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Relaxation Time Spectrum of Hydrogels by CONTIN Analysis

R. MAO, J. TANG, AND B.G. SWANSON

ABSTRACT: CONTIN is a general-purpose program for inverting noisy linear algebraic and integral equations by means of inverse Laplace transform. This study explored the application of CONTIN analysis to determine the relaxation time distribution spectra for food gels, including gellan, carrageenan, whey protein, and gelatin gels, based on stress-relaxation data. CONTIN results represent the continuous relaxation time spectra when the number of the terms in the discrete Maxwell stress-relaxation model approached infinity. The CONTIN results for gellan gels were correlated to the texture properties of gels from compression tests with respect to the effects of calcium concentrations. CONTIN analysis may be a very effective tool in elucidating the microstructural properties of a hydrogel from mechanical testing.

Key Words: stress relaxation, relaxation time distribution, CONTIN, food gel

Introduction

THE STRESS-RELAXATION TEST IS WIDELY USED IN RHEOLOGICAL studies of food products (Mitchell 1976,1980). Stress-relaxation data may provide information on permanent cross-linking (Ziegler and Rizvi 1989; Hsieh and Regenstein 1992), can characterize the effects of different chemicals and enzymatic additives on baking quality (Wikstrom and Eliasson 1998), distinguish products from different origins (Safari-Ardi and Phan-Thien 1998), and form an objective method for the quality assessment of food products (Huang and others 1995), as well as a number of other theoretical and practical applications.

Traditionally, relaxation data are interpreted by fitting equations derived from discrete Maxwell models (Sherman 1970; Mohsenin 1970):

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

where $E(t)$ is the modulus decaying curve determined from experiments, t is the experimental decay time, τ_i is the relaxation time of the i-th Maxwell element, and E_e represents the equilibrium or residual modulus at the fully decayed state, that is, when all relaxable stress is fully relaxed. For liquid foods, which are polymers without permanent cross-linking, E_e=0. For solid foods, polymers with permanent cross-links, E_e is a non-zero constant (Mitchell 1980).

When the number of Maxwell elements approaches infinity, the summation given in Eq. 1 is replaced by an integral:

$$E(t) = E_e + \int_0^{\infty} E(\tau)\exp\left(-\frac{t}{\tau}\right)d\tau \quad (2)$$

Where $E(\tau)$ is a continuous function over relaxation time τ, which may span from milliseconds to thousands of minutes. The relaxation time τ is usually presented on a logarithm scale. Thus, Eq. 2 can be written as,

$$E(t) = E_e + \int_{-\infty}^{\infty} H(\tau)\exp\left(-\frac{t}{\tau}\right)d\ln\tau \quad (3)$$

where $H(\tau)$ [$=\tau E(\tau)$] is called the relaxation time distribution function (Fried 1995). The relaxation time spectrum is a fundamental quantity in the linear theory of viscoelastic materials (Honerkamp and Weese 1993). If the relaxation time spectrum is known, other material functions such as storage modulus (G') and loss modulus (G″) at various frequencies can be calculated without difficulty (Honerkamp and Weese 1993).

If the equilibrium modulus E_e in Eq. 1 reflects a true material property, then its value should be independent of the imposed small strain (ε) in a stress-relaxation test, and the equilibrium stress σ_e ($= \varepsilon E_e$) should be proportional to the strain. Tang and others (1998), however, observed that this was not true for polysaccharide gellan, carrageenan, and agar gels. Instead, the equilibrium stress σ_e was independent of strain up to ε = 10%, although the initial stress $\sigma(0)$ was proportional to the imposed strain ε. Therefore, σ_e may represent an intrinsic property, which is directly related to the cross-linking properties of polysaccharide gels below 10% strain (Tang and others 1998). The following equation may, therefore, be more appropriate than Eq. 1 to describe stress-relaxation tests in polysaccharide gels:

$$\sigma(t) = \sigma_e + \sum_{i=1}^{n} \sigma_i \exp\left(-\frac{t}{\tau_i}\right) \quad (4)$$

Similarly, when n approaches infinity, Eq. 4 can be written as:

$$\sigma(t) = \sigma_e + \int_0^{\infty} \sigma(\tau)\exp\left(-\frac{t}{\tau}\right)d\tau \quad (5)$$

$$\sigma(t) = \sigma_e + \int_{-\infty}^{\infty} F(\tau)\exp\left(-\frac{t}{\tau}\right)d\ln\tau \quad (6)$$

where $F(\tau)$ [$= \tau\sigma(\tau)$] is the relaxation time distribution function. The difference between $F(\tau)$ and $H(\tau)$ is a proportional constant ϵ [$F(\tau) = \varepsilon H(\tau)$].

Most stress-relaxation decay curves can be well fitted to Eq. 4 with 2 to 3 exponential terms. However, the fitting results may

provide little information relevant to the characterization of intrinsic material properties (Peleg and Pollok 1982). In addition, the derived parameters σ_i and τ_i are strongly affected by the usually arbitrary chosen number of exponential terms, that is, n in Eq. 4. Therefore, multi-exponential analysis of stress-relaxation experiments is subjective. This problem can be overcome by using Eq. 5 or 6. By avoiding the arbitrarily chosen n, the relaxation time distribution function $\sigma(\tau)$ or $F(\tau)$ may represent true material properties. The challenge is to mathematically obtain $\sigma(\tau)$ or $F(\tau)$ in Eq. 5 and 6 from an experimentally determined stress-time relationship $\sigma(t)$. This can be achieved through inverse Laplace transform by a numerical method. Provencher (1982a) pointed out that numerical inverse Laplace transform on an experimental curve was generally an ill-posed problem. That is, one may obtain a number of solutions that all fit the data within experimental error, yet these solutions may be significantly different. Several computer programs (Provencher 1982a, 1982b; Weese 1993) are available to solve some ill-posed problems, including inverse Laplace transform problem.

CONTIN is a general-purpose program developed by Provencher (1982a, 1982b) and originally used in polymer science research. It can be used to invert general noisy linear algebraic and integral equations such as:

$$y(t_k) = \int_a^b s(\tau)G(\tau, t_k)d\tau + \sum_{i=1}^{N_L} \beta_i L_i(t_k) \quad (7)$$

where $s(\tau)$ is an unknown function to be solved, $y(t_k)$ is a known function or an experimentally measurable relationship, and $G(\tau, t_k)$ is a known kernel function, depending on the physical meaning of a specific question. The optional sum over N_L known functions $L_i(t_k)$ permits additional time dependent and/or independent terms to be considered. For a single constant term, Eq.(7) becomes,

$$y(t_k) = \int_a^b s(\tau)G(\tau, t_k)d\tau + \beta_1 \quad (8)$$

CONTIN is used successfully to solve many ill-posed problems. For example, it was used to analyze dynamic light-scattering data to determine polymer molecular weight distribution (Provencher and others 1978), to determine diffusion coefficient distribution (Provencher 1979; Bodycomb and Hara 1995), to determine angular frequency distribution of polymer gels and particle-size distribution of polymer solutions (Mao and others 1998), and to monitor both diffusion-limited and reaction-limited cluster aggregation processes of colloidal aggregates (Ju and others 1992). Recently, CONTIN was also used to analyze experimental data other than dynamic light scattering, such as obtaining free-volume radius distribution from positron annihilation lifetime measurements (Wang and others 1996; Cao and others 1997), and obtaining kinetic and affinity spectra from ion exchange processes (Haber-Pohlmeier and Pohlmeier 1997). CONTIN usually produces 10 to 20 physically permissible solutions and chooses the most appropriate solution based on statistical evaluations (Provencher 1982a, 1982b, 1984). Most CONTIN users accept the computer "chosen solution" as the final answer.

A relaxation time spectrum of dough was obtained from stress-relaxation tests (Safari-Ardi and Phan-Thien 1998). Discrete relaxation time spectra of mozzarella cheeses were obtained by Subramanian and Gunasekaran (1997) using the generalized Maxwell model and nonlinear regression analysis. To the best of our knowledge, there are no reports on the use of CONTIN analyses in food science and food engineering research. The objectives of this study were to explore the application of CONTIN analysis to obtain relaxation time distribution spectra from experimental stress-relaxation data, to test the reliability of CONTIN analysis by comparing the CONTIN results with multi-exponential fitting results, and to obtain the characteristics of relaxation time spectra of selected food gels.

Results and Discussion

CONTIN results

Typical stress decay curves, fitted by CONTIN method, and the corresponding relaxation time distribution spectra for gellan gels, carrageenan gels, whey protein gels, and gelatin gels are presented in Fig. 1 to 4, respectively. Each figure represents a single test. In the stress-relaxation tests for gellan gels (Fig. 1a) and carrageenan gels (Fig. 2a), the fully or nearly fully decayed states were not reached until the remaining stresses were reduced to about 30% of the initial stresses $\sigma(t=0)$. Gelatin gel was very elastic, and the gel stress was reduced to about 80% of the initial stress before the fully decayed state was reached (Fig. 4a). Whey protein gel (Fig. 3a) was far from the equilibrium state at the end of the 270-min test. The CONTIN analyses were effective for all these data, as indicated by the perfect fitting and various relaxation time spectra (Fig. 1 to 4, b). Usually, one main peak is observed in the CONTIN derived relaxation time spectra with several minor adjacent peaks. The main peak represents the major

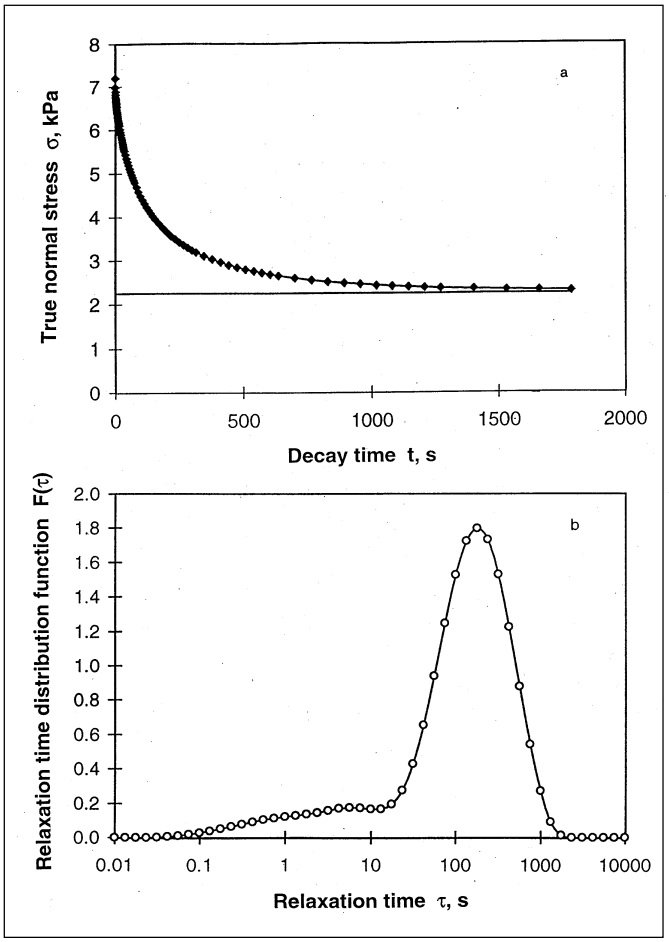

Fig. 1—Stress relaxation of 1% gellan gel with 4mM Ca^{2+}, subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

relaxation process, and the corresponding relaxation time at peak position may be called as characteristic relaxation time τ_c. Minor peaks in relaxation time spectra represent early ($\tau < \tau_c$) or late ($\tau > \tau_c$) relaxation processes other than the major process.

Several observations can be made when comparing the experimentally determined stress decay curves and the CONTIN derived relaxation time spectra. The characteristic relaxation time (τ_c) was positively correlated to the time needed for a gel to reach the fully decayed state, and the area under the relaxation time spectrum curve is positively correlated to total relaxable stress, that is, the difference between the initial stress and the equilibrium stress. For example, the total relaxable stress for the test of a gellan gel shown in Fig. 1a (4.95kPa) is several times higher than that of a carrageenan gel shown in Fig. 2a (0.90kPa). This results in a higher and wider main distribution peak and larger area under the distribution curve for gellan gel than those for carrageenan gel in the relaxation time spectra (Fig. 1b and Fig. 2b). The time needed to reach the fully decayed state for the test of gellan gel (Fig. 1a) was much shorter than that of carrageenan gel (Fig. 2a). As a result the characteristic relaxation time for gellan gel (Fig. 1b) was about one magnitude smaller than that of carrageenan gel (Fig. 2b). The stress decay curve of whey protein gel (Fig. 3a) had two general decaying periods separated by a sudden change of slope in the curve at about 1,000 s decay time. Accordingly, the CONTIN-derivedrelaxation time distribution function showed two similar peaks, one at 237 s and another at 31,600 s (Fig. 3b). The relaxation time of the second peak was well beyond the longest time of test duration (16,200 s). The small amount of relaxable stress for the test of gelatin gel (Fig. 4a) corresponded to a small distribution peak in the relaxation time spectrum (Fig. 4b).

For a relaxation process with only one relaxation time τ_c, the ratio (R_c) of total relaxable stress to the relaxed stress at test time $t = \tau_c$ should be,

$$R_c = \frac{\sigma(0) - \sigma_e}{\sigma(\tau_c) - \sigma_e} = e \approx 2.718 \tag{10}$$

In the presence of multiple relaxation times, however, the value of R_c may deviate from e. For example, the characteristic relaxation times τ_c for the tests of gellan, carrageenan, whey protein, and gelatin gels shown in Fig.1 to 4b were 178, 1780, 237, and 237 s, and their corresponding R_c values were 3.18, 5.29, 1.77, 2.61, respectively. The small amount of early relaxation process in gellan gel before the major relaxation process (Fig. 1b) caused the R_c value to be bigger than e. For the test of carrageenan gel (Fig. 2b), the early relaxation processes were much stronger and the R_c was much larger than e. For the test of whey protein gel (Fig. 3b), a very large late relaxation process resulted in the R_c value much smaller than e. For the gelatin gel (Fig. 4b), on the other hand, the CONTIN-derived relaxation time spectrum appeared to be a sin-

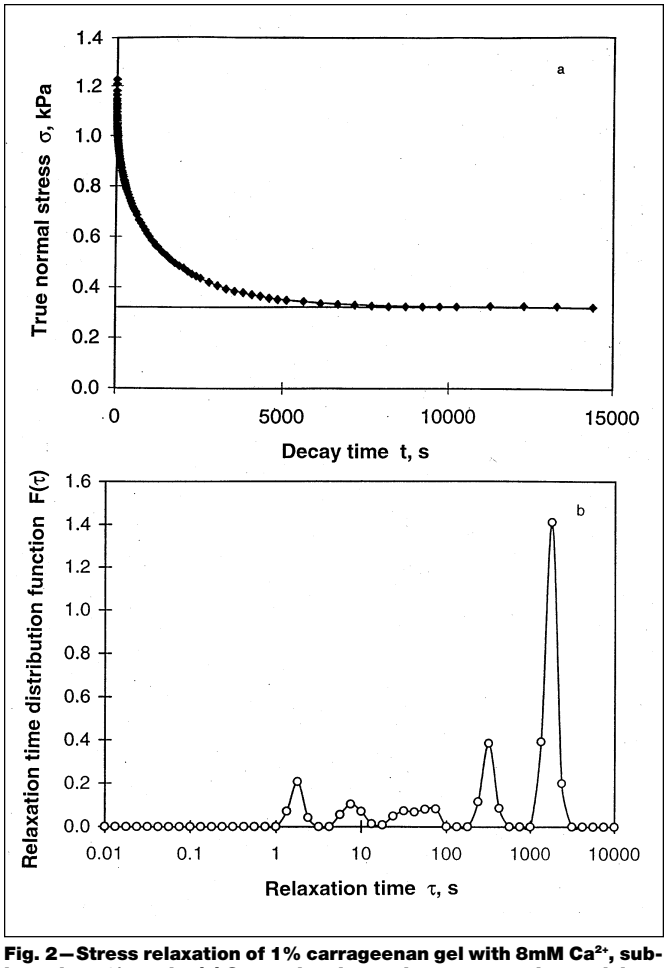

Fig. 2—Stress relaxation of 1% carrageenan gel with 8mM Ca^{2+}, subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

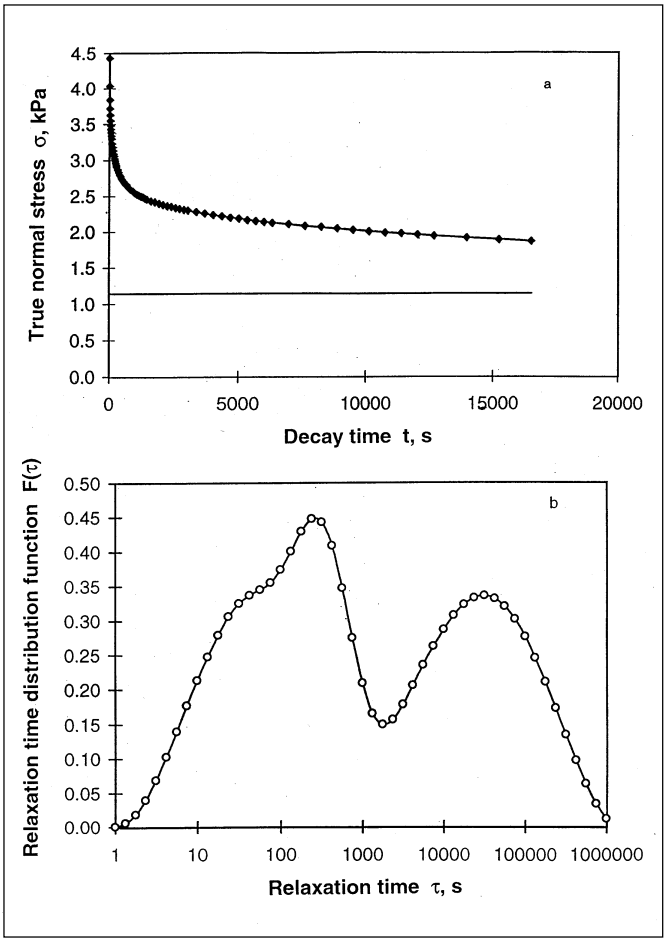

Fig. 3—Stress relaxation of 20% whey protein gel subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

gle peak, and the R_c value was closest to *e*.

While the stress decay curves appeared similar in shape, the CONTIN-derived relaxation time spectra were different for the tested gels, which implies that relaxation mechanisms were different among those gels. For linear polymers, the longest relaxation time corresponds to the relaxation on the entire polymer chain, while the shorter relaxation time corresponds to the relaxation of shorter parts of the macromolecule (Matsuoka 1992; Kontou 1998). Food gels may contain junction zones of various strength, and the strong junction zones may be responsible for the equilibrium stress after relaxation (Mitchell 1976). A wide range of stress-relaxation time spectra suggests a broad range of junction zone strengths and more heterogeneous microstructure. Polysaccharide polymers generally contain more regular chain structure than proteins. For example, gellan and carrageenan are polytetrasaccharide and polydisaccharide, and their polymer chains contain repeating units with four and two sugar residues, respectively. Whey protein and gelatin, on the other hand, are mixtures of proteins. Even a single protein chain may contain 20 different amino acid residues. Therefore, protein gels may contain more heterogeneous junction zones than polysaccharide gels. This may, in part, explain why whey protein and gelatin gels exhibited wider relaxation time distributions (Fig. 3 to 4, b) than those of gellan and carrageenan gels (Fig. 1 to 2, b).

An exothermic crystal formation peak at about 20 °C was observed in the heating DSC curves of carrageenan gels but not in the DSC curves of gellan gels (Nishinari and others 1996), suggesting a more heterogeneous structure in carrageenan gels. This may explain multi-peak relaxation time distribution for the test of carrageenan gels (Fig. 2b) but not for gellan gels (Fig. 1b).

Reproducibility

For the inverse Laplace transform, it is important to be able to obtain repeatable solutions from replicated experiments, although it is unrealistic to expect 2 exact solutions from 2 replicated experimental measurements. However, if a small experimental error causes large deviations in the solutions, the analysis procedure is unreliable. From the CONTIN analyses of many replicated experimental stress-relaxation data, we found that the calculated relaxation time spectra were reproducible, provided that the experimental results were close. Figure. 5 shows 2 typical replicated stress-relaxation test results and the corresponding solutions from CONTIN analyses of 1% gellan gels with 4mM Ca^{2+}. It indicates a good reproducibility for the CONTIN analysis results.

Equilibrium stress

It is sometimes difficult to conduct a stress-relaxation test to a completely or nearly completely decayed state. Biological materials may be particularly difficult because they may undergo rapid biochemical changes, and true equilibrium stress cannot be de-

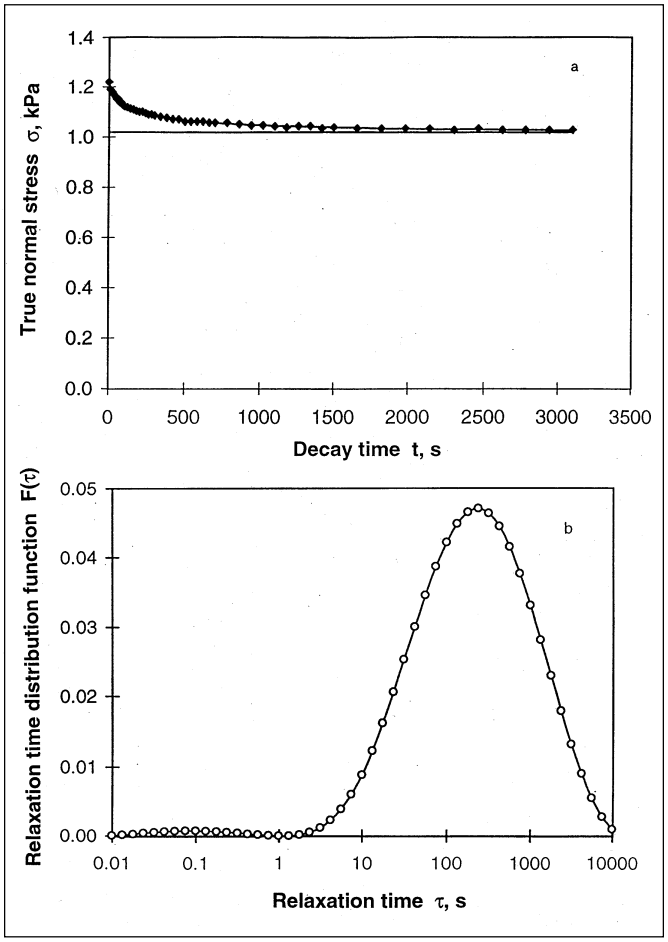

Fig. 4—Stress relaxation of 10% gelatin gel subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

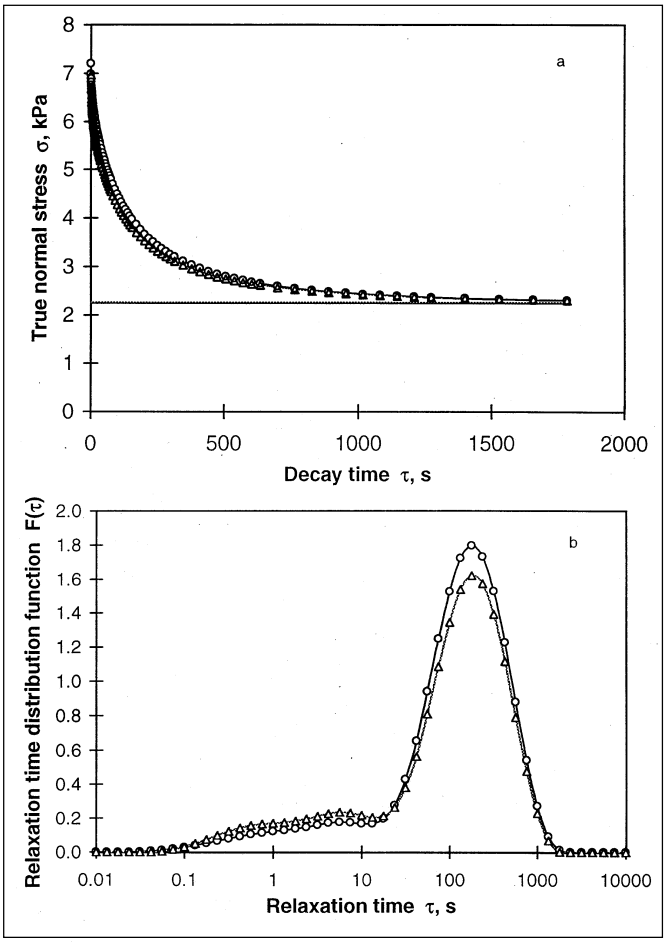

Fig. 5—Replication of stress relaxation of 1% gellan gel with 4mM Ca^{2+}, subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

termined experimentally. Much like fitting a multi-exponential model, CONTIN analysis is able to predict the equilibrium stress. The horizontal lines in Fig. 1 to 5 represent the equilibrium stresses for individual gels in stress-relaxation tests (σ_e=2.25, 0.32, 1.14, 1.02, 2.26 kPa for gels in Fig. 1 to 5, respectively). As shown in Fig. 1 to 5, stresses in gellan gels (Fig. 1 and 5), carrageenan gels (Fig. 2), and gelatin gels (Fig. 4) were relaxed to a near equilibrium state so that the calculated equilibrium stresses were close to the stresses recorded at the end of those tests. Whey protein gels, on the other hand, required a much longer time to reach a completely relaxed state (Fig. 3), and the stress is very difficult to be fully decayed within normal practical experimental time frame. Thus, a large difference was observed between the stress at the end of the experiment period (4.5h) and the calculated equilibrium stress (Fig. 3a).

Influence of the test time duration

Whenever possible, a stress-relaxation test should be carried to the fully or near fully decayed state. However, some food gels require longer time than is practically permissible to reach such a state. An important question arises as to how long a test should last in order to gain most important information. To study the effect of the test time duration on the relaxation time spectra, the test data for the carrageenan gel (Fig. 2a) was shortened to 8 different test periods, ranging from 1000 s to 14,000 s. Carrageenan gel was selected because its relaxation time spectrum was the most complicated among the gels tested, and the CONTIN analysis was hypothesized to be most sensitive to the change of test period. The relaxation time spectra derived from the test results corresponding to those 8 different test periods were shown in Fig. 6, and the predicted equilibrium stresses were listed in **Table** 1. The main peak position of the relaxation time spectra can be located even for the very short duration of 1000 s test time, at which the stress was far from being fully decayed (Fig. 6). The equilibrium stresses were also predicted well (**Table** 1). Therefore, CONTIN analysis of the results from an incomplete stress-relaxation tests can still provide some fundamental information about the relaxation time spectrum. With an increase in test duration, the peaks of relaxation time spectra become higher and narrower (Fig. 6), suggesting an improved resolution of the spectrum is with an increased test duration.

Setting relaxation time range

The CONTIN program does not require initial assumptions about the relaxation time distribution function, nor does contemporary non-linear regression software. The CONTIN program, however, requires an input of the lower and upper limits for the relaxation time spectrum, that is, a and b in Eq.(8). If the time range $[a, b]$ does not include all possible relaxation times, in other words, if the distribution function $F(\tau)$ is not 0 at $\tau < a$ or $\tau > b$, the obtained distribution spectrum may be distorted. The limits of a = 0.01 s and b = 10,000 s are appropriate for most gels tested in this work. However, the upper limit of b = 10,000 s was too

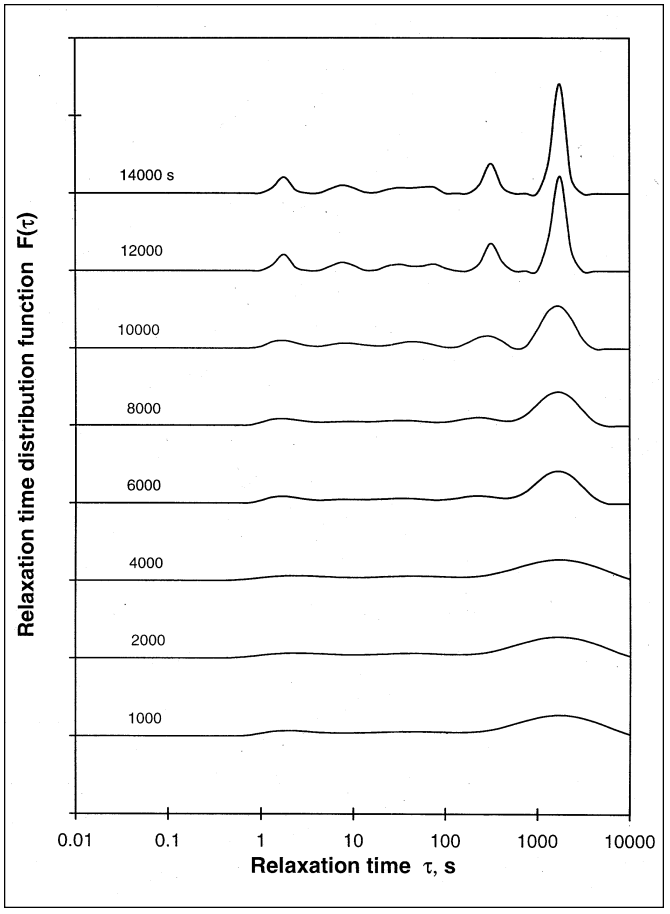

Fig. 6—CONTIN-derived relaxation time distribution functions influenced by different duration of test time for 1% carrageenan gel with 8mM Ca^{2+} subjected to 5% strain.

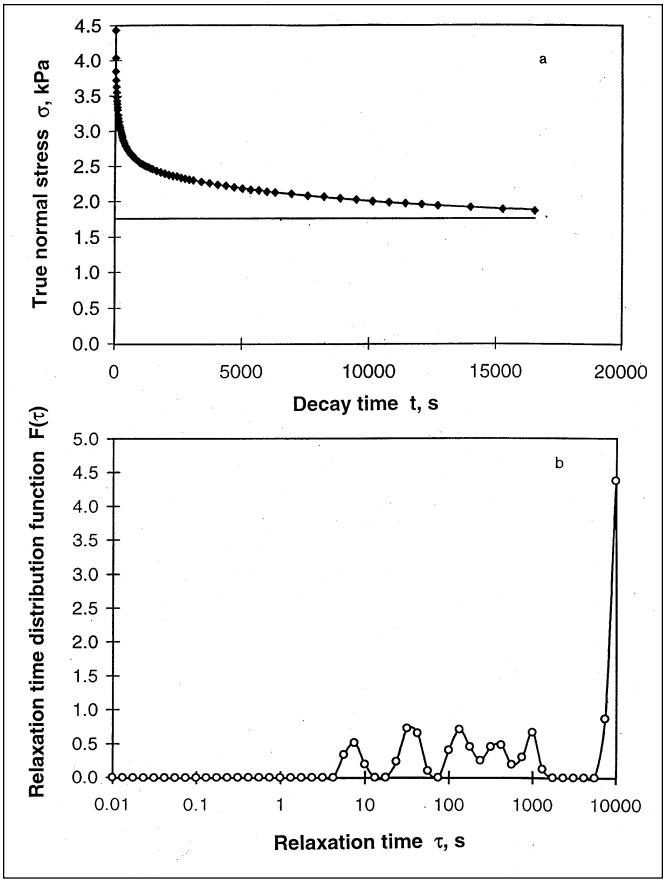

Fig. 7—Inappropriate set relaxation time limits for analyzing the stress-relaxation data of 20% whey protein gel subjected to 5% strain. (a) Scattering data points are experimental data; continuous curve is the fitting curve from CONTIN analysis; horizontal line is the calculated equilibrium stress. (b) Relaxation time distribution function F(τ) obtained from CONTIN analysis.

Table 1—CONTIN-predicted equilibrium stresses influenced by test time for 1% carrageenan gel with 8mM Ca^{2+} subjected to 5% strain

Duration of test (s)	σ_e (kPa)	Standard error (kPa)
1000	0.27	0.014
2000	0.27	0.004
4000	0.27	0.002
6000	0.31	0.003
8000	0.31	0.001
10000	0.32	0.001
12000	0.32	0.001
14000	0.32	0.001

Table 2—A summary of the results from multi-exponential analyses for the stress-relaxation test of 1% gellan gel with 4mM Ca^{2+}

n	2		3		4		5		6	
i	σ_i (kPa)	τ_i (s)	σ_i (kPa)	τ_i (s)	σ_i (kPa)	τ_i (s)	σ_i (kPa)	τ_i (s)	σ_i (kPa)	τ_i (s)
1	1.30	26.7	0.51	2.73	0.35	0.90	0.26	0.54	0.16	0.31
2	3.19	230	1.76	58.8	0.49	12.0	0.31	4.50	0.24	1.84
3			2.52	294	2.01	87.0	0.70	31.9	0.32	10.2
4					2.04	356	2.05	121	0.98	50.9
5							1.60	419	1.92	153
6									1.31	472
σ_e (kPa)	2.39		2.33		2.30		2.29		2.27	
R^2	0.998		0.9998		0.99998		0.999996		0.999998	

small for the selected whey protein gel (Fig. 7). This can be seen clearly from the corresponding relaxation time distribution spectrum $F(\tau)$ (Fig. 7b). Only a small portion of a peak in $F(\tau)$ was included in the specified time limits. When the upper time limit b was set to 1,000,000 s, more complete $F(\tau)$ was obtained (Fig. 3). It should be noted that although the relaxation time limits a and b were inappropriately set and an incorrect relaxation time spectrum was obtained (Fig. 7b), the stress decay curve was still fitted very well (Fig. 7a). This example demonstrates well the ill-posed nature of inverse Laplace transform, that is, good fitting cannot always guarantee the solution was correct.

Comparison of CONTIN result with multi-exponential fitting results

The regression procedure of the SigmaPlot 4.0 (SPSS Inc. 1997) was chosen to fit the multi-exponential model of Eq. 4 to the stress decay curve for the gellan gel shown in Fig. 1. The chosen exponential term n ranged from 2 to 6. These values represent the range for n often used in the literature for multi-exponential models. Table 2 lists the results of the analyses. The value of R^2 indicated that all curve fittings were very good, but the calculated τ_i and σ_i varied significantly as the value of n changed. Theoretically, the multi- exponential analysis becomes inverse Laplace transform when n approaches infinity. At first glance, the results from multi-exponential analysis (Table 2) cannot be seen to be approaching the CONTIN results, except that the equilibrium stress σ_e approached the CONTIN obtained value (2.25 kPa, Fig. 1a) as n increased. However, when the scattered points were connected with smooth curves for each n, it became evident that the outlines of the results of multi-exponential analysis approached the CONTIN results as n increased (Fig. 8). This suggests that CONTIN results indeed represent the continuous relaxation time distribution when n approaches infinity and further justifies the CONTIN analysis.

Influence of the calcium concentration in gellan gels

The potential for using CONTIN analysis to correlate relax-

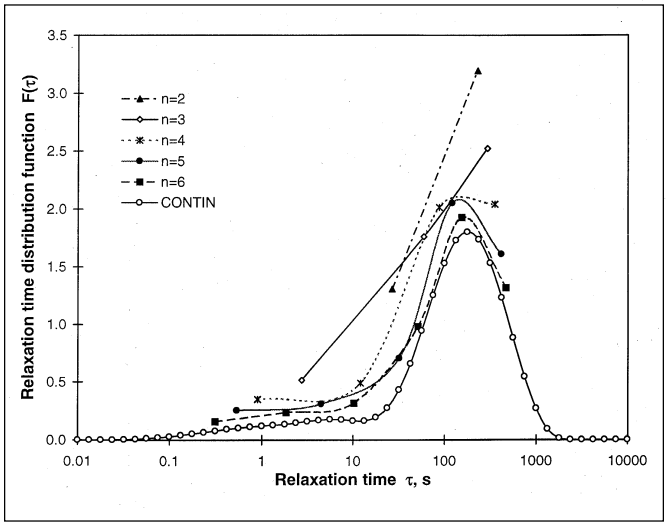

Fig. 8—Multi-exponential fitting results and the CONTIN analysis result for 1% gellan gel with 4mM Ca^{2+} subjected to 5% strain.

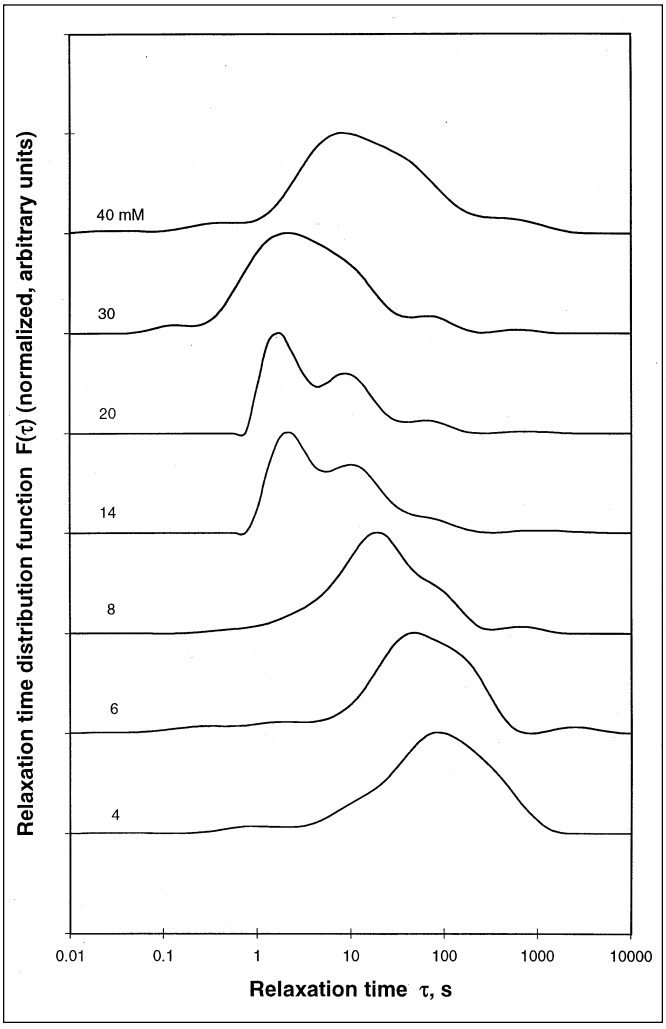

Fig. 9—CONTIN-derived relaxation time distribution function of 1% gellan gels with 4 to 40 mM Ca^{2+} subjected to 10% strain.

ation time spectra to gel compositions was examined, using gellan gel as a model. The relaxation time distribution spectra of 1% gellan gels prepared with calcium concentrations ranging from 4 to 40 mM are presented in Fig. 9. The characteristic relaxation time τ_c shifted to a shorter time as Ca^{2+} concentration increased from 4 mM to 14 mM, then τ_c value remained almost constant with further increase in Ca^{2+} concentrations to 40 mM. This trend is similar to the change in failure strain of gellan gels with respect to the changes in Ca^{2+} concentrations (Tang and others 1994, 1995). Similar results were observed in stress-relaxation tests of whey protein isolate gels, where gels with large relaxation time corresponded to high failure strain (Foegeding 1992).

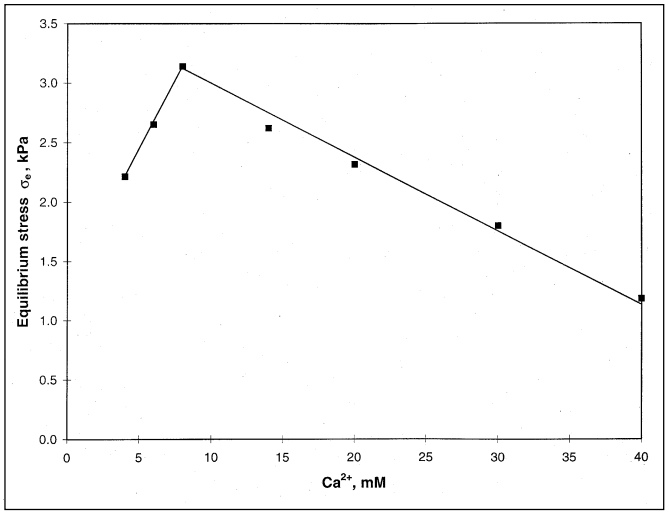

Fig. 10—CONTIN-derived equilibrium stresses of 1% gellan gels with 4 to 40 mM Ca^{2+} subjected to 10% strain.

Tang and others (1998) observed a linear relationship between the equilibrium stresses from stress-relaxation tests and the failure stresses from compression tests for gellan gels. A similar result was observed in the equilibrium stresses from CONTIN analysis with respect to the calcium concentrations for 1% gellan gels (Fig. 10). This is very reasonable because the equilibrium stresses obtained from the CONTIN analyses were very close to the experimental observed final stresses in gellan gels.

The correlations between characteristic relaxation time and failure strain, and between equilibrium stress and failure stress of gellan gels, suggest that the mechanisms between the stress-relaxation test and compression test are interrelated. These mechanisms may include seepage of water from the gels, dissociation of weak bonds, and the breaking of cross-links. The multiple peaks in the relaxation time distribution spectra for gellan gels (Fig. 9) suggests more than one mechanism responsible for the stress-relaxation process. The underlying mechanism for these peaks requires future research.

Conclusions

RELAXATION TIME DISTRIBUTION SPECTRA CAN BE DERIVED FROM stress-relaxation studies using CONTIN analyses. The CONTIN results may provide insight into the mechanism of stress relaxation in food gels. The CONTIN results from stress-relaxation tests were correlated to the failure properties of compression tests in respect to calcium concentrations of gellan gels.

Materials and Methods

Preparation of gels

Gellan gum (KELCOGEL F, NutraSweet Kelco Company, San Diego, Calif., U.S.A.) or κ- carrageenan (Gelcarin GP-812NF, FMC Corporation, Newark, Del., U.S.A.) was dispersed in deionized distilled water at room temperature (22 °C) to make 1% solutions. The solutions were heated to the boiling point (98 °C) and held for 1 min. A pre-weighed amount of $CaCl_2$ was added to the boiling solutions and stirred for another min to prepare 4, 6, 8, 14, 20, 30, 40 mM Ca^{2+} gellan gels or 8 mM Ca^{2+} carrageenan gel. The solutions were weighed, and hot water at about 90 °C was added to make up the lost water due to vaporization. The solutions were briefly mixed, poured into metal tubes with an inner dia of 21 mm, and cooled in running tap water (15 °C) for 15 min to set the gels. A 10% gelatin (BDH inc.) gel was made similarly, except no $CaCl_2$ was added. Whey protein concentrate (ALACEN 882, New Zealand Milk Products Inc., Santa Rosa, Calif., U.S.A.) was dispersed into deionized distilled water, vigorously stirred at room temperature (22 °C) for 20 min, and held until the air bubbles disappeared. The suspension containing 20% whey protein concentrate was poured into the metal tube of 21 mm dia, sealed at both ends, and heated in a water bath at 80 °C for 1 h to form a gel. All gels were stored at room temperature (22 °C) for 24 h prior to stress-relaxation tests.

Stress-relaxation test

The gels were removed from the metal tubes and sliced into 21 mm long cylindrical specimens. Each gel specimen was placed between 2 lubricated Teflon plates fitted to The TA.XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, N.Y., U.S.A./Stable Micro Systems, Godalming, Surrey, U.K.) with a 5 kg load cell interfaced with Texture Expert software (version 1.17). To avoid water evaporation from the gel during prolonged testing, the gel specimen and the Teflon plates were immersed in a 22 °C water bath. To ensure accurate measurements, distance measurement was calibrated in air, while the force measurement was calibrated when the Teflon plate was immersed in the water bath to the same position as the gel samples to eliminate the effect of buoyant force imposed by the water.

Tang and others (1998) observed that when 1% gellan gels were subjected to strains up to 15% during stress-relaxation tests, the gel matrixes were not permanently damaged. The tested gels could regain their lost water and restore their structures when immersed in water after relaxation tests. Therefore, in our tests a constant compression strain of 5% or 10% was imposed on the gels at 5 mm/s crosshead speed. This strain was maintained for test times ranging from 0.5 to 4.5 h, depending the stress-decay rate. The decaying force-time curve was recorded by a personal computer. The time corresponding to the maximum force was selected as 0 time.

Data processing

In a stress-relaxation test, the stress in a gel decays very rapidly at the initial stage, and the data must be collected at very small time intervals. The stress decay, however, slows

down as the test progresses. The Texture Expert software can collect up to 30,000 data points in one test at equal time intervals. It is time-consuming and unnecessary to use all data points for calculating the relaxation time distribution function in the CONTIN analyses. The data points used in these analyses were selected in a quasi logarithmic manner, that is, the time interval between selected adjacent data points was doubled after every 10 selected data points. In this way, a total of 100 to120 data points were selected for calculations. The force at each selected data point was converted to true normal stress according to Tang and others (1997).

CONTIN was used to invert both Eqs. 5 and 6. Comparing Eq. 8 to 5 or 6, β_1 corresponds to σ_e and $y(t_k)$ corresponds to $\sigma(t)$. To invert Eq. 5, $s(\tau)$ corresponds to $\sigma(\tau)$, and $G(\tau, t_k)$ corresponds to $\exp(-t/\tau)$.

Eq. 6 can be re-written as,

$$\sigma(t) = \sigma_e + \int_{-\infty}^{\infty} F(\tau)\left[\frac{1}{\tau}\exp(-\frac{t}{\tau})\right]d\tau \quad (9)$$

therefore, $s(\tau)$ corresponds to $F(\tau)$ and $G(\tau, t_k)$ corresponds to $1/\tau \exp(-t/\tau)$.

Preliminary results indicated that the resulted $\sigma(\tau)$ from inverting Eq. 5 is not sensitive to the gel composition. Therefore, only Eq. 6 was analyzed by CONTIN to obtain the relaxation time distribution function $F(\tau)$. Like many CONTIN users, the computer "chosen solution" (Provencher 1984) was accepted as the final solution.

References

Bodycomb J, Hara M. 1995. Light scattering study of ionomers in solution. 5. CONTIN analysis of dynamic scattering data from sulfonated polystyrene ionomer in a polar solvent (dimethylformamide). Macromolecules 28:8190-8197.

Cao H, Dai GH, Yuan JP, Jean YC. 1997. Reliability of ortho-positronium lifetime distribution analysis in polymers by using CONTIN program. Materials Science Forum. Vols. 255-257. Switzerland: Trans Tech Publications. p 238-242.

Foegeding EA. 1992. Rheological properties of whey protein isolate gels determined by torsional fracture and stress relaxation. J Texture Studies 23:337-348.

Fried JR. 1995. Viscoelacticity and rubber elasticity. In: Fried JR. Polymer Science and Technology. Upper Saddle River, N.J.: Prentice Hall PTR. p 182-231.

Haber-Pohlmeier S, Pohlmeier A. 1997. Kinetics and equilibrium of the ion exchange of Cd^{2+} at Na-montmorillonite: analysis of heterogeneity by means of the regularization technique CONTIN. J Coll Inter Sci 188:377-386.

Honerkamp J, Weese J. 1993. A nonlinear regularization method for the calculation of relaxation spectra. Rheol Acta 32:65-73.

Hsieh YL, Regenstein JM. 1992. Elastic attributes of heated egg protein gels. J Food Sci 57:862-868.

Huang S, Quail K, Moss R, Best J. 1995. Objective methods for the quality assessment of northern-style Chinese steamed bread. J Cereal Sci 21:49-55.

Ju RTC, Frank CW, Gast AP. 1992. CONTIN analysis of colloidal aggregates. Langmuir 8:2165-2172.

Kontou E. 1998. Relaxation time spectra of linear and crosslinked polymers. J Appl Polym Sci 67:679-684.

Mao R, Liu Y, Huglin MB, Holmes PA. 1998. Dynamic light scattering from polymer gels: spring-rotor model. Polym Int 45:321-326.

Matsuoka S. 1992. Stress and strain. In: Matsuoka S. Relaxation Phenomena in Polymers. New York: Hanser Publishers, distributed by Oxford University Press. p 1-41.

Mitchell JR. 1976. Rheology of gels. J Texture Studies 7:313-339.

Mitchell JR. 1980. The rheology of gels. J Texture Studies 11:315-337.

Mohsenin NN. 1970. Physical Properties of Plant and Animal Materials. Vol.1. New York: Gordon and Breach Scientific Publishers. p 112-123.

Nishinari K, Watase M, Rinaudo M, Milas M. 1996. Characterization and properties of gellan__-carrageenan mixed gels. Food Hydrocolloids 10:277-283.

Peleg M, Pollak N. 1982. The problem of equilibrium conditions in stress relaxation analyses of solid foods. J Texture Studies 13:1-11.

Provencher SW, Hendrix J, De Maeyer L, Paullussen N. 1978. Direct determination of molecular weight distributions of polystyrene in cyclohexane with photon correlation spectroscopy. J Chem Phys 69:4273-4276.

Provencher SW. 1979. Inverse problem in polymer characterizations: direct analysis of polydispersity with photon correlation spectroscopy. Makromol Chem 180:201-209.

Provencher SW. 1982a. CONTIN: a general purpose constrained regularization program for inverting noise linear and integral equations. Comput Phys Commun 27:229-242.

Provencher SW. 1982b. A constrained regularization method for inverting data represented by linear algebraic or integral equations. Comput Phys Commun 27:213-227.

Provencher SW. 1984. CONTIN Users Manual - Technical Report EMBL-DA07, Part 1. Germany: Gottingen. Max-Planck-Institut für biophysikalische Chemie.

Safari-Ardi M, Phan-Thien N. 1998. Stress relaxation and oscillatory tests to distinguish between doughs prepared from wheat flours of different varietal origin. Cereal Chem 75: 80-84.

Sherman P. 1970. Industrial Rheology. New York: Academic Press. p 1-31.

SPSS Inc. 1997. Transforms & Regressions Reference Manual (SigmaPlot 4.0 for Windows 95, NT & 3.1), Chicago: SPSS Inc.

Subramanian R and Gunasekaran S. 1997. Small amplitude oscillatory shear studies on mozzarella cheese. Part II. Relaxation spectrum. J Texture Studies 28:643-655.

Tang J, Lelievre J, Tung MA, Zeng Y. 1994. Polymer and ion concentration effects on gellan gel strength and strain. J Food Sci 59:216-220.

Tang J, Tung MA, Zeng Y. 1995. Mechanical properties of gellan gels in relation to divalent cations. J Food Sci 60:748-752.

Tang J, Tung MA, Lelievre J, Zeng Y. 1997. Stress-strain relationships for gellan gels in tension, compression and torsion. J Food Eng 31:511-529.

Tang J, Tung MA, Zeng Y. 1998. Characterization of gellan gels using stress relaxation. J Food Eng 38:279-295.

Wang CL, Wang SJ, Qi, ZN. 1996. Interaction of two phases in PP/EPDM polymer blend probed by positron annihilation: CONTIN analysis. J Polym Sci: Part B: Polym Phys 34:193-199.

Weese J. 1993. A regularization method for nonlinear ill-posed problem. Comput Phys Commun 77:429-440.

Wikstrom K, Eliasson AC. 1998. Effects of enzymes and oxidizing agents on shear stress relaxation of wheat flour dough: additions of protease, glucose oxidase, ascorbic acid, and potassium bromate. Cereal Chem 75:331-337.

Ziegler GR, Rizvi SSH. 1989. Determination of cross-link density in egg white gels from stress relaxation data. J Food Sci 54:218-219.

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