apparent activation energy (kcal/mol)
5	53.90
8	52.38
15	49.25
25	45.58
Mean	50.28

to the right at temperatures higher than 15°C (Fig. 1). The shift factor (a_t), indicating the degree of curve movement at the reference temperature of 15°C, was 1, and the shift factor was 0.067 at 5°C and 0.15 at 8°C. The shift factor at 25°C was 30. The master curve for Cheddar cheese constructed in this study was temperature dependent, and the elastic modulus decreased from 2.35 to 1.70 as temperature increased from 5 to 25°C.

Pappas and Rao (9) studied temperature dependency and moisture content of cowpeas using a master curve and showed that as the storage temperature and moisture contents of cowpeas decreased, the initial stress increased. Katsuta and Kinsella (23) studied whey protein isolate gel using a master curve and suggested that temperature dependency was related to the protein concentration. Yoon *et al.* (24) studied the storage modulus of fish proteins at different temperatures and showed that the storage modulus tended to increase linearly as the frequency increased and the storage temperature decreased. Jang *et al.* (17) used a master curve for tofu at different storage temperatures to show that elasticity decreased linearly as storage temperature increased, similar to results reported herein.

Prediction of the shelf life and calculation of activation energy The activation energy of Cheddar cheese was measured based on viscoelastic parameters using the time-temperature superposition principle. Correlation between the shift factor and temperature is shown in Fig. 3. The shift factor at different storage temperatures was linear (correlation coefficient=0.994), and the activation energy (ÄH) value of 50.25 kcal/mol was obtained from the straight line. ÄH values at each temperature were obtained from Eq. 7 and 8 (Table 2). The apparent activation energy at each temperature ranged from 45.56 to 53.90 kcal/mol, and the average activation energy was 50.28 kcal/mol, which is similar to the 50.25 kcal/mol value using a_t and the 1/T linear equation. The decrease in activation energy based on temperature reflected non-covalent coherence equating to hydrogen bonds. The activation energy also reflected the solidity or the density of cross-links in the structure (23). Thus, non-covalent bonds were dominant in Cheddar cheese stored at low temperature.

The activation energy of tofu was also temperature dependent with a value of 41.36 kcal/mol at 5°C and 22.24 kcal/mol at 25°C (17). The activation energy obtained from uniaxial compression at 10 to 60°C after mixing whey protein, caseinate, egg white, soy protein isolate, and gelatin with mozzarella cheese was between 2.9 and 3.8 kcal/mol (25). Tunick (6) claimed that the protein and moisture contents were related to the activation energy in Cheddar, Colby, mozzarella, and Parmesan cheeses and that a lower moisture content and higher protein content produce higher activation energies.

The value of C_1 was determined based on calculation using Eq. 10 and the inclination, $1/C_1$, and the intercept C_2/C_1 (Fig. 4). The value of C_1 was 10.99 and C_2 was 84.70. Based on the modulus value of Cheddar cheese stored at 15°C for 15 min, similar results were obtained with a storage time of 225 min at 5°C, which was approximately 15 times longer than predicted. Changes in the cheese matrix were affected by values of C_1 and C_2, which were apparently a function of the protein content of Cheddar cheese (23).

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Disclosure The authors declare no conflict of interest.

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