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# A Modified Maxwell and a Nonexponential Model for Characterization of the Stress Relaxation of Agar and Alginate Gels

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## ABSTRACT

Compressive stress relaxation curves of agar and alginate gels of different gum concentration (1.3% and 0.5–2%, respectively) were fitted by a two parameter nonexponential empirical model and a three term modified Maxwell model with two fixed relaxation times (10 and 100s). The asymptotic portion of the residual (unrelaxed) stress calculated by the two models for each gel had a similar magnitude, and therefore could serve as an objective measure of the gels degree of solidity. The coefficients of the modified Maxwell model provided a simple but meaningful means to compare, in quantitative terms, the differences in the relaxation time spectra that were associated with the gels' stiffness and strength.

## INTRODUCTION

THE STRESS-RELAXATION CURVES of gels, as well as many solid foods, have traditionally been described in terms of a discrete linear-Maxwell model (Mitchell, 1976); i.e.

$$E(t) = a_0 + \sum_{i=1}^n a_i \exp - \left( \frac{t}{\tau_i} \right) \quad (1)$$

where  $E$  is the decaying modulus (or sometimes the stress or force),  $a_i$  coefficients, and  $\tau_i$  relaxation times of the model. It has been repeatedly demonstrated that a model having two to four terms is sufficient to describe experimental curves with a high degree of fit, e.g. Gross et al. (1980), Comby et al. (1986), Costell et al. (1986). Theoretically, the constant  $a_0$  in Eq. (1) represents the amount of stress that remains unrelaxed. If  $a_0 = 0$ , all the stress relaxes, although at a progressively decreasing rate, and the material is considered liquid. If  $a_0 > 0$ , that is, there is a residual stress even when  $t \rightarrow \infty$ , the material is considered solid and the magnitude of  $a_0$  can serve as a measure of solidity. In nonlinear viscoelastic materials, the magnitude of  $a_0$  can depend on the deformation history of the specimen and consequently the specimen can exhibit different degrees of solidity at different strains.

Since gels are not physically stable and they tend to exchange moisture with the environment, tests for long term determination of their relaxation pattern are difficult to perform. Consequently, the physical meaning of  $a_0$  when determined in experiments of short duration, that is on the order of a few minutes, is only relevant to the gel's short term response. In other words, a gel's mechanical behavior on a time scale of a few minutes is equivalent to that of a viscoelastic solid with a residual modulus of magnitude  $a_0$ . Furthermore, if the constants of Eq. (1) are determined by a curve fitting technique their magnitude can depend on the test duration, which makes their significance as true material characteristics highly questionable. In liquid polymers this problem has been bypassed by assigning fixed values to the relaxation times and letting

only the coefficients vary (Chang and Lodge 1972; Wagner and Laun 1978). This resulted in a model of the kind:

$$E(t) = b_1 \exp - \left( \frac{t}{100} \right) + b_2 \exp - \left( \frac{t}{10} \right) + \dots + b_n \exp - \left( \frac{t}{0.1} \right) + \dots \quad (2)$$

where the  $b$ 's are the coefficients.

The advantage of this type of model when used to compare different materials or to assess the effects of test conditions, such as strain, on the relaxation behavior is obvious. This kind of model, although with a smaller number of terms, was also proposed for the characterization and classification of solid foods (Peleg, 1984). Its capabilities were demonstrated in selected foods by Miller et al. (1986) who showed that models with two to three terms are sufficient to capture the main characteristics of the stress-strain and stress-relaxation relationships. They also showed, however, that the model is not mathematically unique, and that the relaxation time spectrum can be selected in different ways. If, however, the relaxation times were representative of the relaxation behavior then the same basic picture emerged irrespective of the relaxation time selection and the number of terms in the model.

The problem with the asymptotic or equilibrium modulus was tackled in a different manner. If the relaxation curve can be represented by (Peleg, 1980):

$$\frac{F(t)}{F_0} = 1 - \frac{t}{k_1 + k_2 t} \quad (3)$$

or in its linearized form:

$$\frac{F_0 \cdot t}{F_0 - F(t)} = k_1 + k_2 t \quad (4)$$

where  $F_0$  is the initial force,  $F(t)$  the decaying force, and  $k_1$  and  $k_2$  constants, then a hypothetical asymptotic modulus,  $E_\infty$ , can be calculated from

$$E_\infty = \frac{F_0}{A\epsilon} \left( 1 - \frac{1}{k_2} \right) \quad (5)$$

where  $A$  is the specimen's cross-sectional area and  $\epsilon$  the strain. The physical significance of  $E_\infty$  as calculated by Eq. (5) has been demonstrated and discussed elsewhere (Peleg and Pollock, 1984; Finkowski and Peleg, 1981; Purkayastha and Peleg, 1987). The model expressed by Eq. 3, it should be added, has no direct account of the relaxation time spectrum. The momentary decay rate is expressed by:

$$\frac{d}{dt} \left( \frac{F(t)}{F_0} \right) = \frac{k_1}{(k_1 + k_2 t)^2} \quad (6)$$

and the initial rate by  $1/k_1$ .

Since the models expressed in Eq. (2) and (3) describe the

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same physical phenomenon but have different mathematical properties, it is interesting to compare their performance when applied to the same system. The objective of this work was to test the two models and their predictions in characterizing the relaxation behavior of agar and alginate gels of different concentrations.

### MATERIALS & METHODS

#### Sample preparation

Food grade commercial agar-agar and alginate (Kelgin LV, Kelco Division of Merck & Co.) were used for gel preparation. The agar powder (1–3%) was dispersed in distilled water and heated to boiling. The alginate powder (0.5–2.0%) and calcium-hydrogen orthophosphate ( $\text{CaHPO}_4$ ) were added slowly to stirred distilled water at ambient temperature until complete dissolution of all the ingredients. A freshly prepared solution of glucono- $\delta$ -lactone was then admixed using vigorous stirring.

The hot solution of the agar and the cold solutions of the alginate were poured into special split metal molds (shown schematically in Fig. 1). The molds consisted of metal rings held together with adhesive tape while mounted on a special rod having the rings' internal diameter. After cooling for 1 hr at 20°C, the tape and gel were cut with a sharp blade and the cylindrical specimens (1.5 cm  $\times$  1.5 cm) were removed from the rings using the metal rod as shown in the figure. The exact dimensions of each specimen were determined with a caliper. The initial composition of the alginate solution was 1%  $\text{CaHPO}_4$  and 1% glucono- $\delta$ -lactone. Mechanical tests were done at ambient temperature (20  $\pm$  1°C) on gels that had been aged for 24 hr. The alginate gels underwent syneresis during aging resulting in an increase in the effective polysaccharide concentration. Since no polysaccharide is lost by syneresis, the effective concentration of the alginate could be calculated by mass balance.

#### Mechanical testing

Specimens of the agar and alginate gels were compressed to failure by an Instron Universal testing machine model 1000. The Instron was connected to a Macintosh II computer by an analog to digital con-

version interface card from Strawberry Tree Computers. A specially developed program performed data acquisition from the Instron to the computer and conversion of the Instron continuous voltage vs time output into digitized force-deformation, force-time, stress-strain or stress-time values with any desired definition of the stress and strain. The program also performed linear or nonlinear regression on the data using special built-in subroutines or could write the data to files for regression and plotting using the SYSTAT package.

Agar specimens were compressed to 10% deformation and were allowed to relax for about 3–4 min. The alginate gels relaxed at 20% deformation. The deformation rate in all the tests was 10 mm·min<sup>-1</sup> and all the tests were performed in triplicate.

The voltage vs time data from the Instron were converted to true stress,  $\sigma(t)$ , vs Hencky's strain,  $\epsilon_H(t)$ , relationships according to the following definitions:

$$\sigma(t) = \frac{F(t) [H_0 - \Delta H(t)]}{A_0 H_0} \quad (7)$$

and

$$\epsilon_H(t) = \ln \left[ \frac{H_0}{H_0 - \Delta H(t)} \right] \quad (8)$$

where  $H_0$  is the initial specimen length,  $\Delta H(t)$  the momentary absolute deformation, and  $A_0$  the cross-sectional area of the original specimen.

The slope of the linear portion of the stress-strain relationship was defined as the deformability modulus,  $E_D$ , i.e.

$$E_D = \frac{\sigma(t)}{\epsilon_H(t)} \quad (9)$$

It has stress units and can be treated as a measure of the gel stiffness.

The force-time relationships in relaxation were fitted by Eq. (4) using linear regression to yield the constants  $k_1$  and  $k_2$ . The same relationships were also normalized and fitted, using nonlinear regression, to a shortened and modified version of the model expressed by Eq. (2); i.e.,

$$\frac{F(t)}{F_0} = C_0 + C_1 \exp \left( -\frac{t}{10} \right) + C_2 \exp \left( -\frac{t}{100} \right) \quad (10)$$

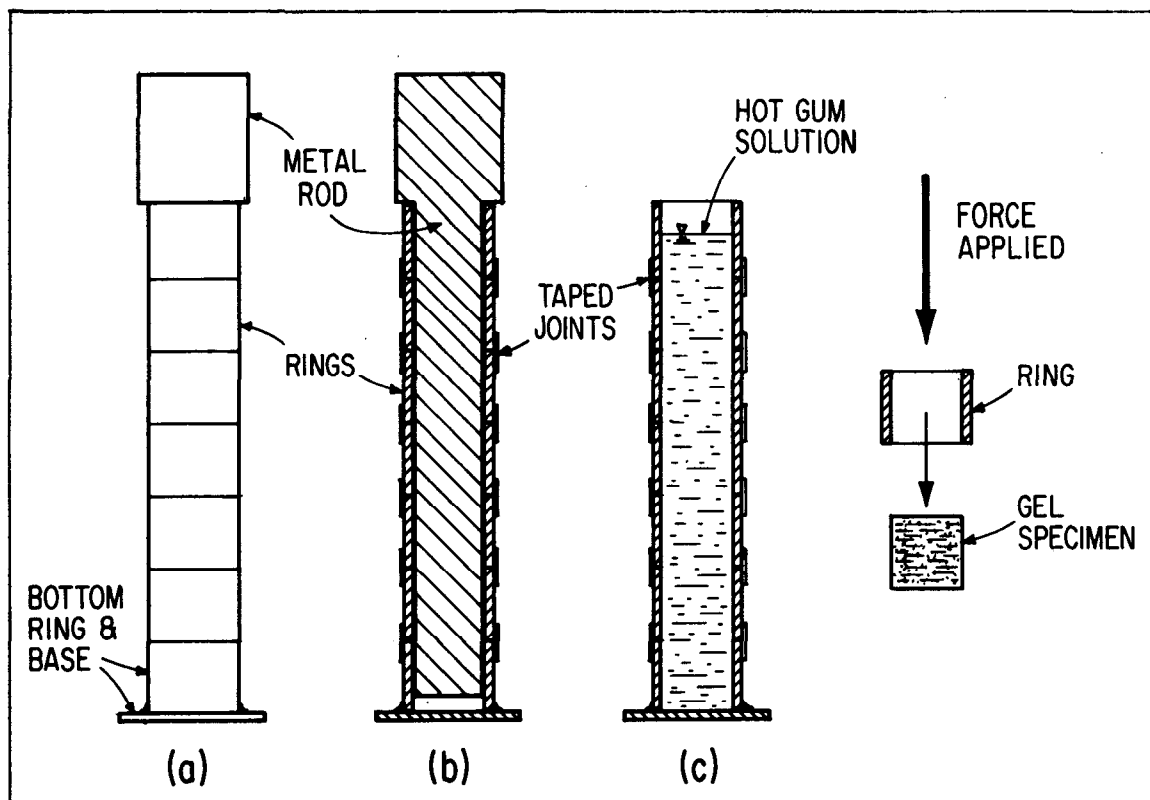


Fig. 1 — Schematic view of the special split mold for making cylindrical gel specimens for mechanical testing.

where 10 and 100 are the fixed relaxation times in seconds. Since the decaying parameter was a ratio, the coefficients  $C_0$ ,  $C_1$ , and  $C_2$  are dimensionless.

## RESULTS & DISCUSSION

THE FIT of the models expressed by Eq. (3) and (10) to experimental relaxation data of agar and alginate gels is demonstrated in Fig. 2. It shows that the two models have the same degree of fit and that, apart from a slight discrepancy in the initial part, the fitted curves of the two models are practically indistinguishable. The regression parameters are listed in Table 1.

As could be expected, an increase of the gum concentration

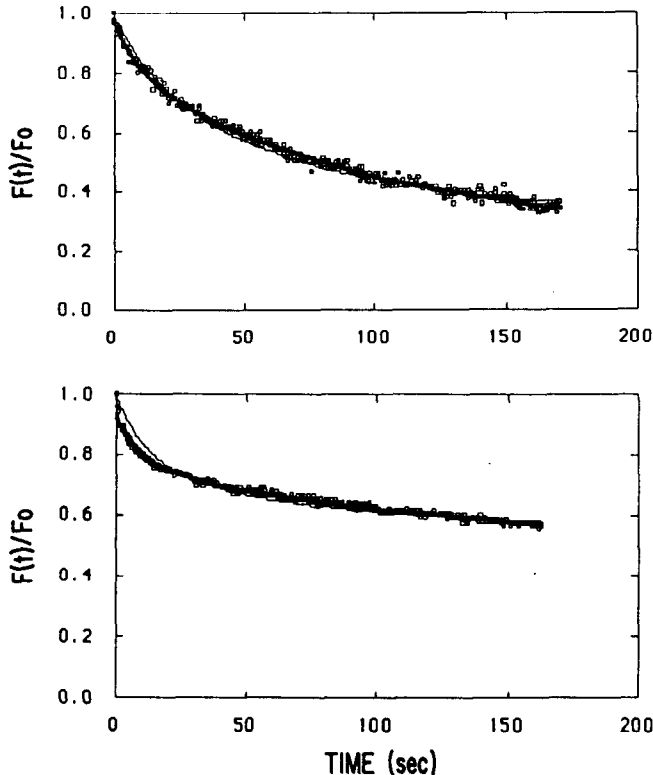


Fig. 2 — Demonstration of the fit of the two models expressed by Eq. (3) and (10) to experimental relaxation data of agar (top) and alginate (bottom) gels. Squares—experimental data; solid lines—Eq. (10); dashed lines—Eq. (3). Note that the fitted curves using the two models are practically indistinguishable over most of the experimental range.

within the reported range resulted in a firmer gel. This was manifested in the gel's stiffness, as expressed by its deformability modulus and its strength, i.e. its failure stress. The magnitudes of the deformability moduli and failure stresses are presented graphically in Fig. 3.

The two models for the relaxation data presentation [Eq. (3) and (10)] have different mathematical structure. They were also fitted by two different regression procedures, linear and nonlinear. Therefore, the fact that both represented the experimental data well within a given range is not in itself proof that their consequences outside that range are also the same. Testing their compatibility, therefore, must be based on comparison of calculated values. The most convenient parameter to compare is the magnitude of the asymptotic portion of the stress that remains unrelaxed. In terms of the two models in question [Eq. (3) and (10)], compatibility will be expressed by  $C_0 = 1 - 1/k_2$ . As can be seen from Table 1, the agreement between the values of  $C_0$  and  $1 - 1/k_2$  was between about 2 to 20% in the agar gels and less than 5% in the alginate gels. In both gel types there was not always an agreement between the values of the initial decay rate calculated by the two models. For the models to be truly compatible, the condition that  $1/k_1 = 0.1 C_1 + 0.01 C_2$  ought to be satisfied. The initial rate calculated by Eq. (3), however, was about three to five times higher in some gels than that calculated on the basis of Eq. (10).

An agreement between the models with respect to both stress and rate was restored shortly after the initial stages of the relaxation (Fig. 2). Since the initial decay rate is strongly influenced by the specimen deformation history and is likely to be influenced by instrumental artifacts, it carries much less useful rheological information than the asymptotic portion of the unrelaxed stress, i.e.  $1 - 1/k_2$  or  $C_0$ . Therefore, the lack of agreement between the two models on this point had little impact on the gel's evaluation. The changes in the gels' stiffness and strength were accompanied by a distinct alteration of the relaxation pattern (Table 1). It was primarily expressed by the portion of the stress that remained unrelaxed, i.e. by the magnitude of  $1 - 1/k_2$  or  $C_0$ , or the magnitude of the asymptotic residual modulus,  $E_A$ , which is shown at the bottom of Fig. 3. The shift in the relaxation pattern was also clearly evident in the ratio between  $C_1$  and  $C_2$  which represents the relative contribution of the short and long relaxation times. Since the latter was defined in terms of standard representative relaxation times, comparison of the relaxation patterns between and within the gels is given in meaningful quantitative terms.

The observed shifts in the relaxation time spectra as a result of increasing the gum concentration came as no surprise. Intuitively, one can expect that stiffening of the gel will be accompanied by an increase in the contribution of long relaxation times at the expense of the shorter relaxation times. This, how-

Table 1—Relaxation parameters of agar and alginate gels calculated by two models<sup>a,b</sup>

Gel	Concentration (% wt)	Relaxation parameters calculated from:							
		Eq. (10)				Eq. (4)			
		Asymptotic residual stress portion <sup>c</sup> $C_0$	Coef. of $\tau = 10s$ $C_1$	Coef. of $\tau = 100s$ $C_2$	$X^2$	$k_1$	$k_2$	$r^2$	Asymptotic residual stress portion <sup>c</sup> $(1 - 1/k_2)$
Agar	1.0	<u>0.24</u>	0.16	0.59	0.068	55	1.25	0.992	<u>0.20</u>
	1.5	<u>0.30</u>	0.13	0.55	0.016	61	1.35	0.992	<u>0.26</u>
	2.0	<u>0.38</u>	0.10	0.48	0.023	67	1.54	0.989	<u>0.35</u>
	2.5	<u>0.40</u>	0.12	0.44	0.004	60	1.63	0.992	<u>0.39</u>
	3.0	<u>0.44</u>	0.12	0.39	0.004	61	1.77	0.993	<u>0.43</u>
Alginate <sup>d</sup>	0.5(1.18)	<u>0.39</u>	0.23	0.26	0.039	22	1.69	0.998	<u>0.41</u>
	1.0(1.68)	<u>0.53</u>	0.16	0.25	0.024	42	2.16	0.995	<u>0.54</u>
	1.5(1.81)	<u>0.59</u>	0.13	0.21	0.016	46	2.48	0.996	<u>0.60</u>
	2.0(2.20)	<u>0.78</u>	0.06	0.14	0.022	112	4.63	0.989	<u>0.78</u>

<sup>a</sup> The agar gels were tested at 10% deformation and the alginate at 20%.

<sup>b</sup> The stiffness of the gels, expressed in terms of the deformability modulus, is given in Fig. 3.

<sup>c</sup> The values of the calculated asymptotic residual stress portion, calculated by the two models, are underlined to facilitate comparison.

<sup>d</sup> Figures in parentheses are the effective gum concentrations in the gel after the syneresis.

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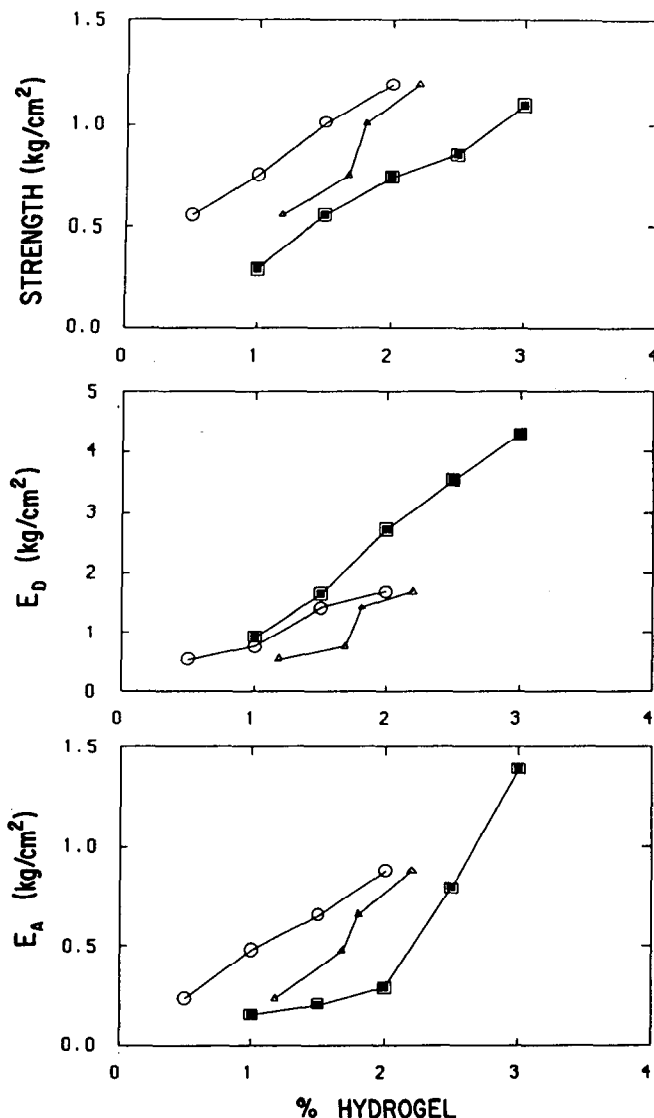


Fig. 3 — Effect of gum concentration on the strength deformability modulus,  $E_D$ , and asymptotic residual modulus  $E_A$  of agar and alginate gels. ■ agar gels; ○ alginate data plotted vs nominal concentration; △ alginate data plotted vs effective hydrogel concentration.

ever, need not be the case in all gels. There are gels, of carageenn for example, where stiffening is only expressed in the overall stress level without a significant shift in the relaxation time spectrum. In other words, although the stress-levels of such gels increase with the gum concentration, the general shape of the normalized relaxation curves remains practically unchanged. For this reason the relaxation data that are reported in Table 1 are qualitative as well as quantitative characteristics of the tested agar and alginate gels.

### Advantages and limitations of the two models

The merits of the model presented by Eqs. 3 and 4 have been discussed in detail elsewhere (Peleg, 1980). Its main ad-

vantages are a simple mathematical form and the possibility of calculating its constants by linear regression. The model expressed by Eq. (10) is mathematically more elaborate but it provided a more detailed account of the shape of the relaxation curves of the gels. This, however, comes at the expense of having to use a nonlinear regression procedure to determine its coefficients.

With appropriate software and a sufficiently powerful computer, the calculation itself poses no serious difficulty. The main problem is that the fixed relaxation times need to be carefully chosen or otherwise the model will not fit. In other words, the desired number of terms and the relaxation time ranges need to be initially selected on the basis of trial and error if the gel's general properties are not known a priori. Reasonable initial guesses of the parameters' values and their limits may also be required for proper functioning of the nonlinear regression procedure. These, however, can easily be made because of the limited range (0–1) in which the magnitude of  $C_0$ ,  $C_1$ , and  $C_2$  can vary. Once the appropriate model format had been found the program worked smoothly. This was evident from the degree of fit and from the fact that the sum of  $C_0$ ,  $C_1$ , and  $C_2$  was approximately unity as it ought to be. Thus, the model made it possible to compare the relaxation patterns of the different gels in terms of the relative magnitude of coefficients that refer to the same relaxation times, an impossible situation if the relaxation times are treated as variables as in conventional methods of relaxation data presentation using the standard form of the discrete Maxwell model.

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