STRESS RELAXATION OF STORED STIRRED CHEDDAR CURD

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ABSTRACT

An introspective empirical method for reducing stress relaxation data of certain foods was proposed by Peleg (1979). In his method relaxation curves are normalized with respect to initial force. In the method described herein his resulting equation is rearranged as a straight line but with the normalized force and time variables written as reciprocals $1/f(t) = (1/ab)(1/t) + (1/a)$, a plot of $1/f(t)$ versus $(1/t)$ will yield a more severe test of the experimental data since the time variable "t" no longer appears on both sides of the equation as it does in the former case. This empirical method has been applied to relaxation data of stirred curd cheddar cheese manufactured under government specifications and stored at −2 to 0°C. With this method there are apparently at least two relaxation periods for cheese, a primary period which occurs for about 2 min and a secondary period which commences thereafter. When the separate periods are compared to one another values of the "a" and "b" constants are completely different and show that the secondary relaxation rate is substantially slower than the first. This method provides a more sensitive tool for comparing aging effects in stored cheese.

INTRODUCTION

The stress-relaxation curves of solid foods have usually been fit to an exponential expression based on a Maxwell model as discussed by Sherman (1970) and Peleg (1979).

The equation is of the form:

$$F(t) = \sum_{j=1}^{m} A_j e^{-(\alpha_j t)} \tag{1}$$

Here, the constants A and α are related to the particular food under investigation and F(t) represents a force imposed on the food sample at time zero which declines with time as the time t increases. It is known that, ordinarily, two to three terms in the expansion of Eq. (1) are necessary to obtain a satisfactory fit to the stress-relaxation curve. Consequently four to six constants appear in the expanded series. In order to ease the comparison of data, Peleg (1979) suggested an introspective empirical method in which: (1) the relaxation curves are normalized with respect to initial force F(o), and (2) the resulting dimensionless function is a normalized relaxation stress and is expressed in the form of a hyperbolic equation, a conjecture based on the shape of the relaxation curve. For example in step one,

$$f(t) = \frac{F(o) - F(t)}{F(o)} \tag{2}$$

where F(t) is the time dependent declining force measured during relaxation and, in step (2)

$$f(t) = \frac{ab\,t}{1 + bt} \tag{3}$$

According to Peleg (1979), the constant "a" represents the asymptotic or equilibrium residual values of f(t) when $t \rightarrow \infty$. The constant b is, according to Peleg (1979), reflective of the "rate" at which the stress relaxes and the reciprocal 1/b, is the time necessary for the normalized relaxation stress f(t) to reach $\frac{a}{2}$. Hence, b equals zero corresponds to an ideal elastic solid and the stress does not relax. Peleg rearranges Eq. (3) in the form of a straight line

$$\frac{t}{f(t)} = \frac{1}{ab} + \frac{t}{a} \tag{4}$$

an plots t/f(t) against t.

According to Peleg, Eq. (4) presents a simple way of describing a curve by means of two constants while still maintaining the character of the curve.

This also follows the recommendation of Hunston (1974) who suggested that the form of Eq. (4) "usually provides the best presentation of the data". However, in contrast it had been pointed out by Mickley *et al.* (1957) that correlations in the form of Eq. (4) can be misleading, "any correlation of experimental data based on a graph in which the same variable appears in both ordinate and abscissa should be viewed with suspicion".

An alternative approach is to rearrange Eq. (3), also in the form of a straight line, but as follows:

$$\frac{1}{f(t)} = \frac{1}{ab}\,\frac{1}{t} + \frac{1}{a} \tag{5}$$

In this form, $\frac{1}{f(t)}$ is plotted against $(\frac{1}{t})$ with slope $(\frac{1}{ab})$ and intercept $\frac{1}{a}$. Equation (5) has the advantage that the same variable (time) does not appear on both the ordinate and abscissa and should therefore represent a critical test of the experimental data. (Incidentally the form of Eq. (5), is, according to Hunston, "a less desirable form" as compared to Eq. (4)).

MATERIALS AND METHODS

Samples of stirred curd cheddar were prepared from cheese blocks which had been stored at −2 to 0 °C. The specimens were 20 mm in diameter and 20 mm thick. The cheese used in the experiments was a commercial stirred curd cheddar which was purchased from a local dairy; it was manufactured according to government specifications.

Two Plexiglas plates, 172 mm and 167 mm diameter, were used. One was attached to the crosshead and one to the load cell of the Instron Machine. All specimens contacted only the plexiglas plates during compression and subsequent relaxation. In some cases, specimens were lubricated at the ends by applying G.E. silicone 192 m Pa-s or 12 Pa-s (12,500 centistoke) viscosity. The specimens were subjected to a constant strain at 20 °C in the Instron machine and allowed to "relax" for at least 15 min. The initial crosshead speed used was 50 mm/min with a chart speed of 200 mm/min. Force-time data were read directly from the strip chart recorder.

RESULTS AND DISCUSSION

Stress relaxation curves of commercial stirred curd both fresh and aged 11 months are shown in Fig. 1 and 2. The samples were taken from different blocks of the same batch. The data in these two figures are presented in both normalized form, according to Peleg's approach and in reciprocal normalized form according to Eq. (5). Results of the experimental series which examined specimens at various age increments to 14 months are shown in Table 1.

As may be noted in Fig. 1 and 2, two separate straight lines may be fit to the experimental data when the reciprocal method is used, suggesting that a primary and secondary relaxation occurs in stirred curd cheese. Stress relaxation curves with two regions were also observed recently by Bagley and Christianson (1986) in a study involving dough rheology. In each case the change from a primary to secondary relaxation occurs at about 2 min under the experimental conditions employed. The values of "a" and "b" increased as aging increased during primary and secondary relaxation. The value of "b" (indicative of the "rate" of relaxation) increased by about a factor of two over the 14 months aging period in both primary and secondary relaxation while the values of "a" increased by about 25% in primary relaxation. There is significant reduction in the magnitude of the "rate" "b" during secondary relaxation when compared to the primary relaxation. In secondary relaxation the values of the "rate" "b" were found to have changed from 1/3 to 1/2 of those observed in primary relaxation. It was also noted that even at the relatively low compression levels employed (4 to 7%), lubrication of the specimens resulted in lowered force measurements; however, in general, there was not a great difference between the computed "a" and "b"

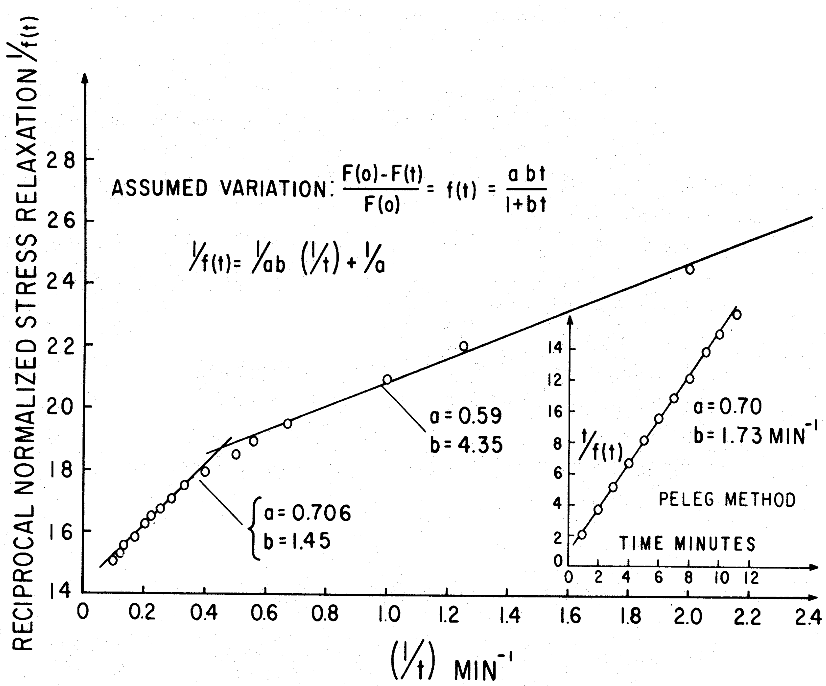

FIG. 1. RECIPROCAL BASELINE DATA-NORMALIZED STRESS RELAXATION $\frac{F(o)-F(t)}{F(o)}$ STIRRED CHEDDAR CURD; 6% COMPRESSION

Stress level 0.322 kg./cm.^{2} Crosshead speed 50 mm/min. No treatment.

values whether the specimens were treated or not treated.

An evident change in the "a" and "b" values occurs at 7 months, as shown in Table 1. The "rates" of relaxation as reflected by "b" have about doubled from their initial value. Additional changes in "a" appear inconclusive based on the values shown. Definite increases in the primary relaxation rate still occur at 14 months, based on the increased value of b, almost a factor of 2, although the secondary relaxation rate as reflected by changes in "b" does not seem to have changed much during the latter 7 months.

It was also observed that an empirical "power" law fit could be made from the data occurring during secondary relaxation. The fit used took the simple form

$$f(t) = c\,t^n \qquad 0 < t < 10 \tag{6}$$

(where t is the time in min) with r^2 at least 0.98 in each data set examined.

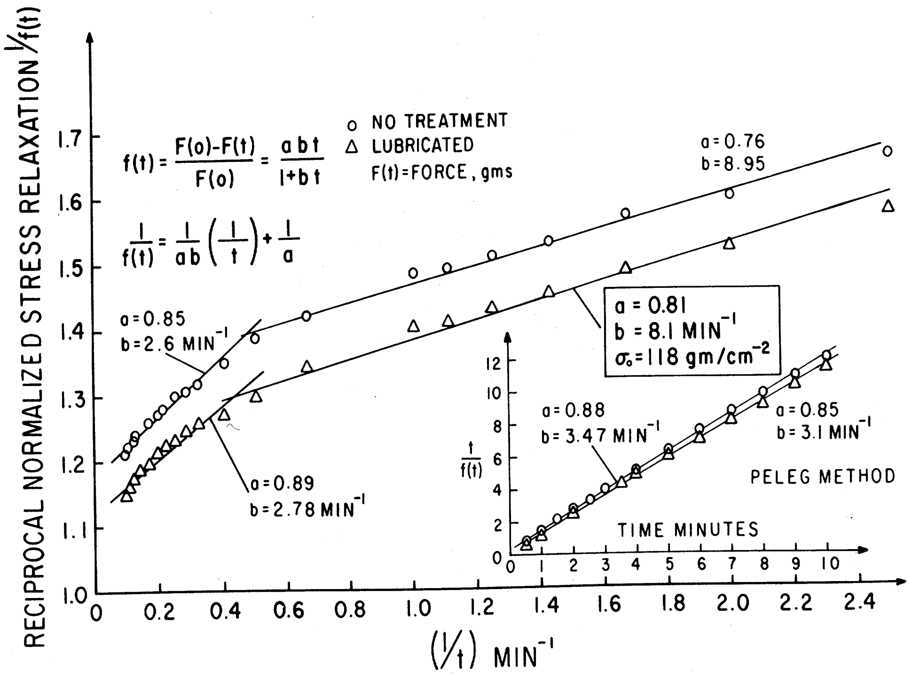

FIG. 2. RECIPROCAL NORMALIZED STRESS RELAXATION $\frac{(F(o)-F(t))}{F(o)}$
STIRRED CHEDDAR CURD AGED 11 MONTHS
6% compression stress level 0.131 kg/cm.[2] Crosshead speed 50 mm/min.
Lubricated with GE Viscasil 12 Pa-s; (12,500 centistokes).

The numerical values of the constants c and n obtained from the power law fit are also shown in Table 1. Thirty-nine points were considered in fitting the power law expression. The values of "c" and "n" shown represent 95% confidence limits. No theoretical deductions should be inferred from this empirical calculation except that the results are useful when comparing one cheese versus another. Moreover, regarding the power law fit, it appears that the exponent "n" is a better indicator of relaxation changes during aging than is the constant "c". There is clear evidence of a significant decrease in "n" in a given block as time progresses. (i.e. the different blocks are all obtained from the same batch, however). Notice that the value "n" has decreased by about a factor of 2 during the 14 months of aging. The values of "b", (Eq. 3) reflective of the rate during relaxation, have increased also by about a factor of 2 over the same time period. This increase in the rate of relaxation suggests that irreversible changes have occurred internally in the body of the cheese. Cheese is primarily a mixture of fat, water and protein (essentially casein) distributed in roughly equal proportions in which the protein contributes the solid form of a mature cheese, Prentice (1972).

TABLE 1.
EFFECTS ON AGING ON "a" *AND* "b" (EQ. 3) AND POWER LAW COEFFICIENTS "n" AND "c" (EQ. 6); STORED CHEDDAR CURD

Months Aged	Primary Relaxation			Secondary Relaxation			Treatment	Apparent Stress[3]	Power Law Fit Secondary Relaxation		% Compression
	a	b	r^2	a	b	r^2			n	C	
0	0.59	4.35	0.99	0.71	1.45	0.98	none	0.332	0.133 ± .007	0.495 ± .007	6
1	0.59	4.50	0.99	0.71	1.57	0.98	none	0.193	0.134 ± .006	0.497 ± .006	6
2	0.60	5.30	0.99	0.71	1.96	0.99	none	0.221	0.121 ± .007	0.526 ± .007	6
2	0.59	5.50	0.99	0.82	2.90	0.98	none	0.255	0.126 ± .007	0.518 ± .007	4
7	0.71	9.10	0.98	0.81	3.00	0.98	lubricate[1]	0.322	0.088 ± .004	0.654 ± .004	7
7	0:68	9.40	0.98	0.77	3.30	0.98	none	0.383	0.080 ± .004	0.636 ± .004	7
11	0.76	9.00	0.97	0.85	2.76	0.98	none	0.131	0.079 ± .002	0.670 ± .002	6
11	0.81	8.10	0.98	0.89	2.80	0.97	lubricate[2]	0.118	0.074 ± .004	0.735 ± .004	6
13	0.73	11.00	0.99	0.81	3.60	0.98	lubricate[2]	0.234	0.073 ± .004	0.685 ± .004	5
14	0.73	9.30	0.98	0.82	2.90	0.97	none	0.240	0.078 ± .002	0.671 ± .002	6
14	0.75	9.00	0.98	0.83	3.00	0.98	none	0.224	0.073 ± .002	0.690 ± .002	6

1 GE Silicone Viscasil - 12,500 cs (12 Pa-s)
2 GE Silicone - 200 cs (192 m Pa-s)
3 Apparent stress $= \frac{\text{Force}}{\text{Initial Area of Sample}}$; Kg/cm²

It is the action of an enzyme (chymosin) during manufacture which results in the decomposition of the α-casein during aging, Kim (1985); moreover the casein undergoes a change from its spherical form to a filament structure and subsequently during aging to a three dimensional fibrous network, Shama and Sherman (1973), and hence these internal structural changes are not reversible. One may infer that the corresponding changes in the value of the power law exponent "n" is also suggestive of the aforementioned internal structural changes in the cheese matrix.

CONCLUSIONS

A fairly straightforward technique has been discussed for comparing the relaxation characteristics of cheeses; this technique is a more severe test of the data than the method suggested by Peleg (1979). The method proposed is also empirical and infers that two relaxation periods can be identified even at relatively low compression levels. Interpretating the constant "1/a" in terms of a strain in difficult but it is likely that it is related to an equilibrium modulus (Peleg 1979). The constant, "b" is easier to interpret since it has dimensions of reciprocal time and is thus indicative of a rate of relaxation. It was found that one could also fit a power law curve to the secondary relaxation data; statistically the fit is about as good as the straight line fit (i.e. r^2 about equal). The experimental relaxation data were obtained over a rather low level of strain; the results, however, may still be strain dependent because the data may not be in the linear range. The method proposed does allow one to compare aging effects in stored cheeses in a straightforward manner.

NOMENCLATURE

A	= Coefficient in Eq. (1), units of force
a	= Constant in Eq. 3, 4 and 5, dimensionless
b	= Constant in Eq. 3, 4 and 5 having units of reciprocal time
C	= Constant in Eq. (6)
f(t)	= Stress relaxation force function defined in Eq. 1
F(t)	= Time dependent force (see Eq. 2)
F(o)	= Initial force at time zero
n	= exponent, constant in Eq. 6
r^2	= correlation coefficient
t	= time

greek

(alpha) α = exponential constant (min^{-1}) in equation 1 related to relaxation time

(sigma) σ = Initial stress level kg/cm^2

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