ELSEVIER

Journal of Food Engineering **38** (1998) 279–295
© 1999 Elsevier Science Limited. All rights reserved
Printed in Great Britain
0260-8774/98/$ — see front matter

PII: S0260-8774(98)00114-9

Characterization of Gellan Gels Using Stress Relaxation

Juming Tang,[a]* Marvin A. Tung[b] & Yanyin Zeng[c]

[a]Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164-6120, USA
[b]Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada
[c]Information Technology Center, Washington State University, Pullman, WA 99164-6120, USA

(Received 13 April 1998; accepted 29 July 1998)

ABSTRACT

The effect of testing parameters on stress relaxation characteristics and the relationship between those characteristics and intrinsic gel properties were investigated. Gellan gels were tested in stress relaxation using different crosshead speeds (3–300 mm/min) to apply strain (3–20%) to specimens of 21 and 31 mm diameter with aspect ratios of 0·5, 1·0 and 1·5. Relaxation appeared to be associated with a release of hydraulic pressure in the gel matrix. The relaxation rate was inversely related to specimen diameter, but positively related to the pore sizes in the gel matrix. Increasing the applied strain resulted in larger initial stresses but slightly lower equilibrium stresses. The equilibrium stresses were positively related to the strength of the gels and, thus, to the degree of crosslinking in the polymer network. As long as the polymer networks were not permanently damaged during relaxation tests, the gel structure could be restored upon soaking in water.

INTRODUCTION

Gellan gum is an extracellular polysaccharide secreted by the bacterium *Pseudomonas elodea* in aerobic fermentation and appears to possess unique gel-forming properties that are attractive to the food industry (Pszczola, 1993). The mono-

---

*To whom correspondence should be addressed. Tel.: +1-509 335 2140; Fax: +1-509 335 2722; E-mail: jtang@mail-wsn.edu saccharide units, β-D-glucose, β-D-glucuronic acid and α-L-rhamnose, are combined in a polymer that forms gels in the presence of cations in water solution (Sanderson, 1990), possibly through three-fold double-helical junctions (Upstill *et al.*, 1986; Chandrasekaran *et al.*, 1988). The effects of polymer and cation concentrations on the strength and deformability of gellan gels has been studied using large deformation tests (Sanderson, 1990; Tang *et al.*, 1994; Tang *et al.*, 1995). In general, higher polymer and cation concentrations yield stronger gels; however, the presence of excessive cations tends to weaken the gels (Tang *et al.*, 1994; Tang *et al.*, 1995).

Gels formed by gellan may be soft or brittle, depending on composition (Tang *et al.*, 1995) and exhibit viscoelastic behavior evident in creep compliance and stress relaxation experiments (Nussinovitch *et al.*, 1990). The rheological properties of food gels as determined by stress relaxation tests are related to the properties of cross-linking in gel networks (Mitchell, 1980; Ziegler & Rizvi, 1989). In stress relaxation tests, a food sample is compressed at a controlled crosshead speed to a desired strain. This strain is maintained as a constant, while the accompanying stress decays with time to provide the characteristic relaxation behavior. The stress relaxation can be described by (Mohsenin, 1970):

$$\sigma(t)=\sigma_e+f(t) \tag{1}$$

where $\sigma(t)$ is the transient stress, $f(t)$ represents the decaying component of the stress, and σ_e is the equilibrium stress after infinite time. For solids σ_e is a non-zero constant, while for liquids $\sigma_e=0$. Several test parameters such as the imposed strain, crosshead speed when applying the load, and the aspect ratio of the specimen affect stress relaxation results (Culioli & Sherman, 1976; Peleg & Pollak, 1982; Goh & Sherman, 1987) and, thus, also affect the form of eqn (1). It is necessary to understand the effects of these parameters on the rheological behavior of the materials, so that meaningful information can be obtained from the test data.

The objective of this study was two-fold: (1) to study the effects of operating variables including loading speed, strain and specimen dimensions on the relaxation characteristics of gellan gels; and (2) to relate information from the stress relaxation tests to intrinsic properties of the gels, such as microstructure and strength.

MATERIALS AND METHODS

Sample preparation

Gellan polymer (KELCOGEL, Kelco Company, San Diego, CA) was added to distilled deionized water at room temperature (22°C) to prepare dispersions containing 1 and 2% (w/w) of gellan. The mixtures were heated on hot plates while being stirred constantly to obtain clear solutions at 90°C. Predetermined amounts of calcium chloride were added to provide 2, 4, 6, 8, 16 and 32 mM Ca^{2+}, the solutions were cooled in air to about 70°C and poured into cylindrical stainless steel molds which were preheated to 70°C to prevent partial gelling along a cold metal wall during pouring. The molds were 140 mm long with internal diameters of 21 or 31 mm. The molds were sealed at both ends and cooled in running water at 15°C for 15 min and then held overnight at room temperature.

Stress relaxation tests

Gels were removed from the metal molds and specimens were cut to form cylindrical shapes for compression between two Teflon plates on an Instron machine (Model 1125, Instron Corporation, Canton, MA). The contact surfaces were lubricated with silicone oil to reduce friction so that the samples would retain their cylindrical shape under compressive loading. During the relaxation tests, a constant compressive strain was imposed at a controlled crosshead speed. This strain was maintained constant for 20 min, while stress decay was monitored.

Variables studied in the relaxation tests were: (1) specimen diameter of 21 and 31 mm with aspect ratios (height to diameter) of 0·5, 1·0 and 1·5; and (2) crosshead speeds of 3, 30 and 300 mm/min. In compression, maximum strain for linear stress–strain behavior of gellan gels was between 15 and 25% strain (Tang *et al.*, 1997). The compressive strain (or compression ratio) imposed on gels during relaxation tests in the current study were 3, 5, 7, 10, 15 and 20%. The tests were conducted in triplicate at room temperature. Variability in recorded engineering stresses (force divided by the initial sample cross-section area) among the replicates was less than 5%; the means of the replicates were plotted and discussed. Statistical analyses were made with reference to a significance level of $P < 0{\cdot}05$.

Cryo-scanning electron microscopy (Cryo-SEM) studies

A small section, 1–2 mm^2, of gellan gels was mounted in the cryo-holder for the Emscope 2000 A cryo-preparation unit (Ashworth, Kent, UK), and plunged into propane, and then cooled further with liquid nitrogen. Our preliminary tests showed that use of propane helped to reduce distortion to the gel structure. The frozen sample was fractured to expose a fresh surface, and sublimated for one hour at −80°C to expose the underlying structure. The exposed structure was sputter coated with 30 nm of gold. Partially freeze-dried samples were viewed and photographed in the Hitachi S-570 scanning electron microscope (Tokyo, Japan) at 10 kV and below −135°C.

Compression tests

To study the relationship between the experimental data of stress relaxation and the large deformation tests, cylindrical gellan specimens of diameter 21 mm and length 20 mm were compressed to failure between lubricated plates. Detailed information on the test procedure and data reduction is reported in Tang *et al.* (1995).

Data reduction

Stress relaxation data can be reduced to viscoelastic parameters by fitting a suitable model to the stress–time relationship. A common model for such purposes is the modified Maxwellian equation, which includes a number of discrete exponential terms for the decaying component of engineering stress (Shama & Sherman, 1973; Peleg, 1980; Peleg and Normand, 1998):

$$\sigma(t) = \sigma_c + \sum_{i=1}^{n} \sigma_i \, e^{-t/\tau_i} \tag{2}$$

where, σ_i is the coefficient and τ_i is the relaxation time of the ith term. Most relaxation curves can be fitted by eqn (2) with two to three exponential terms (Peleg & Pollak, 1982). A simplified form of the above equation, similar to that in Nussinovitch *et al.* (1989), was used to describe the relaxation curves of gellan gel in this study:

$$\sigma(t) = \sigma_e + \sigma_1 e^{-t/10} + \sigma_2 e^{-t/100} + \sigma_3 e^{-t/1000} \tag{3}$$

Fixed relaxation times of 10, 100 and 1000 s were chosen based on a previous study (Tung *et al.*, 1994). Constant σ_e to σ_3 were obtained by fitting eqn (3) to relaxation data using a nonlinear regression procedure (SAS Institute Inc., 1985). The above equation was rearranged in the following dimensionless form:

$$\frac{\sigma(t)}{\sigma(0)} = C_0 + C_1 e^{-t/10} + C_2 e^{-t/100} + C_3 e^{-t/1000} \tag{4}$$

in which $\sigma(0)$ is the stress at the start of the relaxation, and $C_0 = \sigma_e/\sigma(0)$. $C_i = \sigma_i/\sigma(0)$, where $i = 1$–3. The initial decay rate of stress ratio is:

$$\frac{1}{\sigma(0)} \left. \frac{d\sigma(t)}{dt} \right|_{t=0} = -\left(\frac{C_1}{10} + \frac{C_2}{100} + \frac{C_3}{1000} \right) \tag{5}$$

According to the above equation, the value of C_1 dominates the initial stress decay rate.

Peleg (1980) proposed an empirical model as an alternative to the above approach. In this method, the relaxation curves were normalized with respect to the initial relaxation stress $\sigma(0)$ and the resulting model was expressed in a linear form:

$$\frac{\sigma(0)t}{\sigma(0) - \sigma(t)} = k_1 + k_2 t \tag{6}$$

Consants k_1 and k_2 were obtained by linear regression. An advantage of this model is that if the data follow the linear relationship shown in eqn (1), constant k_1 and k_2 are independent of the test duration (Peleg & Pollak, 1982). The above equation was rearranged so that the transient stress was expressed as the sum of the equilibrium stress and a decaying stress:

$$\sigma(t) = \sigma_e + \sigma(0) \left(\frac{k_1/k_2}{k_1 + k_2 t} \right) \tag{7}$$

where the residual stress σ_e is calculated as:

$$\sigma_e = \sigma(0)\left(1 - \frac{1}{k_2}\right) \tag{8}$$

The rate of stress decay was derived from eqn (7) as:

$$\frac{d\sigma(t)}{dt} = -\sigma(0)\frac{k_1}{(k_1+k_2t)^2} \tag{9}$$

and the initial decay rate of stress ratio is:

$$\frac{1}{\sigma(0)}\frac{d\sigma(t)}{dt}\bigg|_{t=0} = -\frac{1}{k_1} \tag{10}$$

The goodness of fit of selected models to the stress relaxation data was determined using the root mean square (RMS) error calculated by:

$$\text{RMS} = \sqrt{\frac{1}{n}\sum_{i=1}^{N}\left(\frac{x'_i - x_i}{x'_i}\right)^2} \tag{11}$$

where x_i was the predicted value and x'_i was experimental data.

RESULTS AND DISCUSSION

Figure 1 illustrates typical behavior of gellan gels when subjected to different strains in relaxation tests. Equations (3) and (6) were fitted to the relaxation portion of the data to obtain stress relaxation parameters (Tables 1–3). As indicated by the values of root mean square errors, eqn (3) describes the stress relaxation behavior better than eqn (6). Parameters from eqn (3) and (6) will be used for discussion in the following sections.

Effect of strain on stress relaxation

Stresses developed rapidly to reach maximum values when samples were compressed to desired strains (Fig. 1). The magnitudes of those maximum stresses, $\sigma(0)$, were proportional to the imposed strains (Table 1). Each stress decayed with time to approach an equilibrium value. The initial decaying rate increased with the amount of imposed strain as demonstrated by the increasing C_1 in eqn (5) and $1/k_1$ in eqn (10) (Table 1). The equilibrium stress, σ_e, of a gellan gel decreased slightly with increased strain up to 15% in the case of 1% gel and up to 10% in the case of 2% gel (Table 1). When subjected to larger 20% strain for 1% gel, and 15% strain for 2% gel, however, the equilibrium stresses were significantly reduced (Fig. 1). In those cases, the stress relaxation rates were greatly increased and miniature cracks developed in the specimens. The deviation of these relaxation behaviors from those under smaller strains was likely due to breaking up of cross-links in the gel system, which resulted in significantly smaller equilibrium stresses.

Effect of crosshead speed

The data in Fig. 2 represent typical results to show the effect of crosshead speeds. Greater crosshead speeds resulted in significantly larger initial stresses. When compared to the effect of the imposed strains (Table 1), however, the influence of the crosshead speeds on the initial stress was less prominent (Table 2), because two orders of magnitude increase in the crosshead speed only resulted in an increase in the initial relaxation stress by 1·5–1·9 times. Higher crosshead speeds also corresponded to larger initial relaxation rates, but crosshead speed did not affect the equilibrium stress σ_e as derived from eqn (5) and (10) (Table 2).

Effect of sample diameter and aspect ratio

The experimental data in Fig. 3 show the effect of specimen diameter and aspect (height to diameter) ratio on the relaxation curves of 2% gellan gels. For a given diameter, the relaxation curves of gel specimen of 0·5, 1·0 and 1·5 aspect ratios were identical (Table 3). Thus, the specimen height did not affect the relaxation behavior of the gels. The specimen diameter, on the other hand, had a marked effect on the

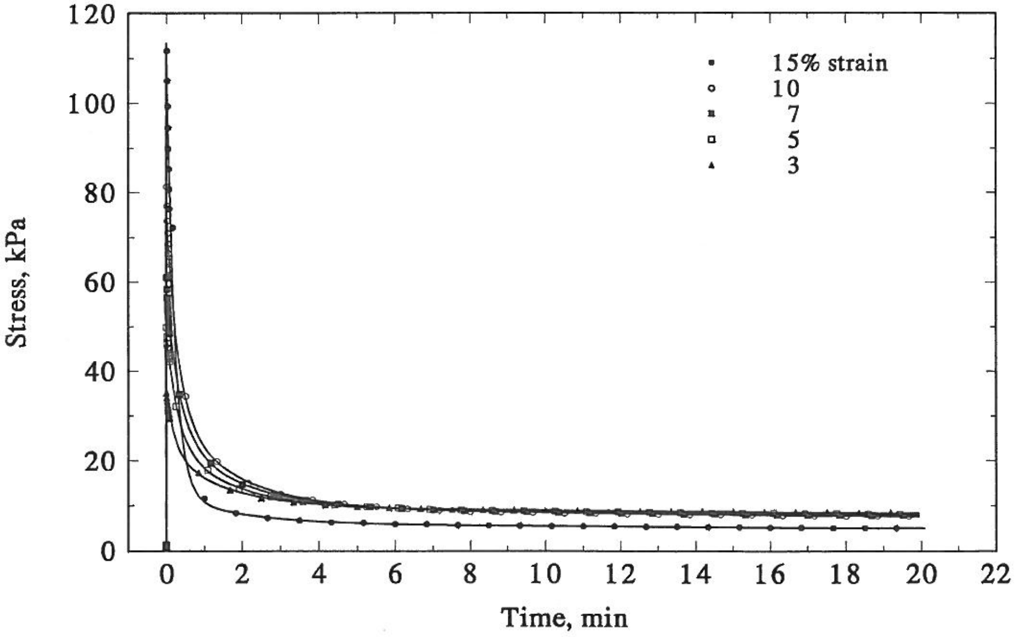


Fig. 1. Stress relaxation of gellan gels containing 2% gellan and 8 mM Ca^{2+}, subjected to five strains. Crosshead speed, 300 mm/min; specimen diameter, 21 mm.

TABLE 1
Relaxation Parameters for Gellan Gels as Affected by Strain at 300 mm/min Crosshead Speed

Gel type	*Strain (%)*	*Equations (3) and (4)*				*Equation (6)*		
		$\sigma(0)$ *(kPa)*	σ_e	C_1*	*RMS*	σ_e	$1/k_1(s^{-1})$	*RMS*
1% Gellan	3	5·4	2·09	0·02	0·014	2·2	0·012	0·058
4 mM Ca^{2+}	5	7·6	1·98	0·07	0·017	2·1	0·016	0·077
	7	10·3	1·86	0·16	0·014	2·2	0·020	0·084
	10	18·0	1·62	0·28	0·039	1·9	0·034	0·092
	15	29·9	1·19	0·43	0·032	1·7	0·046	0·088
	20	44·1	0·31	0·48	0·059	0·5	0·044	0·073
2% Gellan	3	37·3	8·20	0·30	0·027	8·2	0·053	0·045
8 mM Ca^{2+}	5	53·6	8·03	0·43	0·026	7·8	0·067	0·048
	7	65·6	7·88	0·45	0·024	7·4	0·074	0·065
	10	90·0	7·20	0·55	0·036	7·2	0·101	0·083
	15	137·4	5·68	0·82	0·049	4·5	0·228	0·055

*C_1 is dimensionless.

rates of stress relaxation, as stresses in gels of 21 mm diameter decayed more rapidly than gels of 31 mm (Fig. 3). The equilibrium stresses were not affected by the aspect ratio (Table 3).

Consecutive stress relaxation tests

Consecutive tests on the same sample using identical test conditions resulted in shorter specimens with smaller initial stresses but the same equilibrium stresses (Fig. 4). When a specimen was soaked in distilled water for 2 h after a 20 min stress relaxation test, the original geometry was restored, and subsequent stress relaxation

TABLE 2
Relaxation Parameters for Gellan Gels as Affected by Crosshead Speed at 5% Strain

Gel type	Crosshead speed *(mm/min)*	*Equations (3) and (4)*				*Equation (6)*		
		$\sigma(0)$ *(kPa)*	σ_e	C_1	*RMS*	σ_e	$1/k_1(s^{-1})$	*RMS*
1% Gellan	3	4·4	1·85	0·05	0·027	1·7	0·003	0·047
4 mM Ca^{2+}	30	5·0	1·81	0·02	0·016	1·8	0·009	0·059
	300	6·5	1·70	0·02	0·021	1·8	0·015	0·086
2% Gellan	3	23·5	7·29	0·20	0·021	7·2	0·015	0·012
8 mM Ca^{2+}	30	29·6	7·11	0·23	0·045	7·3	0·028	0·042
	300	44·7	7·16	0·35	0·054	7·4	0·051	0·073

TABLE 3
Relaxation Parameters for Gellan Gels as Affected by Specimen Diameter and Aspect (Height to Diameter) Ratio at 5% Strain and 300 mm/min Crosshead Speed

			Equations (3) and (4)				*Equation (6)*		
Gel type	*Diameter (mm)*	*Aspect ratio*	*$\sigma(0)$ (kPa)*	*σ_e*	*C_1*	*RMS*	*σ_e*	*$1/k_1(s^{-1})$*	*RMS*
1% Gellan 4 mM Ca^{2+}	21	0·5	10·2	1·83	0·15	0·022	1·9	0·023	0·088
		1·0	9·3	1·78	0·14	0·017	1·9	0·021	0·089
		1·5	11·0	1·76	0·16	0·015	1·9	0·024	0·097
	31	0·5	10·5	1·47	0·17	0·011	1·5	0·019	0·087
		1·0	9·3	1·49	0·15	0·016	1·7	0·016	0·097
		1·5	9·6	1·53	0·15	0·022	1·7	0·016	0·089
2% Gellan 8 mM Ca^{2+}	21	0·5	45·7	7·30	0·43	0·025	7·6	0·058	0·059
		1·0	44·5	7·67	0·41	0·024	7·7	0·052	0·056
		1·5	45·8	7·66	0·40	0·031	7·6	0·053	0·063
	31	0·5	50·7	6·59	0·34	0·032	7·7	0·064	0·071
		1·0	50·9	6·10	0·38	0·025	7·2	0·052	0·084
		1·5	51·3	6·16	0·38	0·033	7·4	0·049	0·092

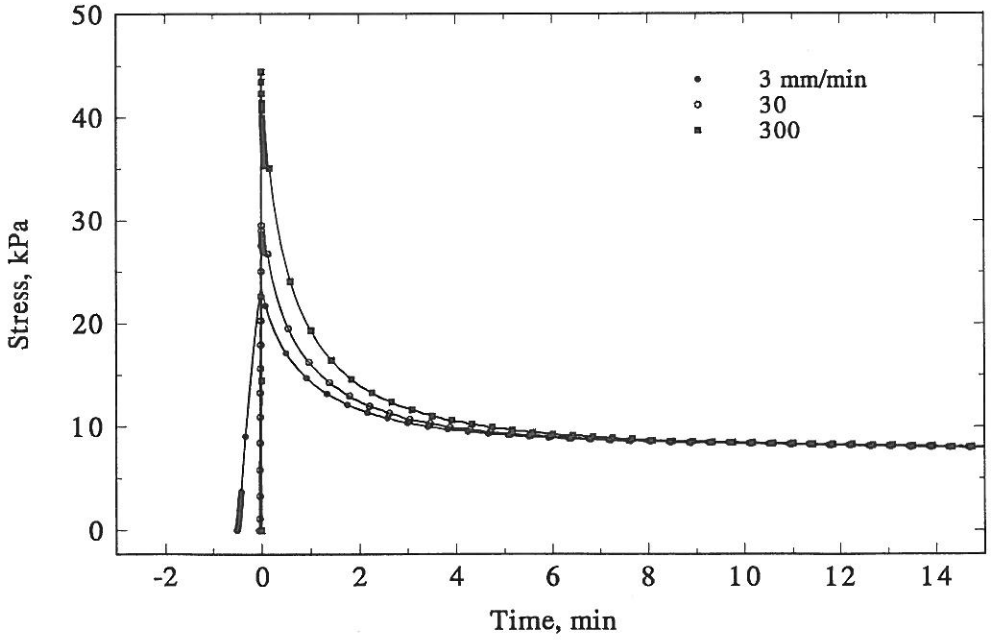


Fig. 2. Stress relaxation of gellan gels containing 2% gellan and 8 mM Ca^{2+}, subjected to 5% strain at three different crosshead speeds. Relaxation strain, 5%; specimen diameter, 21 mm.

curves were identical to the previous ones (Fig. 5). When the gel was subjected to 20% of strain at 300 mm/min, structure was irreversibly altered and the geometry was not restored in soaking (Fig. 6). Both the initial and residual stresses in the soaked gels of the second test were significantly smaller than the first one. Similar stress relaxation characteristics were observed with 1% gellan gels at other Ca^{2+} levels (Table 4) and also with 2% gellan gels.

Equilibrium stress

The effect of gel composition on the equilibrium stresses of 1 and 2% gellan gels relaxed under 5% strain are shown in Fig. 7. In general, 2% gels had higher equilibrium stresses than 1% gels. At a given gellan concentration, the equilibrium stresses increased with Ca^{2+} concentration up to a certain level, and then decreased with extra cations. The pattern of changes in the equilbrium stresses in stress relaxation with respect to gellan and cation concentrations resembles that of the dependence of failure stresses (which indicate the strength of the gels) on Ca^{2+} concentrations in large deformation compression tests reported by Tang *et al.* (1994, 1995). Fig. 8 shows a close correlation ($r^2 = 0{\cdot}998$) between equilibrium stresses from stress relaxation tests and the failure stresses obtained in compression tests for ten different gellan gels. Gel failure stresses reflect the strength of gel systems (larger failure stress corresponds to a stronger gel system). Therefore, the equilibrium stresses in stress relaxation should be directly related to the degree of

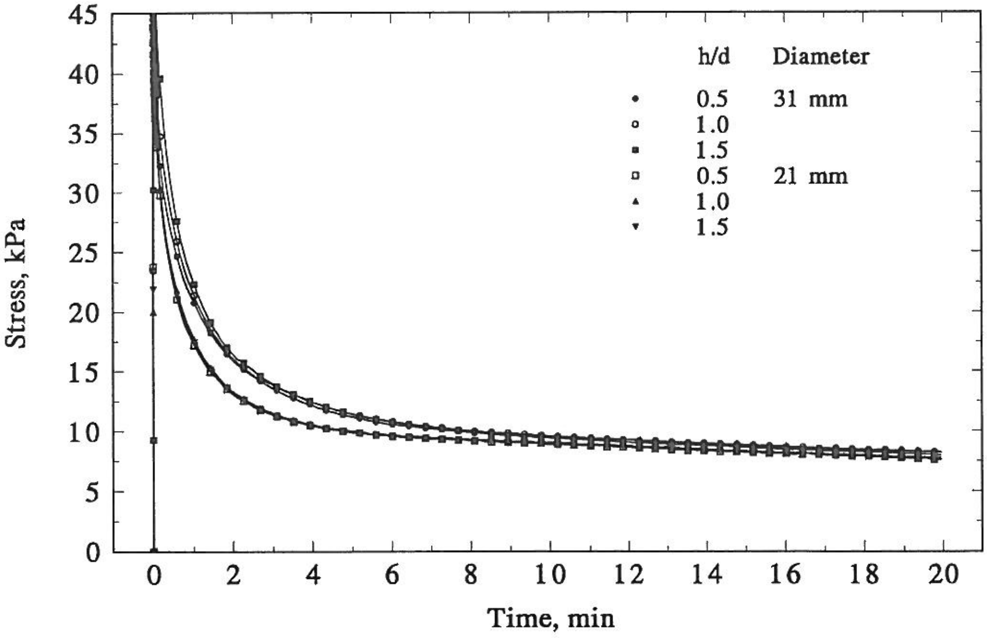


Fig. 3. Stress relaxation of gellan gels containing 2% gellan and 8 mM Ca^{2+} showing two diameters and three aspect ratios. Imposed strain was 5% at 300 mm/min crosshead speed.

crosslinking in the polymer network. Nussinovitch *et al.* (1989) also suggested that the equilibrium stresses in agar and alginate gels were related to stiffness and strength.

Mechanism for stress relaxation

Although relaxation tests are commonly used to characterize properties of food gels, the mechanism involved in the relaxation behavior of those materials is not well understood. Mitchell (1980) suggested that time dependent mechanical behavior in stress relaxation was due to entanglement coupling of larger polymer chains in covalent crosslinked gel, and the shifting of crosslinks in noncovalent crosslinked gels. Peleg & Pollak (1982) and Nussinovitch *et al.* (1990), on the other hand, attributed the time dependent characteristics of gels to the release of hydraulic pressure induced within gel specimens during loading. It is possible that all the above mechanisms contributed to stress relaxation in gellan gels. Our observations, especially those on the effects of specimen diameter and consecutive stress relaxation, suggest that a release of hydraulic pressure was a major factor responsible for stress relaxation in gellan gels.

Gellan gels are two-phase systems consisting of 98–99% water in a supporting matrix (or network) of crosslinked polymer chains or bundles of chains. In function, the polymer network resembles a sponge (Fig. 9), but the pores in gel networks are

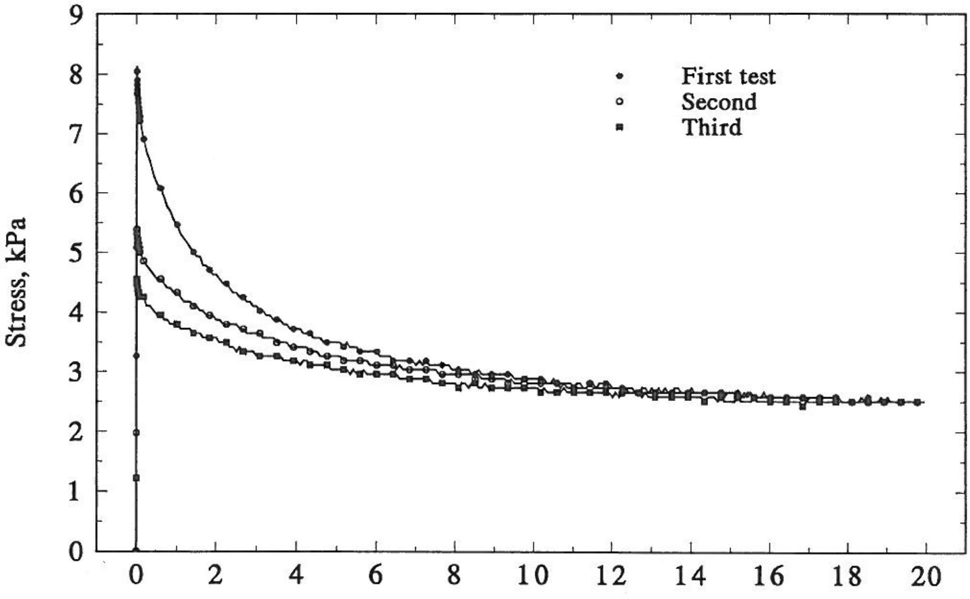


Fig. 4. Stress relaxation of gellan gels containing 1% gellan and 4 mM Ca^{2+} and subjected to three successive compression tests. Specimen diameter, 21 mm; imposed strain, 5%; and crosshead speed, 300 mm/min.

much smaller, in the order of 0·1–1 μm. Water is held in the pores of the matrix mostly via capillary forces. Pore sizes and the strength of the matrix depend upon gel composition and, perhaps, the gel preparation method. Rapid compression of the polymer/water system at the start of relaxation tests resulted in a build-up of hydraulic pressure, registered as a normal stress or shear stress. The larger the imposed strain and the more rapid the loading rate, the larger the stresses. When the stress magnitude exceeded a certain limit, the polymer network failed, most probably at weak crosslinks and/or in concentrated stress areas. As a result, cracks developed, as in the cases when 1% gellan was subjected to 20% strain and 2% gels to 15% strain at a crosshead speed of 300 mm/min. At smaller compression strains, the polymer matrix deformed without fracturing, but an internal hydrostatic pressure developed due to the resistance of the network to the liquid seepage.

Differential hydraulic pressures between the interior and the cylindrical surface of a compressed specimen might have forced water held in the polymer matrix to migrate towards the free surfaces, which released some of the hydraulic pressure and contributed to stress relaxation. Thus, the rate of stress relaxation would, to a large degree, depend on the magnitude of capillary forces that hold the water, the resistance to water seepage through the polymer matrix, and the distance for the water to flow. The first two factors depend on pore size of the gel network, the third factor depends upon the diameter of the specimen. Therefore, higher stress relaxa-

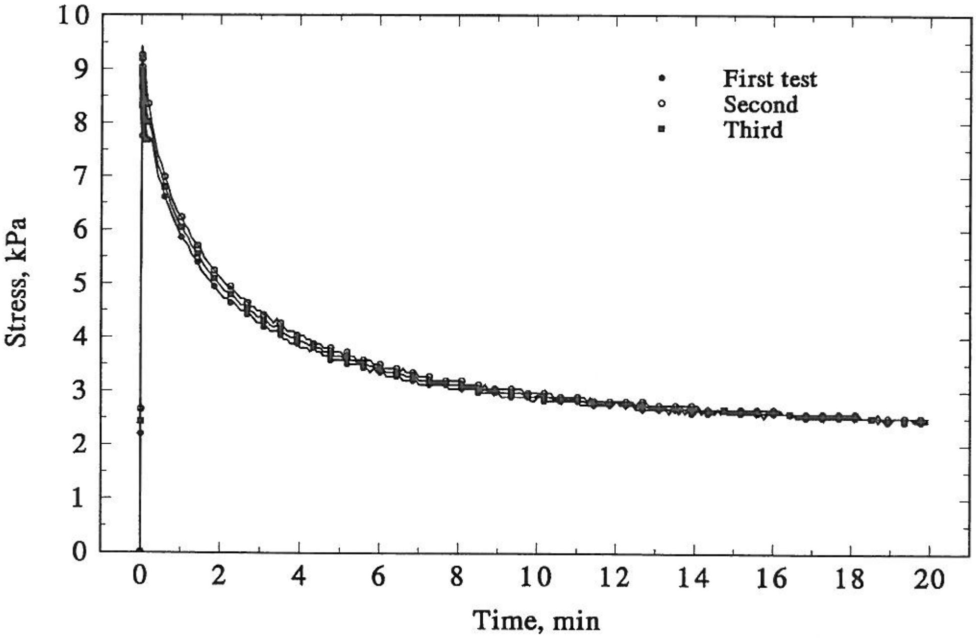


Fig. 5. Stress relaxation of gellan gels containing 1% gellan and 4 mM Ca^{2+} and subjected to three successive compression tests with interim soaking in distilled water for 2 h. Specimen diameter, 21 mm; imposed strain, 5%; and crosshead speed, 300 mm/min.

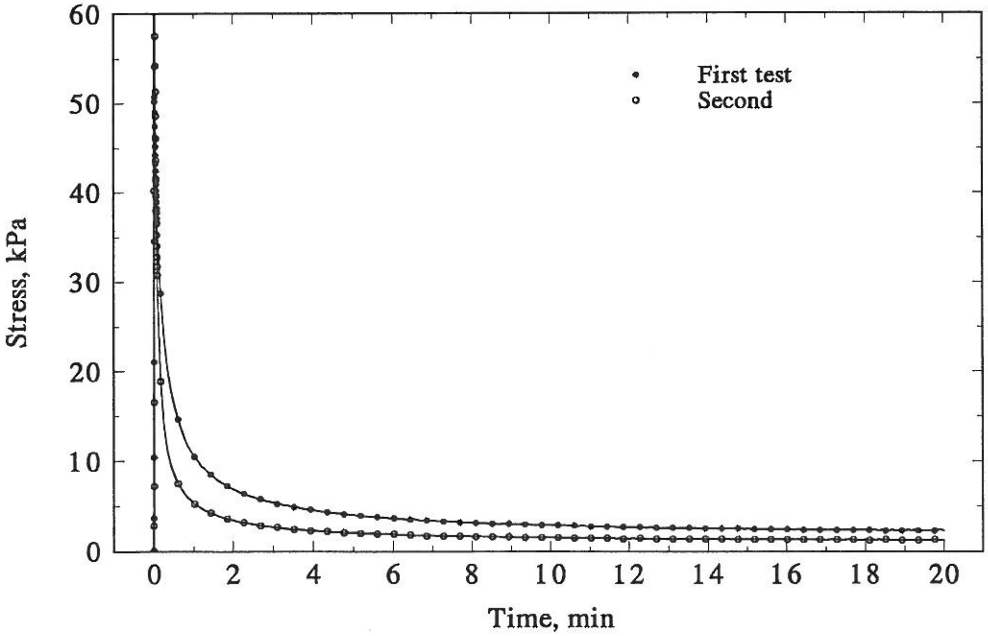


Fig. 6. Stress relaxation of gellan gels containing 1% gellan and 4 mM Ca^{2+} and subjected to two consecutive tests with interim soaking in distilled water for 2 h. Specimen diameter, 21 mm; imposed strain, 20%; and crosshead speed, 300 mm/min.

TABLE 4
Values of k_1 and k_2 in Eqn (6) for 1% (w/w) Gellan Gels in Three Consecutive Relaxation Tests for Three Ca^{2+} Concentrations at 5% Strain and 300 mm/min Crosshead Speed

Consecutive test no.	*4 mM Ca^{2+}*				*8 mM Ca^{2+}*				*32 mM Ca^{2+}*			
	$\sigma(0)$	k_1 (s)	k_2	r^2	$\sigma(0)$	k_1 (s)	k_2	r^2	$\sigma(0)$	k_1 (s)	k_2	r^2
1	8·1	59·4	1·35	1·00	22·31	12·6	1·16	1·00	20·0	3·0	1·08	1·00
2	5·5	102	1·82	0·99	15·57	20·4	1·27	1·00	11·6	10·8	1·15	1·00
3	4·6	146	2·11	0·99	13·05	23·4	1·34	1·00	8·8	15·6	1·21	1·00
1	8·8	57·6	1·36	0·99	23·62	12·0	1·14	1·00	20·7	2·9	1·08	1·00
2*	9·0	56·4	1·36	1·00	23·43	12·6	1·15	1·00	20·2	2·9	1·07	1·00
3*	8·9	58·2	1·34	1·00	24·01	12·0	1·14	1·00	20·0	2·9	1·08	1·00

*Samples were soaked in water for 2 h after each consecutive test.

tion rates are expected in gels with larger pore sizes, as in the sample of gels made of 1% gellan and 32 mM Ca^{2+} (Fig. 9), and smaller specimen diameters.

Water loss associated with stress relaxation at a constant strain resulted in reduced sample height after the imposed deformation was removed. As long as the polymer matrix was not permanently damaged by excessive stresses, the gel could regain its lost water and restore its structure when immersed in water. Only when the gels were subjected to large stresses, the polymer network may have been permanently damaged so that the gel structure was irreversibly altered. The cracks in the damaged gels facilitated the release of hydraulic pressure and, thus, speeded up the stress relaxation process.

Mechanical models consisting of spring (representing the elastic component) and dashpot (representing viscous fluid) elements are often used to explain rheological properties of hydrogels (Mitchell, 1980). Those models suggest that, for a solid, a larger imposed strain would lead to a larger equilibrium stress in stress relaxation. Models based on Gaussian network theory developed for rubber materials also suggest that larger strains would result in larger stresses in equilibrium conditions. Our results, however, indicate that the equilibrium stresses of gellan gels after stress relaxation under small strains were independent of or slightly decreased with the imposed strain. Similar observations were made with two other polysaccharide hydrogels: carrageenan (1·75%) and agar (5%) tested using the same test conditions for gellan gels (Figs 10 and 11). Our observations suggest that the solid matrix in

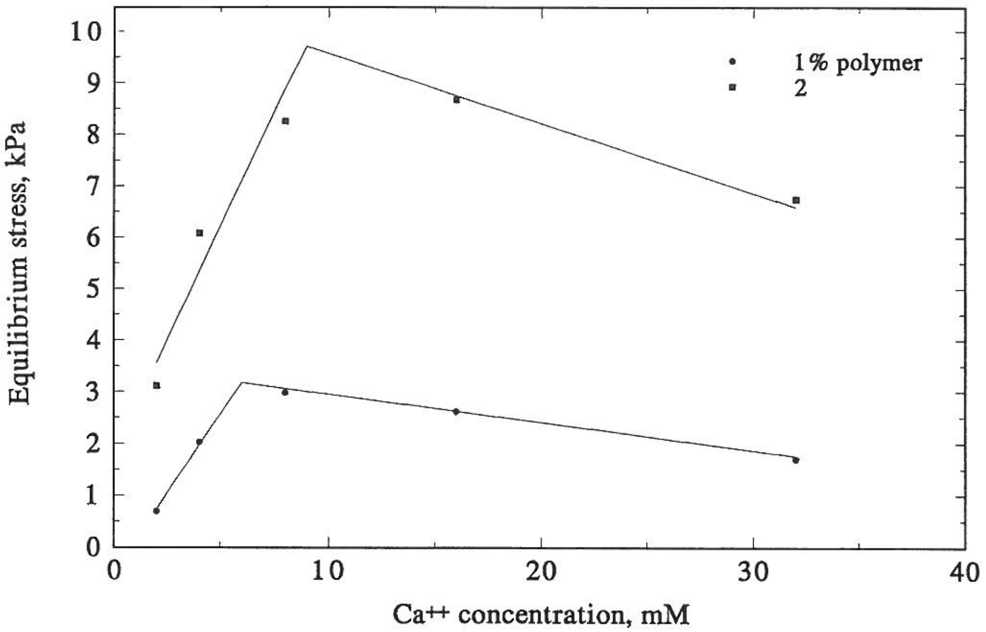


Fig. 7. Equilibrium stresses in gellan gels in stress relaxation as affected by polymer and Ca^{2+} concentrations. Specimen diameter, 21 mm; crosshead speed, 300 mm/min; imposed strain, 5%. The data points are means of three replicates.

those polysaccharide gels did not behave like a spring or a combination of springs and dashpots, nor like a Gaussian network. The underlying mechanism for this interesting phenomenon warrants further investigation.

CONCLUSIONS

Our results indicate that stress relaxation in gellan gels is mainly associated with a release of hydraulic pressure caused by compression of the gellan gel matrix. Increasing the loading speed and the magnitude of the imposed strain resulted in larger initial stresses during relaxation tests. Higher stress relaxation rates were associated with larger pore sizes of the gel matrix and smaller specimen diameter. The equilibrium stresses following relaxation were not affected by test parameters, such as specimen geometry and loading speed, but positively related to gel strength. It is, thus, very likely that equilibrium stress reflects the degree of crosslinking in the polymer network.

Stress relaxation was associated with water loss from the gel matrix and reduction in specimen height. As long as the polymer network was not permanently damaged by excessive stresses, the gel structure could be restored upon soaking in water.

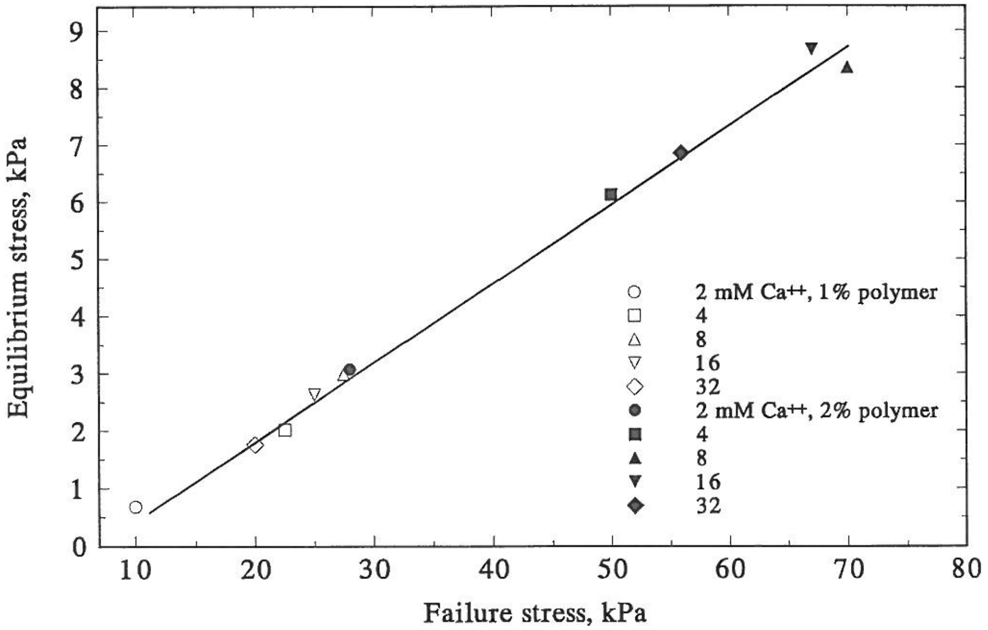
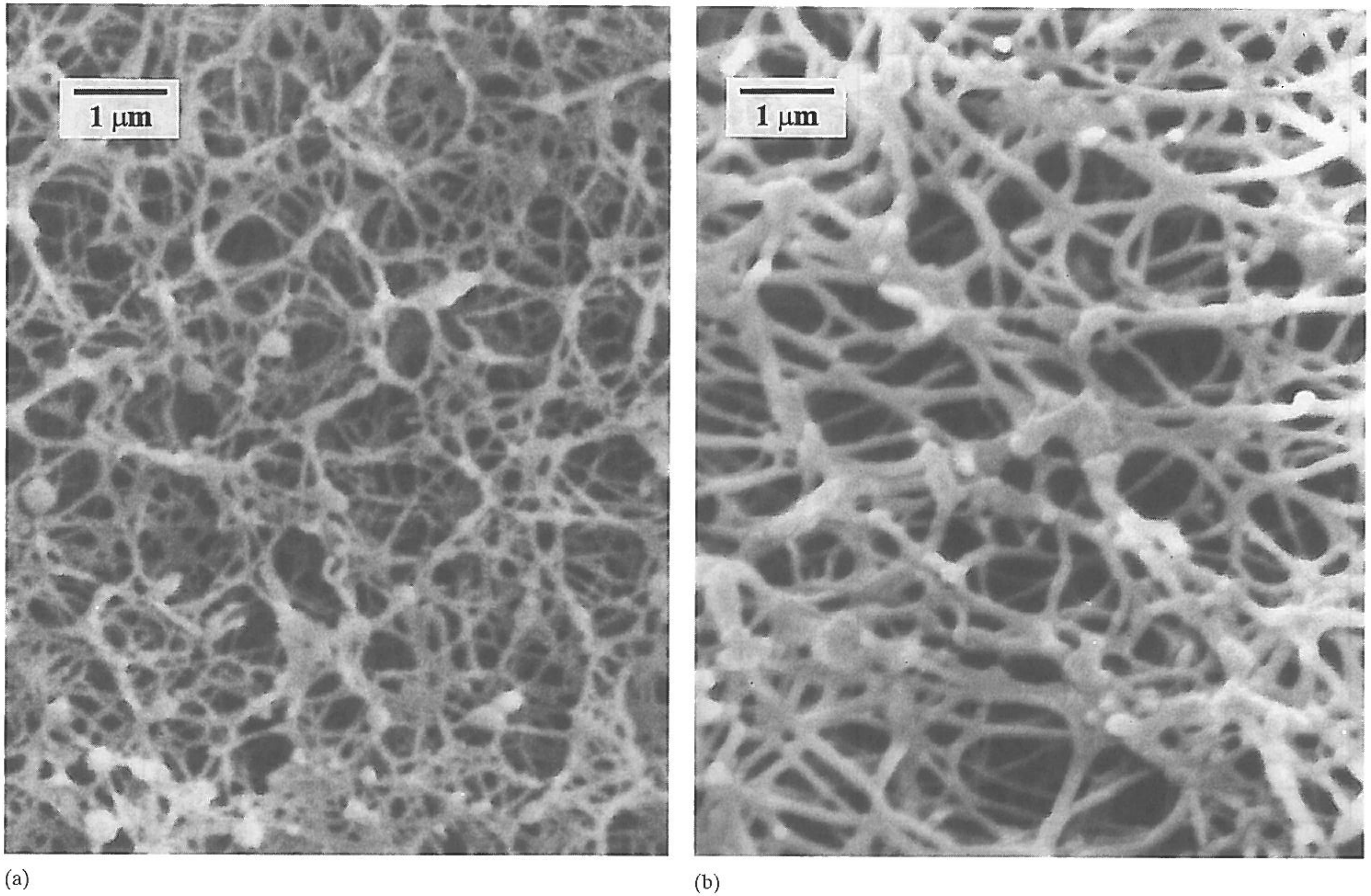


Fig. 8. Correlation between equilibrium stress from relaxation tests and failure shear stresses from compression tests for gellan gels containing different concentrations of polymer and Ca^{2+}. For both tests, specimen diameter was 21 mm and crosshead speed was 300 mm/min. For relaxation tests, 5% strain was imposed.



(a) (b)

Fig. 9. Cryo-SEM image of gellan gels containing 1% gellan and (a) 4 mM Ca^{2+}; (b) 32 mM Ca^{2+}.

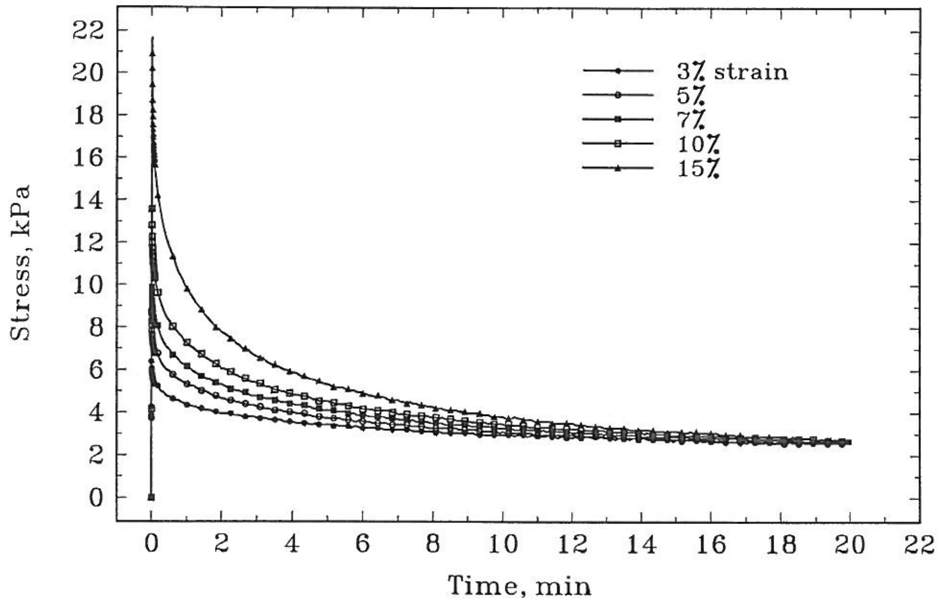


Fig. 10. Stress relaxation of 1·75% κ-carrageenan gel subjected to five strains. Crosshead speed, 300 mm/min; specimen diameter, 21 mm.

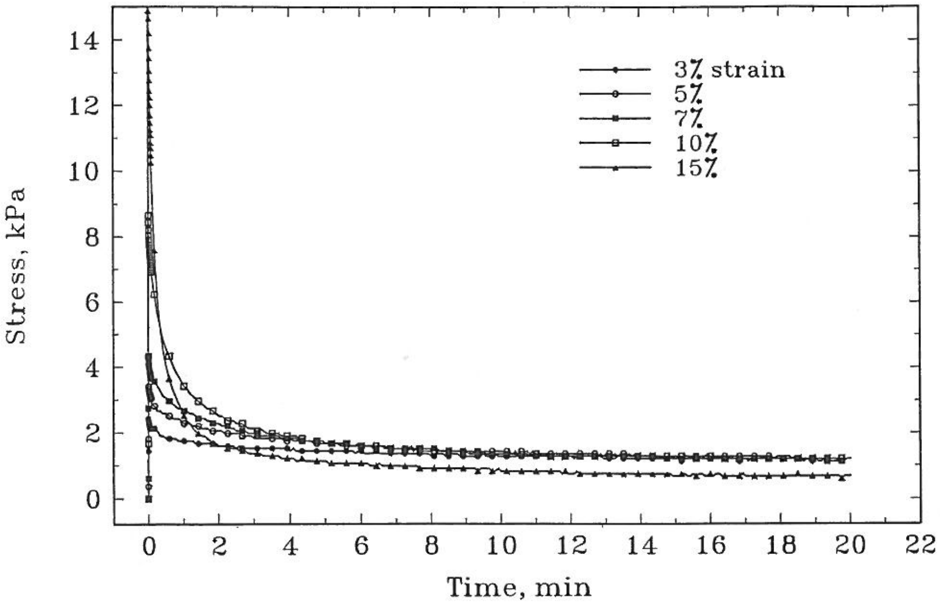


Fig. 11. Stress relaxation of 5% agar gel subjected to five strains. Crosshead speed, 300 mm/min; specimen diameter, 21 mm. Gel structure failed at 15% strain.

ACKNOWLEDGEMENTS

This project was supported by Washington State Agricultural Research Center, Pullman, WA and by the Natural Sciences and Engineering Research Council of Canada. We thank Alexandra K. Smith at the University of Guelph, Guelph, ON, for preparing the Cryo-SEM images.

REFERENCES

Chandrasekaran, R., Puigjaner, L. C., Joyce, K. L. & Arnott, S. (1988). Cation interactions in gellan: an X-ray study of the potassium salt. *Carbohydrate Research*, **181**, 23–40.

Culioli, J. & Sherman, P. (1976). Evaluation of Gouda cheese firmness by compression tests. *Journal of Texture Studies*, **7**, 353–372.

Goh, H. C. & Sherman, P. (1987). Influence of surface friction on the stress relaxation of Gouda cheese. *Journal of Texture Studies*, **18**, 389–404.

Mitchell, J. R. (1980). Review paper: the rheology of gels. *Journal of Texture Studies*, **11**, 315–337.

Mohsenin, N. N. (1970). *Physical Properties of Plant and Animal Materials*. Gordon and Breach Science Publishers, New York.

Nussinovitch, A., Peleg, M. & Normand, M. D. (1989). A modified Maxwell and a non-exponential model for characterization of the stress relaxation of agar and alginate gels. *Journal of Food Science*, **54**(4), 1013–1016.

Nussinovitch, A., Ak, M. M., Normand, M. D. & Peleg, M. (1990). A research note: characterization of gellan gels by uniaxial compression, stress relaxation and creep. *Journal of Texture Studies*, **21**, 37–49.

Peleg, M. (1980). Linearization of relaxation and creep curves of solid biological materials. *Journal of Rheology*, **24**(4), 451–463.

Peleg, M. & Pollak, M. (1982). The problem of equilibrium conditions in stress relaxation analyses of solid foods. *Journal of Texture Studies*, **13**, 1–11.

Peleg, M. & Normand, M. D. (1983). Comparison of two methods for stress relaxation data presentation of solid foods. *Rheologica Acta*, **22**, 108–113.

Pszczola, D. E. (1993). Gellan gum wins IFT's food technology industrial achievement award. *Food Technology*, **9**, 94–96.

Sanderson, G. R. (1990). Gellan gum. In *Food Gels*, ed. P. Harris, pp. 201–230. Elsevier Science Publishers Ltd, New York.

SAS Institute Inc. (1985). *SAS Users Guide: Statistics*, 5th edn. SAS Institute Inc., Cary, NC.

Shama, F. & Sherman, P. (1973). Stress relaxation during force–compression studies on foods with the Instron universal testing machine and its implications. *Journal of Texture Studies*, **4**, 353–362.

Tang, J., Lelievre, J., Tung, M. A. & Zeng, Y. Y. (1994). Polymer and ion concentration effects on gellan gel strength and strain. *Journal of Food Science*, **59**(1), 216–220.

Tang, J., Tung, M. A. & Zeng, Y. Y. (1995). Mechanical properties of gellan gegls in relation to divalent cations. *Journal of Food Science*, **60**(4), 748–759.

Tang, J., Lelievre, J., Tung, M. A. & Zeng, Y. Y. (1997). Stress–strain relationships for gellan gels in tension, compression and torsion. *Journal of Food Engineering*, **31**, 511–529.

Tung, M. A., Britt, I. J. & Tang, J. (1994). Controlled biaxial extension of food polymer gels. In *Proceedings of the 6th International Congress on Engineering and Food*, ed. T. Yano. R. Matuno and K. Nakamura, Blackie Academic and Professional, London.

Upstill, C., Atkins, E. D. T. & Attwool, P. T. (1986). Helical conformations of gellan gum. *International Journal of Biological Macromolecules*, **8**, 275–288.

Ziegler, G. R. & Rizvi, S. S. H. (1989). Determination of cross-link density in egg white gels from stress relaxation. *Journal of Food Science*, **54**(1), 218–219.