

Rheological properties of skim milk gels at various temperatures; interrelation between the dynamic moduli and the relaxation modulus*)

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Abstract: The rheological properties of rennet-induced skim milk gels were determined by two methods, i.e., via stress relaxation and dynamic tests. The stress relaxation modulus $G_c(t)$ was calculated from the dynamic moduli G' and G'' by using a simple approximation formula and by means of a more complex procedure, via calculation of the relaxation spectrum. Either calculation method gave the same results for $G_c(t)$. The magnitude of the relaxation modulus obtained from the stress relaxation experiments was 10% to 20% lower than that calculated from the dynamic tests.

Rennet-induced skim milk gels did not show an equilibrium modulus. An increase in temperature in the range from 20° to 35 °C resulted in lower moduli at a given time scale and faster relaxation. Dynamic measurements were also performed on acid-induced skim milk gels at various temperatures and $G_c(t)$ was calculated. The moduli of the acid-induced gels were higher than those of the rennet-induced gels and a kind of “permanent” network seemed to exist, also at higher temperatures.

Key words: Milk gels; rheology; stress relaxation; dynamic moduli; temperature

Notation:

G'	– storage shear modulus, $N \cdot m^{-2}$;
G''	– loss shear modulus, $N \cdot m^{-2}$;
G'_c	– calculated storage shear modulus, $N \cdot m^{-2}$;
G''_c	– calculated loss shear modulus, $N \cdot m^{-2}$;
G_e	– equilibrium shear modulus, $N \cdot m^{-2}$;
G_{ec}	– calculated equilibrium shear modulus, $N \cdot m^{-2}$;
$G(t)$	– relaxation shear modulus, $N \cdot m^{-2}$;
$G_c(t)$	– calculated relaxation shear modulus, $N \cdot m^{-2}$;
$G^*(t)$	– pseudo relaxation shear modulus, $N \cdot m^{-2}$;
H	– relaxation spectrum, $N \cdot m^{-2}$;
t	– time, s;
τ	– relaxation time, s;
ω	– angular frequency, $rad \cdot s^{-1}$.

1. Introduction

Milk contains about 3.3% protein, of which about 80% consists of casein. Almost all the casein in uncooled milk is present in roughly spherical particles, with sizes ranging from 20 to 300 nm. An important

step during cheesemaking is the rennet-induced coagulation of milk. Rennet is an extract from calves' stomachs. It contains proteolytic enzymes which hydrolyze a specific peptide bond of one of the caseins. The casein particles lose their colloidal stability and a gel is formed under quiescent conditions. Milk can also be coagulated by acidification. It occurs in the manufacture of products such as yoghurt and quark.

Recently, extensive studies on the structure and mechanical properties of milk gels have been performed by Van Dijk and coworkers [1–3], Roefs et al. [4–6], Zoon et al. [7–12], Tokita et al. [13–17], and Van den Bijgaart et al. [18–19]. The rheological behavior of rennet-induced milk gels made at the natural pH of milk (pH \approx 6.65) was studied by Tokita et al. [13–17] and by Zoon et al. [7–12]. The latter investigated the effect of variables, known to be important for cheesemaking, such as pH, temperature, ionic strength, calcium phosphate content by performing dynamic, stress relaxation and creep experiments. Electron microscopy was performed, e.g., by Kalab et al. [20] and Knoop et al. [21, 22], whereas

*) Partly presented at the “Conference on Rheology of Food, Pharmaceutical and Biological Materials”, Warwick, UK, September 13–15, 1989 [33].

Van Dijk et al. [1–3] and Van den Bijgaart et al. [18–19] investigated the structure and syneresis behavior of this type of gels. The structure and rheological properties of casein gels formed by cold acidification and subsequent heating were studied by Roefs et al. [4–6] through rheological and permeability measurements and electron microscopy. The main conclusions of these investigators, relevant to the topic of this paper, were that skim milk gels were built of aggregated casein particles; the gel was a viscoelastic system and mainly interactions of enthalpic nature contributed to the storage and loss modulus [23]. The temperature-time superposition could not be applied [4, 9].

To obtain information on the viscoelastic behavior of the milk gels over a relatively long time-scale, it was necessary to combine the results of different kinds of measurements. Dynamic experiments provide information at relatively short and stress relaxation at relatively long time-scales. If the viscoelastic behavior can be described by a generalized Maxwell model, it is, within the linear region, possible to calculate any viscoelastic function from any other, provided the latter is known over a sufficiently wide range of time or frequency [24]. Moreover, if the same time-dependent rheological data can be calculated from different types of experiments, this is a strong indication that true material properties have been measured. In this study the stress relaxation modulus was calculated from the dynamic moduli by two methods and the calculated relaxation modulus was compared to the relaxation modulus obtained from stress-relaxation experiments for rennet-induced milk gels. The influence of temperature on the stress relaxation was studied and a comparison was made with acid-induced skim milk gels.

2. Theory

It was assumed that the linear viscoelastic behavior of a milk gel could be described by the properties of a generalized Maxwell model. Each of the relaxation modes (Maxwell element) constitutes to the viscoelastic functions by [24]:

$$G_m(t) = G_m \exp(-t/\tau_m) \quad (1)$$

$$G'_m(\omega) = G_m \omega^2 \tau_m^2 / (1 + \omega^2 \tau_m^2) \quad (2)$$

$$G''_m(\omega) = G_m \omega \tau_m / (1 + \omega^2 \tau_m^2) \quad (3)$$

The behavior of the milk gel is then modeled by the sum of the contributions of the individual elements.

If some of the bonds in the network are permanent, one of the relaxation times is chosen to be infinite and the corresponding modulus contribution is G_e , the equilibrium modulus. Increasing the number of elements without limit and using a logarithmic time scale leads to a continuous relaxation spectrum $H(\tau)$. The functions described in Eqs. (1)–(3) then become [24]:

$$G_c(t) = G_e + \int_{-\infty}^{+\infty} H(\tau) \exp(-t/\tau) d \ln \tau \quad (4)$$

$$G'_c(\omega) = G_e + \int_{-\infty}^{+\infty} H(\tau) \omega^2 \tau^2 / (1 + \omega^2 \tau^2) d \ln \tau \quad (5)$$

$$G''_c(\omega) = \int_{-\infty}^{+\infty} H(\tau) \omega \tau / (1 + \omega^2 \tau^2) d \ln \tau \quad (6)$$

Several methods have been developed for the calculation of one function from the other [24, 26]. In this study, two methods were used to calculate $G(t)$ from the dynamic moduli G' and G'' as described in Section 3.2.

3. Materials and methods

3.1 Experimental methods

3.1.1 Preparation of rennet-induced milk gels: 10.4 g of a commercial low-heat skim milk powder (Krause, Heino) was brought into 100 g of demineralized water containing 0.015% thiomersal (BDH chemicals) or 0.02% sodium azide (Merck) to prevent bacterial growth. To allow equilibrium the dispersion was stirred for about 16 h at 30°C. 0.025% calf rennet (10800 SU; from CSK, The Netherlands) was added to the milk (pH 6.65), which was then put into the rheological measuring apparatus.

For the dynamic experiments, the gels were aged for 10 h at 30°C before the measurement started (30°C) or the temperature was changed. At a testing temperature of 25°C or higher the measurements started 1 h after the temperature change and at 20°C 2.5 h after the change.

For the stress relaxation experiments, the samples were aged for 6 h at 30°C before testing (30°C) or temperature change. At 25° and 20°C the measurements started 1.5 h after the water temperature had been adjusted. (A more extensive description has been previously published [9].)

3.1.2 Preparation of acid-induced milk gels: 12 g of commercial low-heat skim milk powder was dissolved in 100 g of demineralized water and 0.01% of

thiomersal was added to the milk. The milk was stirred for 16 h at 30 °C. The temperature was brought at 2 °C and the pH was slowly and, while continuously stirring, lowered to pH 4.6 by adding HCl. The milk was transferred to the rheometer and the temperature was raised to 30 °C at a rate of 0.5 °C per min. The gels were aged for 16 h at this temperature and the temperature was changed to 20° or 40 °C for some tests. After 1 h the measurement was started. A more extensive description is given in [4].

3.1.3 Dynamic measurements with the “Den Otter” rheometer: The rheometer was developed and described by Duizer [28] and Den Otter [29]; a brief description is given here. The apparatus consisted of two coaxial cylinders. The stainless steel inner cylinder had a length of 15 cm and a radius of 3.75 mm; it was suspended between a torsion wire fixed to a drive shaft and a strain wire. The outer cylinder was made of glass and had a radius of 4.5 mm; it was surrounded by a water jacket to control the temperature within 0.1 °C.

The gel was formed in the apparatus. During the measurements a sinusoidal oscillation was applied to the inner cylinder. The amplitude of the drive shaft and of the inner cylinder were measured, as well as the phase difference. From these the storage modulus G' and the loss modulus G'' were calculated [4]. The amplitude of the drive shaft was small enough to ensure linear behavior of the milk gel, which appeared to exist if the maximum strain was smaller than 0.03 [4]. The angular frequency was varied between 10^{-3} and $10 \text{ rad} \cdot \text{s}^{-1}$.

3.1.4 Stress relaxation measurements: A Weissenberg R 18 Rheogoniometer was used, (a brief description is given here; a more detailed description is given by Bloksma and Nieman [27]). The apparatus consisted of a cone (top) and a plate (bottom), both having a radius of 37.52 mm. The stainless steel surfaces had been blasted with corundum to a roughness of about 4 μm . The angle between the cone and the plate was 0.0549 rad. The cone was truncated over a distance of 157 μm of its axis. The temperature was controlled by pumping water through a double-walled chamber enclosing the cone and plate.

The gels were formed in the apparatus. During the measurements a constant shear strain of about 0.03–0.04 was applied to the gel after moving the plate at a constant rate of 0.0143 s^{-1} for 2–3 s. The resulting stress was recorded until 2 h after deformation. To minimize drying of the sample two troughs

with water were placed between the sample and the chamber.

3.2 Mathematical procedure

The methods used to calculate $G(t)$ from the dynamic moduli were:

Method I: a simple approximate equation derived by Ninomiya and Ferry [25]:

$$G(t) = G'(\omega) - 0.40G''(0.40\omega) + 0.014G''(10\omega)|_{\omega=1/t}; \quad (7)$$

Method II: calculation of the relaxation spectrum from G'' and, subsequently, calculation of $G(t)$, as described partly by De Cindio et al. [26].

The first step was to estimate $H(\tau)$ from $G''(\omega)$ obtained by dynamic measurements by applying:

$$H(\tau) = (2/(3\pi))[G''(\omega) + G''(10^{0.2}\omega) + G''(10^{-0.2}\omega)]_{\omega=1/\tau}. \quad (8)$$

The dynamic moduli were obtained over a frequency range from 10^{-3} to $4.5 \text{ rad} \cdot \text{s}^{-1}$. $H(\tau)$ was estimated at several values of τ ($\tau = 1/\omega$) within this range. In all of the calculations the steps between two succeeding values of $\log \tau$ was 0.2.

It was then checked whether the estimate of $H(\tau)$ was correct by calculating the loss modulus G''_c with Eq. (6). Because of the finite range over which the dynamic moduli were obtained, the limits of the integral were not $-\infty$ and $+\infty$, but were the inverse of the upper and lower limit of ω . This also applies to the use of Eqs. (4), (5), and (11). The integrals were calculated by a step method. First an auxiliary variable A was calculated:

$$A = H(\tau)\omega\tau/(1 + \omega^2\tau^2) \quad (9)$$

in which ω was kept constant. A was calculated for all values of τ (with steps of 0.2 between the succeeding values of $\log \tau$) within the range over which the dynamic moduli were determined. The average value of every two succeeding A 's was calculated and multiplied by $\ln 10^{0.2}$. Then the obtained values were summed, giving G'' at the chosen value of ω .

If the difference between the calculated and measured loss moduli was on average larger than 2%, a new estimate for $H(\tau)$ was made:

$$H(\tau)_{\text{new}} = H(\tau)_{\text{old}} + \Delta H(\tau), \quad \text{with} \quad (10)$$

$$\begin{aligned} \Delta H(\tau) = & (2/(3\pi))\{[G''(\omega) - G_c''(\omega)] \\ & + [G''(10^{0.2}\omega) - G_c''(10^{0.2}\omega)] \\ & + [G''(10^{-0.2}\omega) - G_c''(10^{-0.2}\omega)]\} . \quad (11) \end{aligned}$$

This procedure was repeated until the average difference between the calculated and measured loss moduli was at most 2%. Next, G_c' was calculated:

$$G_c'(\omega) = \int_{-\infty}^{+\infty} H(\tau) \omega^2 \tau^2 / (1 + \omega^2 \tau^2) d \ln \tau , \quad (12)$$

and G_{ec} was calculated:

$$G_{ec}(\omega) = G'(\omega) - G_c'(\omega) . \quad (13)$$

Subsequently, $G_c(t)$ was calculated with Eq. (4).

4. Results and discussion

4.1 Calculation of $G(t)$ from G' and G'' and comparison with $G(t)$ obtained from stress relaxation measurements

Dynamic measurements were performed as described in Section 3.1. The results were published before [4, 7, 9]. In this article the dynamic moduli were used to calculate $G(t)$ as described in Section 3.2. The dynamic moduli were obtained over a finite range. This caused some problem in the calculation of $G_c(t)$ via the relaxation spectrum. Calculation of G_c'' (Eq. (6)) in the first cycle of calculation gave too low values near the limits, because (part of) the contribution of the interactions with relaxation times just below $0.22s$ ($4.5 \text{ rad}\cdot\text{s}^{-1}$) or just above $1000s$ ($0.001 \text{ rad}\cdot\text{s}^{-1}$) were not taken into account. The value of $H(\tau)$ near the limits was then increased (Eqs. (10), (11)) to such an extent that the difference between G_c'' and G'' was on average less than 2%. Therefore, the values of $H(\tau)$, G_{ec} and $G_c(t)$ near the limits calculated in this way were unreliable. Subsequently, $H(\tau)$ was determined over an extended range: from $\tau = 2.2$ to $10000s$. The loss modulus in the extended range was obtained by linear extrapolation in a log-log plot. Probability this procedure does not introduce gross errors, because a straight line of $\log G''$ vs $\log \omega$ was observed in the range between 1 and $10 \text{ rad}\cdot\text{s}^{-1}$ in some experiments in which G'' was determined up to $\omega = 10 \text{ rad}\cdot\text{s}^{-1}$. At long time-scales no irregularities were observed in the curve of $G(t)$ vs t and, therefore, no marked deviation from a straight line of $\log G''$ vs $\log \omega$ between 10^{-3} and $10^{-4} \text{ rad}\cdot\text{s}^{-1}$ is expected. Moreover, it appeared that

small differences in extrapolation did not change G_c' , G_c'' , and $G_c(t)$. Calculations of G_c' , G_c'' , and $G_c(t)$ were performed over the range of ω in which measurements were performed using $H(\tau)$ of the extended range. All of the subsequent results have been obtained by using this procedure.

The relaxation modulus was calculated from the dynamic moduli by the two methods described in Section 3.2 and both gave the same results (Fig. 1), strongly suggesting that the calculations had been performed correctly. A disadvantage of the use of the formula derived by Ninomiya and Ferry (Eq. (7)) was that the relaxation modulus could only be calculated over a range of time-scales that was by 1.5 decades narrower than that tested. Extrapolation of the dynamic moduli to shorter and longer time-scales would increase this range, although this calculation method is more sensitive to deviations in extrapolation than the calculation via the relaxation spectrum. Another advantage of calculation via the relaxation spectrum is that, not only the relaxation modulus may be calculated, but, in principle, also other functions.

To compare $G_c(t)$ calculated from the dynamic moduli with $G(t)$ obtained from relaxation measurements a correction had to be made. The gels tested in the relaxation experiments had been aged for a shorter time than those in the dynamic experiments. The difference in time was due to experimental restrictions: performing the dynamic tests took about a whole day, so the gels were aged overnight. The gels tested in the relaxation test were aged a shorter time, because the samples tended to dry on the edge and to release from the cone after longer times. In the dynamic test it was observed that the storage and loss modulus increased measurably up to about 8 to 10 h after rennet addition. Then the moduli were stable for a few hours [8]. $G(t)$ obtained from stress relaxation was therefore multiplied by 1.13 (G' after 10 h of ageing divided by G' after 6 h of ageing). In Fig. 1 the corrected values are depicted. Moreover, the temperature in the Weissenberg Rheogoniometer was 20.5°C instead of 20.0°C ; no correction has been made for this. $G(t)$ obtained from stress relaxation measurements was somewhat lower than the calculated $G_c(t)$. For the samples tested at 25° and 20°C the measured $G(t)$ was about 20% lower than the calculated $G_c(t)$, and at 30°C this was about 10%. There may be various reasons for the difference:

– Differences between duplicates of about 20% were found in stress-relaxation measurements. The results given in Fig. 1 are mean values of two to four measurements. The differences between duplicates may (partly) have been caused by (micro)syneresis. At

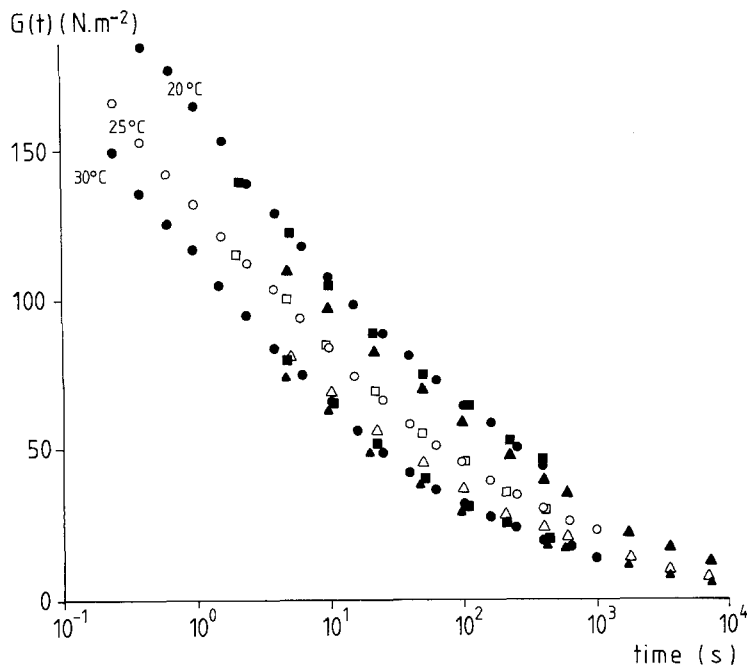


Fig. 1. The relaxation modulus $G(t)$ as a function of time for rennet-induced skim milk gels (pH 6.65), formed and aged at 30°C and tested at the indicated temperatures. Symbols: (Δ , \blacktriangle) obtained from measurements with the Weissenberg Rheogoniometer (corrected values); (\square , \blacksquare) calculated with method I; (\circ , \bullet) calculated with method II. (For further explanation see text)

35°C almost no stress was measured after deformation of the gel. In the Den Otter rheometer this occurred only at temperatures of 40°C or higher. The difference in syneresis is probably caused by the different geometry of the rheometers. Due to its own weight the casein network tends to yield, which results in (micro)syneresis. In the Den Otter rheometer the gel is suspended from the inner and outer cylinder, which diminishes (micro)syneresis.

– The temperature control in the Weissenberg Rheogoniometer, viz. by air thermostating, was less accurate than in the Den Otter rheometer, and this may have contributed to the deviations between the measured and the calculated relaxation modulus for tests at lower temperatures.

– The time needed to apply strain in the stress relaxation experiments of about 2.5 s probably did not contribute largely to the differences. According to the factor-of-ten rule [32] deviating results could be expected upto 25 s, whereas the differences existed also at longer times.

In general the results of the dynamic and stress relaxation experiments agreed fairly well. The same conclusion was obtained for rennet-induced milk gels with pH 6.25 and 5.75 measured at 30°C [33]. This strongly supports the idea that the rheological properties of rennet-induced milk gels determined under widely varying conditions (such as temperature) did not depend on the measuring method and may be considered true material properties.

4.2 Time-dependent rheological behavior of milk gels and the effect of temperature

4.2.1 Rennet-induced milk gels: In Fig. 2 H is depicted as a function of τ in a log-log plot. At 20°C H varied little with τ . With increasing temperature H was almost the same at the shorter times, but the slopes became steeper at longer times. At high temperatures interactions with long relaxation times thus contributed less to the modulus than at lower temperatures, implying that at a higher temperature the stress relaxed in a shorter time. This was already concluded before from the results of the dynamic tests on rennet-induced milk gels [9] and it can also be concluded from the steeper slope of the curves of $G(t)$ vs time at higher temperature in Fig. 3.

Executing the mathematical procedure described in Section 3.2, an equilibrium modulus G_{ec} was calculated (Fig. 4). As it should be, its value was independent of time. However, G_{ec} is not a real equilibrium modulus, since it does not represent the contribution to the storage modulus of interactions with an infinite relaxation time. G_{ec} represents the contribution of interactions with relaxation times longer than about 10^3 s due to the finite range over which the measurements were performed. Therefore, the value of G_{ec} depends on the value of the lowest frequency at which the dynamic moduli were determined. It cannot be considered as a material property. The calculation of G_{ec} was necessary for calculation

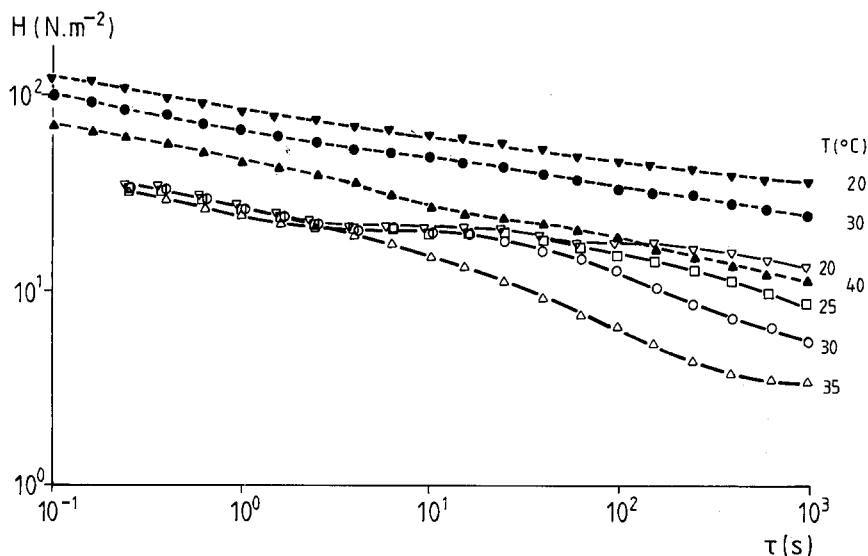


Fig. 2. The relaxation spectrum H calculated from the loss modulus G'' (see text) for rennet-induced skim milk gels (open symbols) and acid-induced skim milk gels (filled symbols) formed and aged at 30°C and tested at the indicated temperatures

of $G_c(t)$ (Eq. (4)), because otherwise the interactions with relatively long relaxation times would not have been taken into account and too low values of $G_c(t)$ would have been obtained. The slope of the curves of the relaxation modulus vs time became steeper with increasing time (Fig. 3). It is therefore not likely that a real equilibrium modulus for rennet-induced milk gels exists under these conditions.

4.2.2 Acid-induced skim milk gels: To compare the moduli of the acid-induced milk gels and rennet-induced milk gels a correction had to be made, because a

higher concentration of milk powder was used in making the acid-induced milk gels. It was found [4, 8] that increasing the concentration of casein in solution by a factor x increased both the storage and loss modulus by a factor $x^{2.5}$. After correction it appeared that the storage and loss moduli of acid-induced milk gels were higher than those of the rennet-induced milk gels (about 2.5 times at 30°C and $\omega = 1 \text{ rad}\cdot\text{s}^{-1}$). Also the dependence on time was different. As can be seen from Fig. 3 the negative slopes of the curves of the acid gels mostly were less steep than those of the rennet-induced gels at the same

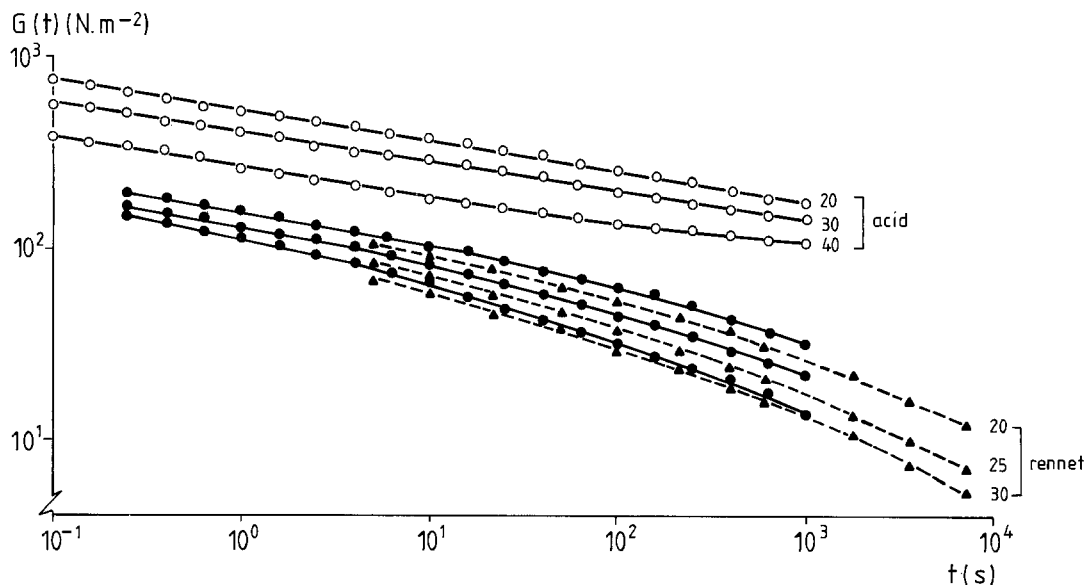


Fig. 3. Log-log plot of the relaxation modulus $G(t)$ vs t for rennet-induced skim milk gels (filled symbols) and acid-induced skim milk gels (open symbols) calculated with method II (see text) (\circ , \bullet) and obtained from stress relaxation measurements (\blacktriangle). The test temperature is indicated

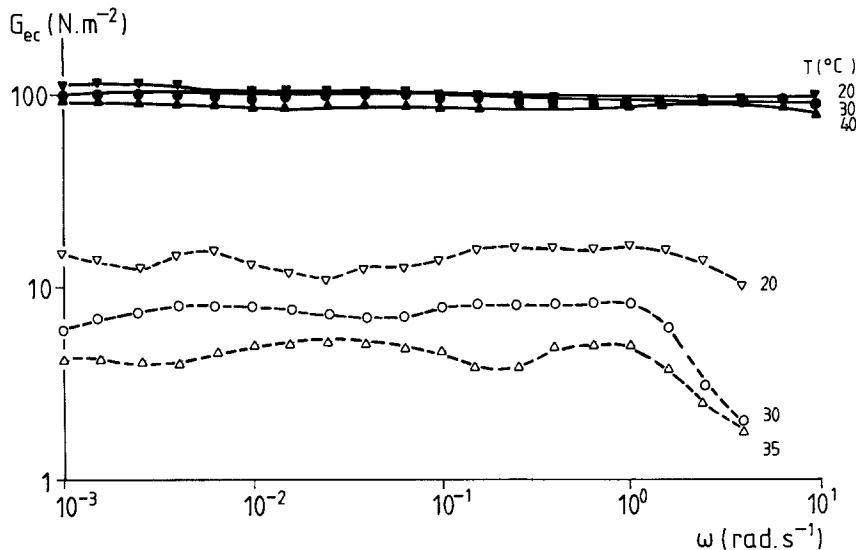


Fig. 4. The “equilibrium” modulus G_{ec} calculated from the dynamic moduli (see text) for rennet-induced skim milk gels (open symbols) and acid-induced skim milk gels (filled symbols) formed and aged at 30 °C and tested at the indicated temperatures

temperature. Increasing the temperature caused a decrease of the relaxation modulus. Qualitatively different from the behavior of the rennet-induced gels, the slope became more flat at longer time-scales with increasing temperature (Fig. 3). This may point to the existence of a true equilibrium modulus. For acid-induced milk gels no true stress relaxation measurements were performed, but the rheometer was used to roughly test the relaxation of stress of acid-induced skim milk gels. For this purpose the drive shaft was set at its maximum displacement (within the linear

region). The displacement of the inner cylinder was measured as a function of time and a pseudo-stress relaxation modulus $G^*(t)$ was calculated as described in [4]. In Fig. 5 $G^*(t)$ is depicted as a function of time. Even after $10^5 s$ (30 h) a substantial value of $G^*(t)$ remained and $G^*(t)$ decreased relatively little with time. This points to the existence of interactions with very long relaxation times, although ongoing gelation may also play a part. As described in a preceding study [4], the dynamic moduli of acid-induced milk gels increased almost linearly with the logarithm of time and even after 7 days the moduli still increased without reaching a plateau value. This alone cannot account for the flattening of the curves at longer times. At 40 °C, for instance, the value of $G^*(t)$ would only be about 60% lower after times longer than $3.10^5 s$ if no ongoing gelation occurred.

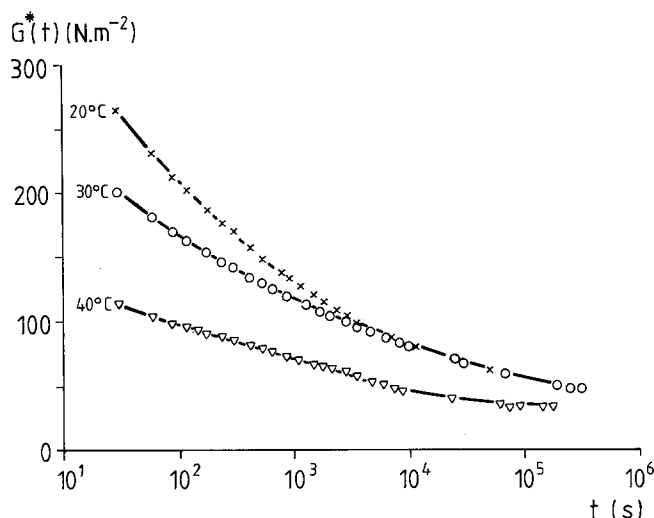


Fig. 5. The pseudo-stress relaxation modulus $G^*(t)$ as a function of the logarithm of time for acid-induced skim milk gels formed and aged for about 20 h at 30 °C and tested at the indicated temperatures

The possible existence of an equilibrium modulus, the higher modulus and less stress relaxation of acid-induced milk gels compared to rennet-induced milk gels may be related to the differences in, for example, microsineresis. For instance, the permeability to whey of rennet-induced gels keeps increasing 24 h after the onset of gelation, whereas the permeability of acid-induced milk gels does not increase between 2 and 20 h after the onset of gelation [1]. This implies that in rennet-induced gels strands break and reform at other places [3], whereas in acid gels rearrangements only take place at a very local scale in the network. The reason for these differences probably stems from the difference in structure of the casein particles at, for example, pH 4.6 and 6.6 [6, 30], and from differences in the main interaction forces between the protein molecules [31].

5. Conclusion

The results of this study show that calculation of the relaxation modulus $G_c(t)$ from the dynamic moduli of rennet-induced milk gels, being particle gels, could be successfully performed by methods described for polymer gels. The relaxation modulus calculated from the dynamic moduli $G_c(t)$ was somewhat lower than the relaxation modulus obtained from stress-relaxation experiments ($G(t)$). This was thought to be mainly due to experimental inaccuracy.

Based on the time-dependency of $G(t)$, it was concluded that rennet-induced milk gels do not have a permanent network.

In comparison with rennet-induced milk gels, $G_c(t)$ of acid-induced milk gels was higher and decreased relatively slower with time.

Acknowledgements

The Institute for Cereals, Flour, and Bread TNO, Wageningen, The Netherlands, kindly allowed us to perform measurements on the Weissenberg Rheogoniometer.

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(Received November 10, 1989;
in revised form February 4, 1990)

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