Cordiales saludos,
Micha Peleg

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Comparison of two methods for stress relaxation data presentation of solid foods

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Abstract: Published exponential relaxation equations, derived from Maxwellian models, were used to generate data for linear representation in the form of $P(0) \cdot t/(P(0) - P(t)) = k_1 + k_2 t$ where $P(t)$ is the decaying parameter (force, stress or modulus), $P(0)$ its initial value (at $t = 0$) and k_1 and k_2 constants. The computer plots indicated that the fit of this normalized and linearized form was excellent for equations containing at least three exponential decay terms. The fit was not as good for some of the two-term exponential equations mainly due to the lack of accurate account for the initial stage of the relaxation process. In all the cases, however, the linear representation could clearly reveal the general rheological character of the analysed materials in terms of the relative degree of solidity.

Key words: Stress relaxation, Maxwellian model, solid food

1. Introduction

Stress relaxation data have traditionally been employed as one of the principal means of quantifying the viscoelastic behavior of foods. Commonly, experimental force decay curves have been presented in the form of a discrete Maxwellian model containing 2–4 elements, i. e. [1]:

$$P(t) = \sum_{i=1}^{n} P_i \exp\left(-\frac{t}{\tau_i}\right) \tag{1}$$

where $P(t)$ is the decaying parameter (i. e. force, stress or modulus) after time t at relaxation, P_i's the representatives of the elastic constants of the individual Maxwell elements and τ_i's the relaxation times of these elements.

The mathematical form of eq. (1) implies that at $t \to \infty$ $P(t) \to 0$ and therefore that a material described by it is a liquid by definition. A truly viscoelastic solid material ought to be described by:

$$P(t) = P_o + \sum_{i=1}^{n} P_i \exp\left(-\frac{t}{\tau_i}\right) \tag{2}$$

where P_o is the residual unrelaxed or asymptotic parameter (which corresponds to the single spring constant in parallel to the group of Maxwell elements in a generalized Maxwell mechanical analog array). It also ought to be mentioned that eqs. (1) and (2) will have the same mathematical character if any τ_i in eq. (1) is allowed to approach infinity. If, however, all the τ_i's in eq. (1) have finite values the question of whether the longest relaxation time has physical significance will naturally arise. This problem as well as a mathematical procedure to deal with its solution were described by Tobolski and Murakami [2].

When models of the kind expressed in eqs. (1) and (2) are applied to food materials in compression, two special theoretical considerations ought to be borne in mind (i. e. apart from the more obvious instrumental considerations associated with the straining rate, friction, the specimen shape, etc.). The first is that food materials, especially under large deformations, exhibit non-linear viscoelastic properties. Therefore, the constants of eqs. (1) and (2) (or any other equation of a similar kind) must depend on both the strain and the strain history of the test.

The second factor is that almost all foods are by nature unstable or biologically active and consequently, long-term experiments for direct determination of equilibrium mechanical parameters or the longest relaxation time cannot yield pertinent results.

It has recently been shown [3, 4] that these two difficulties can be resolved, at least to some extent, by modification of the way by which the relaxation data are presented. According to this method the experimental force relaxation curves are first normalized and then linearized in a form similar to that previously suggested by Hunston [5], i. e.:

$$\frac{F(0) \cdot t}{F(0) - F(t)} = k_1 + k_2 t \tag{3}$$

where $F(0)$ is the initial force, $F(t)$ is the decaying force after time t and k_1 and k_2 are constants. According to this equation the reciprocal of k_1 depicts the initial decay rate, and the reciprocal of k_2 is the representative of a hypothetical asymptotic level of the normalized relaxation parameter $[F(0) - F(t)]/F(0)$. Since the latter is expressed as a dimensionless ratio it has the same value if expressed in terms of stresses or moduli.

According to this model the asymptotic modulus (E_A) after relaxation is given as follows:

$$E_A = \frac{F(0)}{A\varepsilon} \cdot \left[1 - \frac{1}{k_2}\right] \tag{4}$$

where A is the specimen cross-sectional area of the deformed specimen and ε is the fixed strain.

It has previously been shown [4, 6] that E_A is a function of both the initial stress and the fixed strain and that the relationships between E_A and ε (or $\sigma(0)$) are characteristics of the material and carry information that is relevant to its particular physical structure. Other mathematical aspects of this form of relaxation data presentation are discussed by Hunston [5] who also analysed the possibilities of using more than two constants in cases where the curves cannot be linearized.

The mathematical properties of eqs. (1) and (3) are such that they cannot be derived from one another. Any degree of compatibility can only be observed in extreme cases, i. e. for an ideal elastic solid or viscous liquid where both equations degenerate. In the intermediate range, k_2 of eq. (3) is the representative of the degree of solidity and it varies between the value of $k_2 = 1$ for a material that is truly a liquid (i. e. all the stress relaxes) to $k_2 \to \infty$ for an ideal elastic solid where the stress does not relax at all.

The fact that all the experimental evidence obtained so far [3, 4, 6, 7, 8] indicates that eq. (3) is a good representative of stress relaxation curves poses an inevitable question. Are these reported data in conflict with other published data or is there a practical agreement between the results despite the mathematical incompatability of the two types of models?

In this communication we have tried to address this problem through computer generated data obtained from published constants of eq. (1) and analysing their fit to the model presented by eq. (3).

2. Results and discussion

Published exponential stress relaxation equations, from different sources, were utilized to generate data representing the stress or modulus decay with time. By the same computer program the data have been converted into the normalized parameter given by:

$$y = \frac{F(0) - F(t)}{F(0)} \quad \text{or} \quad \frac{\sigma(0) - \sigma(t)}{\sigma(0)}$$

$$\text{or} \quad \frac{E(0) - E(t)}{E(0)} \tag{5}$$

and listed as functions of time (t).

The units of force, stress or modulus are the same as those reported in the original publications. The terms $F(0)$, $\sigma(0)$ or $E(0)$ were calculated as the sum of the F_i's, σ_i's or E_i's in the original exponential equation. Since at $t = 0$ $\exp(-t/\tau) = 1$, Eq. (1) or one of similar type becomes

$$P(0) = \sum_{i=1}^{n} P_i \, . \tag{6}$$

(The implications of this point in the comparison of the two methods will be discussed later.) The data so generated underwent linear regression by the SPSS package to fit the form and to calculate the constants of eq. (3). The process was repeated by data generated at different time intervals so that eq. (3) was fitted with two sets of data points in the range of 14 to 200 points. The created data file as well as the regression equations were then used to plot the following relationships:

a) $F(t)$, $\sigma(t)$ or $E(t)$ vs. t (i. e., the shape of the decay curve produced by the reported exponential equation).

b) $t/Y(t)$ vs. t from the generated data.

c) $t/Y(t) = k_1 + k_2 t$ where k_1 and k_2 are the constants calculated by linear regression of the generated data.

The plots so produced are shown in figures 1 – 7. The equations used as well as the results of the regression analysis are summarized in table 1.

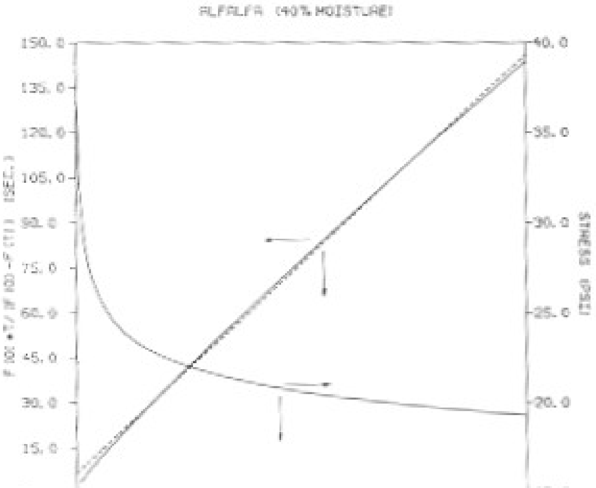

Fig. 1. Exponential and linearized stress relaxation curves of alfalfa. (Solid lines represent the actual data and the dashed line the linear regression.) Data from Ref. [10]

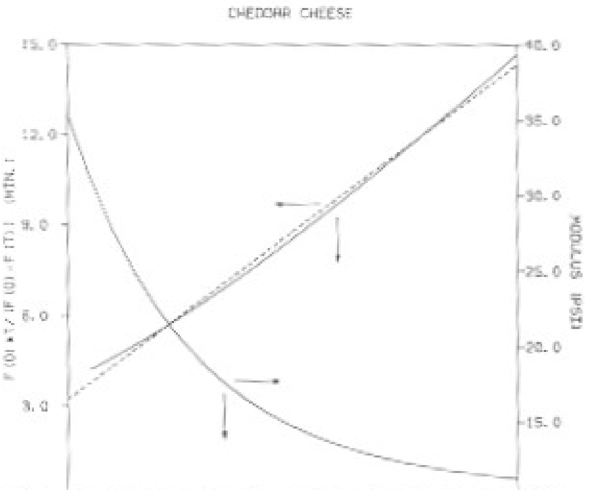

Fig. 2. Exponential and linearized stress relaxation curves of cheddar cheese. (Solid lines represent the actual data and dashed line the linear regression.) Data from Ref. [11]

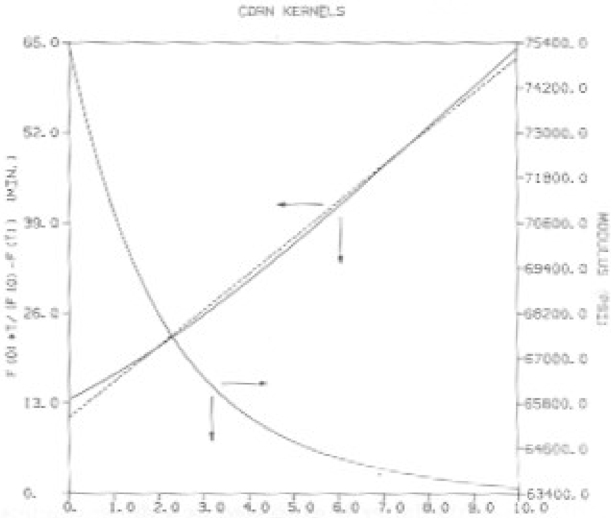

Fig. 3. Exponential and linearized stress relaxation curves of corn grains. (Solid lines represent the actual data and the dashed line the linear regression.) Data from Ref. [11]

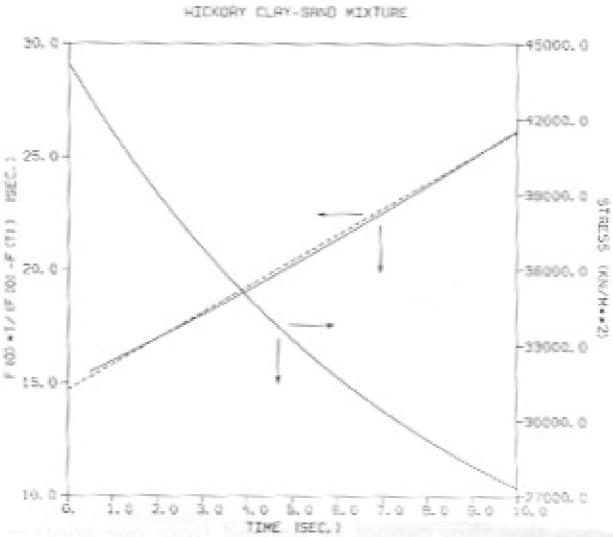

Fig. 4. Exponential and linearized stress relaxation curves of clay-sand mix. (Solid lines represent the actual data and dashed line the linear regression.) Data from Ref. [12]

The results clearly demonstrate that for all the cases in which the original exponential equation contained 3 or 4 terms (i. e., alfalfa, clay sand mixture and potato) the data had excellent fit to eq. (3). Where the exponential decay equation contained only two terms, the goodness of the fit varied according to the material. Although it was generally reasonable, it was clearly not as good as in the former case. One of the reasons for this is that fitted equations with only two exponential terms do not provide an accurate account of the initial part of the relaxation curve where the decay rate is extremely fast. (Compare, for example, [11] where both experimental and fitted curves are shown.) Since the statistical fit is mainly determined by the data beyond the initial stage of the stress decay, this point may easily be overlooked or considered

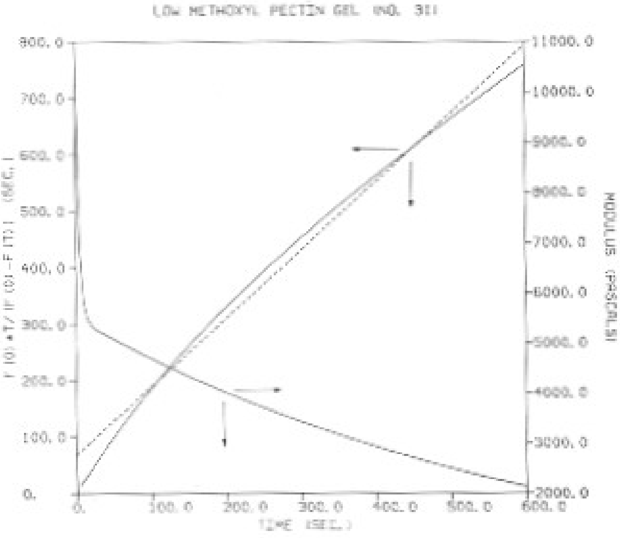

Fig. 5. Exponential and linearized stress relaxation curves of low methoxyl pectin gel. (Solid lines represent the actual data and the dashed line the linear regression.) Data from Ref. [13]

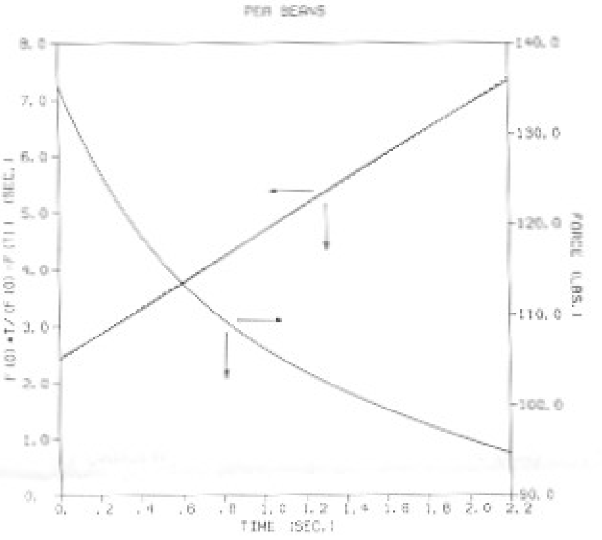

Fig. 6. Exponential and linearized stress relaxation curves of pea beans. (Solid lines represent the actual data and dashed line the linear regression.) Data from Ref. [14]

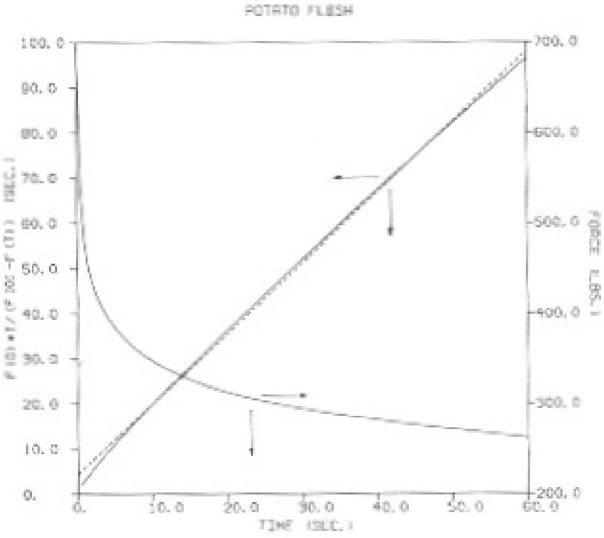

Fig. 7. Exponential and linearized stress relaxation curves of potato flesh. (Solid lines represent the actual data and the dashed line the linear regression.) Data from Ref. [15]

insignificant. The goodness of the fit of eq. (3), in contrast, was influenced by this aspect to a much greater extent. This is for the reason that the terms $F(0)$, $\sigma(0)$ or $E(0)$ were calculated from the sum of the preexponential coefficients (eq. (6)). A missing term in the original exponential equation, dropped because it contains a very short relaxation time, will obviously have very little effect on the magnitudes of the generated values of $\varepsilon(t)$, $\sigma(t)$ or $F(t)$ after a fairly short time. The presence or absence of such a term (or terms) however will have a very significant effect on the preexponential coefficient's sum (eq. (6)) especially if the former has an appreciable magnitude. It is evident (see table 1) that when such terms are added to the exponential equation, the magnitude of their preexponential coefficients are indeed significant. (It is also demonstrated in table 1 that in our case the linear regression coefficient r is not a very reliable index to the goodness of the fit, because its definition and method of calculation do not provide an indication as to the existence of real curvature.)

It can be argued however, on the basis of theoretical and instrumental considerations that the shape of the very initial part of the recorded relaxation curves is strongly influenced by the deformation history of the specimen and in certain instruments by the recorder pen response time also. Therefore, the physical significance of the values of k_1, in table 1 (or more accurately their reciprocal) as a representative of the initial relaxation rate, ought to be interpreted with caution [3, 4]. As a measure of a first-order approximation, however [5], the values do indicate that the materials in question are all fast relaxing materials at least initially. The values of k_2 (see eqs. (3) and (4)) ought to be more indicative of these materials' general rheological characteristics since

Table 1. Linearization of published relaxation curves expressed by exponential decay equations

Material	Exponential Decay Equation	Regression and Fit to eq. (4)				Source
		k_1	k_2	Number of Data Points (Generated)	r	
Alfalfa (40% M)	$\sigma(t) = 21 \exp\left(-\frac{t}{790}\right) + 4.2 \exp\left(-\frac{t}{16.4}\right) + 5.5 \exp\left(-\frac{t}{2.9}\right) + 6.9 \exp\left(-\frac{t}{0.47}\right)$ (σ in psi, t in sec)	6.66 (sec)	1.99	140	0.9995	Mohsenin (1970)
Cheddar Cheese	$E(t) = 23.6 \exp\left(-\frac{t}{2.6}\right) + 11.7 \exp\left(-\frac{t}{115}\right)$ (E in psi, t in min)	3.23 (min)	1.11	20	0.9980	Mohsenin and Morrow (1967)
Corn Grains	$E(t) = 10{,}980 \exp\left(-\frac{t}{2}\right) + 64{,}300 \exp \cdot \left(-\frac{t}{767.6}\right)$ (E in psi, t in min)	10.9 (min)	5.18	200	0.9982	Mohsenin and Morrow (1967)
Clay & Sand Mix	$\sigma(t) = 22{,}064 \exp\left(-\frac{t}{282}\right) + 17{,}238 \exp\left(-\frac{t}{8}\right) + 4{,}896 \exp\left(-\frac{t}{7}\right)$ (σ in $kN \cdot m^{-2}$, t in sec)	14.7 (sec)	1.14	20	0.9993	Rao (1975)
Low Methoxyl Pectin Gel (No. 31)	$E(t) = 5{,}487 \exp\left(-\frac{t}{635}\right) + 4{,}659 \exp\left(-\frac{t}{4.21}\right)$ (E in pascal, t in sec)	68.2 (sec)	1.21	120	0.9955	Gross et al. (1981)
Pea Beans	$F(t) = 109.5 \exp\left(-\frac{t}{14.67}\right) + 25.8 \exp\left(-\frac{t}{0.54}\right)$ (F in lb, t in sec)	2.41 (sec)	2.26	200	0.9999	Zoerb and Hall (1960), in Mohesenin (1970)
Potato Flesh	$F(t) = 319.8 \exp\left(-\frac{t}{301}\right) + 107.3 \exp\left(-\frac{t}{9.49}\right) + 72.3 \exp\left(-\frac{t}{2.03}\right) + 195.6 \exp\left(-\frac{t}{0.44}\right)$ (F in lb, t in sec)	4.40 (sec)	1.56	120	0.9995	Bashford and Whitney (1975)

they represent their relative degree of solidity. Although the original publications from which the data were obtained do not discuss if or how the relaxation equation terms varied with the strain, it is clearly evident that the more obviously solid materials had higher values of k_2 (e. g., corn kernels) while the soft or semi-solid foods (e. g. cheese) had a value close to unity which is an indication of liquid properties.

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