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Stress–Strain Relationships for Gellan Gels in Tension, Compression and Torsion

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ABSTRACT

Formulated foods often contain small amounts of polymeric ingredients that interact to form three-dimensional networks which stabilize structure and provide desirable textural quality. One goal of food engineers is to understand how gels are formed and to be able to predict their mechanical properties. We have studied calcium-crosslinked gels of gellan, a polysaccharide recently introduced to the food industry, in order to understand their stress–strain behavior in tension, compression and torsion. This information will be applied when designing stability and texture for a variety of food systems. Gels were prepared by dispersing gellan polymer in 90°C water, adding calcium chloride and cooling in molds to form the test specimens. Four levels of polymer, ranging from 0·6 to 1·8% w/v, were used with seven calcium concentrations between 1·5 and 60 mM. Molds of differing construction provided specimen shapes that were cylindrical with enlarged ends for tensile tests, cylindrical for compression tests and capstan-shaped for torsion tests. Specimens for tension and torsion testing were modified with plastic adapters to facilitate attachment in mechanical testing machines; whereas compression was carried out between lubricated parallel Teflon plates. Gel properties were influenced strongly by the content and combination of polysaccharide and ion. Shear stress relationships in small deformations were almost identical in the three testing modes for a given gellan and calcium concentration. In large deformations, gels were more rigid in tension than in compression and torsion, but they failed at the same

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maximum shear stress regardless of testing mode. Stress–strain responses were analyzed using constitutive equations based on energy functions. Mooney–Rivlin constitutive equations were applicable for stress–strain relationships for small strains; however, equations based on three-term energy functions fitted the data more accurately at larger strains.

NOTATION

CV	Coefficient of variation
C_1, C_2, C_3	Constants in energy functions (kPa)
E	Modulus of elasticity (kPa)
F	Second order polynomial functions of I_1 and I_2
G	Shear modulus of elasticity (kPa)
I	Strain invariant
K	Specimen shape factor
K'	Correction factor for the end pieces of torsion specimens
L	Initial specimen length (m)
ΔL	Deformation (m)
M	Twisting moment (kNm)
N	Number of data points
Q	Specimen shape factor (m^{-3})
r	Radius of the narrowest section of the capstan specimens (m)
R	Radius of specimens for tension or compression tests (m)
R.M.S	Relative mean square error
Y_i'	Value predicted by the constitutive equation
Y_i	Experimental data
W	Stored-energy function
Φ	Angular deformation (rad)
λ	Ratio of transient sample dimension to the original dimension
σ	Nominal normal stress (kPa)
ε	Nominal normal strain
ν	Poisson's ratio
τ	Nominal shear stress (kPa)
γ	Nominal shear strain

Subscripts

1, 2, 3	In three principal axes
true	True or Hencky's stress or strain

INTRODUCTION

Gel-forming polymers can stabilize components of formulated foods by trapping them in a three-dimensional matrix consisting of the polymer molecules which interact at junction zones to provide a solid-like structure. Some gelling polymers are essentially indigestible, hence have little or no caloric value. These are attractive replacements for starches, proteins, fats and low molecular weight sugars which are commonly used to provide textural properties in sauces, emulsions, custards and protein gel foods. In order to use gelling polymers in the food industry, considerable efforts have been devoted to understanding the functions and characteristics of gelling agents.

Gellan gum is a newly approved gelling agent with interesting properties that are applicable to a wide variety of food systems. It is an extracelluar polysaccharide secreted by the bacterium *Pseudomonas elodea*. This polysaccharide can produce a gel at a concentration as low as 0·2% when in the presence of cations (Tang *et al*., 1995) and provides a wide range of textures at different polymer and ion concentrations, or when used with other gelling agents (Sanderson, 1990). Many applications have been identified and evaluated on a laboratory scale and some have already been successfully tested at the commercial level. In order to utilize its full potential as a functional ingredient for foods, information is needed concerning the mechanical characteristics of gellan gels in large deformations (Bagley & Christianson, 1988; Borwankar, 1992; Lelievre *et al*., 1992a).

Methods for obtaining stress–strain relationships in large deformation include uniaxial tension and compression tests and torsion tests. Uniaxial compression tests are widely used because of simplicity (Diehl *et al*., 1979). Tension tests are more difficult to perform because of difficulty in mounting samples, and care must be taken to prevent premature failure due to stress concentrations adjacent to the specimen attachments (Hamann, 1983; Lelievre *et al*., 1992b). Torsion testing has become a popular method for large deformation testing of foods (Diehl *et al*., 1979; McCarthy, 1987). The experimental results from each of the above three methods may reflect different aspects of the general behavior of a food material. For this reason, it may be possible to obtain more comprehensive information by using all three methods when testing food material properties. Tang *et al*. (1994) studied effects of divalent cation and polymer concentrations on the strength and extensibility of gellan gels using tension, compression and torsion tests. They observed that when more than 0·5 divalent cations were present per repeat gellan polymer unit the gels were relatively brittle and the maximum true shear strains at failure in compression and torsion were about 0·4. These strains were significantly smaller than the maximum true shear strains of 1·02–1·10 for fish gels and 1·04–1·16 for egg white gels in similar test modes (Hamann, 1983). However, at low cation levels, the maximum true shear strain in gellan gels in compression and torsion could be as large as 1·2 before the gels fail (Tang *et al*., 1994). At all cation levels, the maximum true shear strains of gellan gels at failure in tension tests were about half that in compression and torsion tests.

Stress–strain relationships before failure reveal the interactions among functional components of materials in deformation. These relationships may be described by constitutive models. The simplest model for elastic materials in small deformation is Hooke's law, which predicts a linear relationship between stress and strain under a uniaxial load (Ugural & Fenster, 1981). Deformation in rubbers can be described by Gaussian Network Theory, for strains up to 0·2, and by Mooney–Rivlin constitutive equations for larger deformations (McCrum *et al*., 1988). However, there is a lack of constitutive equations applicable to stress–strain relationships in food gels when subjected to large deformations (Bagley, 1983). Gao *et al*. (1993) used a stored energy equation to describe the stress and strain relationship, but only in the compression mode. Treloar (1958) pointed out that any particular type of strain would be too limited to provide the true form of the stored energy function. The objectives of the present study were to investigate the general stress–strain relationships of gellan gels in tensile, compressive and torsion tests, and to explore the possibility of describing these relationships with mathematical models based on stored energy functions.

THEORY

Most food gels are nearly incompressible (Hamann, 1983). When these gels experience large deformations, the constitutive relations may be developed from a stored-energy function:

$$W = W(I_1, I_2) \tag{1}$$

where I_1, I_2 are the strain invariants defined as (Treloar, 1958):

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \tag{2}$$

$$I_2 = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2} \tag{3}$$

where λ_1, λ_2 and λ_3 are the ratios of transient sample dimensions to the original dimensions in the three principal axes. These ratios are related to the principal strains by:

$$\lambda_i = \varepsilon_i + 1, \quad i = 1,2,3 \tag{4}$$

A general stored-energy function for an incompressible isotropic elastic material may be expressed as the sum of a series of terms involving powers of $(I_1 - 3)$ and $(I_2 - 3)$:

$$W(I_1, I_2) = \sum_{i=0, j=0}^{\infty} C_{ij}(I_1 - 3)^i (I_2 - 3)^j \tag{5}$$

where C_{ij} are material constants. For tensile or compressive deformation under an uniaxial load, the three parameters λ_1, λ_2 and λ_3 can be expressed by a single parameter λ because $\lambda_1 = \lambda$ and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$, where λ is in the direction of load. Thus I_1 and I_2 can be expressed as:

$$I_1 = \lambda^2 + \frac{2}{\lambda} \tag{6}$$

$$I_2 = 2\lambda + \frac{1}{\lambda^2} \tag{7}$$

For deformation in the torsion mode, the three principal extension ratios may be written as $\lambda_1 = \lambda$, $\lambda_2 = 1$ and $\lambda_3 = 1/\lambda$, where λ represents the extension ratio in the principal axis of deformation. Therefore, I_1 and I_2 can be written as:

$$I_1 = \lambda^2 + 1 + \frac{1}{\lambda^2} \tag{8}$$

$$I_2 = \frac{1}{\lambda^2} + 1 + \lambda^2 \tag{9}$$

According to Castigliano's theory (Ugural & Fenster, 1981), the nominal (engineering) normal stress (σ) in tension or compression is related to the stored-energy function (W) as:

$$\sigma = \frac{dW}{d\lambda} = \frac{\partial W}{\partial I_1}\frac{dI_1}{d\lambda} + \frac{\partial W}{\partial I_2}\frac{dI_2}{d\lambda} \tag{10}$$

whereas in a simple shear, the shear stress (τ) is related to the shear strain (γ) according to Rivlin (1947):

$$\tau = 2\left(\frac{\partial W}{\partial I_1} + \frac{\partial W}{\partial I_2}\right)\gamma \tag{11}$$

The explicit expression for stress–strain relationships in incompressible gels depends upon the form of the function $W(I_1, I_2)$ in eqn (5).

Mooney–Rivlin constitutive equations developed for elastic rubbers (McCrum *et al.*, 1988) were based on the following first order two-term Mooney energy equation:

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \tag{12}$$

where C_1 and C_2 are material constants. Using eqn (10) and eqn (11), the stress–strain relationships in compression ($\lambda < 1$, $\sigma < 0$) and tension ($\lambda 1$, $\sigma 0$) can be described by:

$$\sigma = 2\left(\lambda - \frac{1}{\lambda^2}\right)\left(C_1 + \frac{C_2}{\lambda}\right) \tag{13}$$

and in the torsion mode by:

$$\tau = 2(C_1 + C_2)\gamma \tag{14}$$

Thus, $2(C_1 + C_2)$ represents the shear modulus of the material.

Equation (13) describes a nonlinear normal stress–strain relationship in uniaxial loading, whereas eqn (14) represents a linear relation under a torsional load. The Mooney–Rivlin constitutive relationship has been used to a limited extent for food gels in compression (Bagley, 1983), although the fits were generally not very satisfactory for large deformations. It will be of interest to examine its applicability to gels in tensile and torsional modes. Improvement may be possible by adding a second order term to the Mooney energy equation:

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) + C_3F(I_1, I_2) \tag{15}$$

where $F(I_1, I_2)$ stands for a second order polynomial function of I_1, and I_2. Equation (15) can be used with eqn (10) to derive the constitutive relationships for tension and compression modes as:

TABLE 1

Possible Forms of the Second Order Polynomial Function $F(I_1,I_2)$ and Their Derivatives

$F(I_1,I_2)$	$\partial F(I_1,I_2)/\partial\lambda$	$\partial F/\partial I_1+\partial F/\partial I_2$
$(I_2-3)^2$	$2C_3(I_2-3)/\lambda$	$2C_3(I_2-3)$
$(I_1-3)^2$	$2C_3(I_1-3)$	$2C_3(I_1-3)$
$(I_1-3)(I_2-3)$	$C_3[(I_1-3)/\lambda+(I_2-3)]$	$C_3[(I_1-3)+(I_2-3)]$

$$\sigma = 2\left(\lambda-\frac{1}{\lambda^2}\right)\left(C_1+C_2\frac{1}{\lambda}\right)+C_3\frac{\mathrm{d}F(I_1,I_2)}{\mathrm{d}\lambda} \tag{16}$$

and with eqn (11) for the torsion mode:

$$\tau = 2(C_1+C_2)\gamma+2\left(\frac{\partial F}{\partial I_1}+\frac{\partial F}{\partial I_2}\right)\gamma \tag{17}$$

The actual forms of the derivatives of $F(I_1, I_2)$ in eqn (16) and eqn (17) are listed in Table 1.

In principle, it would be possible to consider a general three-term polynomial energy equation as follows:

$$W = \sum_{i=0,j=0}^{2} C_{ij}(I_1-3)^i(I_2-3)^j \tag{18}$$

Higher than second order terms would render the constitutive equation more complicated and potentially unrealistic. Theoretically, a truly representative energy equation should be able to describe the mechanical behavior of a material under any loading conditions, including tensile, compressive and torsional modes. The experimental phase of this work involved carrying out tensile, compressive and torsional tests to derive stress–strain relationships which could be used to select the most suitable form of the theoretical energy functions discussed above.

MATERIALS AND METHODS

Preparation of gellan gels

Gellan gum powder (KELCOGEL, The Nutrasweet Kelco Inc, San Diego, CA) was dispersed in deionized and distilled water with magnetic stirrers. The gellan polymer and water mixtures were heated to 90°C to give clear solutions, and calcium chloride was added. Four levels of gellan polymer (0·6, 1·0, 1·4 and 1·8% w/v) were used in combination with seven concentrations of Ca^{++} (1·5, 3·0, 4·5, 6·0, 24·0 and 60·0 mM). In each case the solution was cooled at room temperature to 60°C and filled into molds. The gels were set by cooling in running water for 15 min at 15°C, and held overnight at 22°C before measurements were made.

Testing conditions

Bagley *et al.* (1985) reported that aspect ratio (length/diameter) of cylindrical specimens of gelatin gels did not affect the mechanical response in lubricated compression. Mirza & Lelievre (1992) investigated the effect of strain rate on the mechanical behavior of gellan gels in compression, and the effect of aspect ratio in compression and torsion. For a range of strain rates from 0·05 to 0·25 s^{-1}, no influence of strain rate was detected. As well, the mechanical behavior of gels was not sensitive to aspect ratios close to 1·0. Therefore, only one aspect ratio and one loading speed was used in the experiments. The mechanical tests were carried out using six replicate measurements.

Tension tests

A mold system described by Langley *et al.* (1986) was used to prepare dumbbell-shaped samples. The test section of each gel specimen was 10 mm in diameter and 32 mm in length with the enlarged ends of the gel samples cut to 3 mm to reduce the end effect (Lelievre *et al.*, 1992b). Nylon disks with cylindrical gripping shafts were attached on both ends of the specimen using cyanoacrylate glue. Specimens were mounted in the mechanical testing machine (Model 1125, Instron Corporation, Canton, MA) using drill chucks attached to the load cell and crosshead to clamp the shaft from the plastic disk on each end of the specimen. Tensile testing was carried out at a crosshead speed of 20 mm/min. Load and deformation data were recorded automatically on an IBM compatible microcomputer through an analog to digital conversion card (Model CIO-AD08, Computer Boards Inc., Mansfield, MA). The nominal normal stress and strain were calculated from the load (F) and deformation (ΔL) using the following equations:

$$\sigma = \frac{F}{\pi R^2} \tag{19}$$

$$\varepsilon = \frac{\Delta L}{L} \tag{20}$$

where L and R are the initial length and radius of the test section of the specimens, respectively. The true (Hencky's) normal stress and strains were calculated from Hamann (1983) and Nussinovitch *et al.* (1990):

$$\sigma_{\text{true}} = \frac{F(L+\Delta L)}{\pi R^2 L} \tag{21}$$

$$\varepsilon_{\text{true}} = \ln\left[1+\frac{\Delta L}{L}\right] \tag{22}$$

Compression tests

Cylindrical test specimens of 21 mm diameter and 20 mm length were compressed between lubricated flat Teflon surfaces fitted to the mechanical testing machine. The gels were deformed at a constant crosshead speed of 20 mm/min. The nominal normal stresses and strains were determined using eqn (19) and eqn (20), and the corresponding true stresses and strains were obtained from:

$$\sigma_{\text{true}} = \frac{F(L-\Delta L)}{\pi R^2 L} \tag{23}$$

$$\varepsilon_{\text{true}} = -\ln\left[1-\frac{\Delta L}{L}\right] \tag{24}$$

In both tensile and compressive modes, the maximum shear stresses are on the plane 45 degrees with the direction of the load. The maximum shear stresses and strain are related to the normal stress and strain by (Hamann, 1983):

$$\tau_{\text{true}} = \frac{\sigma_{\text{true}}}{2} \tag{25}$$

$$\gamma_{\text{true}} = \varepsilon_{\text{true}}(1+\nu) \tag{26}$$

The Poisson's ratio, ν, is about 0·5 for most food gels.

Torsion tests

Test samples were prepared in a mold that gave six capstan-shaped specimens, each with a narrow mid-section and enlarged ends as described by Diehl *et al.* (1979). Plastic disks were attached to both ends of the specimen using cyanoacrylate glue. A Bohlin Rheometer (Model VOR, Bohlin Rheology AB, Lund, Sweden) was used to make torsional measurements. Standard Bohlin attachments were modified to mount the plastic end pieces in a manner analogous to that described for Brookfield (Wu *et al.*, 1984) and Ferranti–Shirley (MacDonald *et al.*, 1990) viscometers. The specimens were twisted at a constant strain rate of 0·0583 s^{-1}. Under a torsional load applied at the two ends of a capstan-shaped specimen, maximum shear stress and strain occurred at the surface of the narrowest section. This shear stress and the corresponding nominal shear strain were calculated as (Diehl *et al.*, 1979; Tang *et al.*, 1994):

$$\tau = \frac{2KM}{\pi r^3} \tag{27}$$

$$\gamma = \frac{2K\Phi}{\pi r^3 Q_s} K' \tag{28}$$

where M and r are the twisting moment and the radius of the narrowed section of the capstan, respectively; Φ is the angular deformation of the specimen. K and Q_s are constants depending on the sample geometry; expressions for these two constants were reported by Diehl *et al.* (1979). K' is the correction factor for the end-piece effect (Tang *et al.*, 1994). The principal normal stress and the true normal stress was related to the maximum shear stress as (Hamann, 1983):

$$\sigma = \sigma_{\text{true}} = \tau \tag{29}$$

The principal true normal strain is (Nadai, 1937):

$$\varepsilon_{\text{true}} = \frac{1}{2} \ln \left[1 + \frac{\gamma^2}{2} + \gamma \left(1 + \frac{\gamma^2}{2} \right)^{1/2} \right] \tag{30}$$

and the maximum true shear strain is:

$$\gamma_{\text{true}} = 2\varepsilon_{\text{true}} \tag{31}$$

Data analyses

Material constants in various constitutive equations were obtained by fitting the equations to the nominal normal stress–strain relationships obtained from the combined data of tensile and compressive tests, using the GLM procedure in the Statistical Analysis System software (SAS, 1985). These constants were substituted in corresponding constitutive relations for the torsion mode, and the theoretical curves were compared with the experimental data. The goodness of fit was evaluated by their Relative Mean Square Error (R.M.S.) defined as:

$$\text{R.M.S.} = \sqrt{\frac{1}{N} \sum_{i=1} \left(\frac{Y_i' - Y_i}{Y_i} \right)^2} \tag{32}$$

where Y_i' is the value predicted by the constitutive equation, Y_i are the experimental data and N stands for the number of data points.

RESULTS AND DISCUSSION

The stress–strain curves from six replicates at each polymer and calcium concentration were fairly consistent, with coefficients of variation less than 5% for compression, 9% for tension and 7% for torsion. Representative curves based on the mean failure stress and strain of six replicates were used for analysis.

Stress–strain relations under uniaxial loads

Typical true normal stress–strain curves from uniaxial tension and compression tests are presented in Fig. 1. The slopes of these curves represent transient moduli of elasticity. Tension and compression curves follow essentially the same pathway near the origin, which suggests that gellan gels had identical tensile and compressive moduli when strains were small ($\varepsilon < 0{\cdot}04$). The same was true at other polymer and

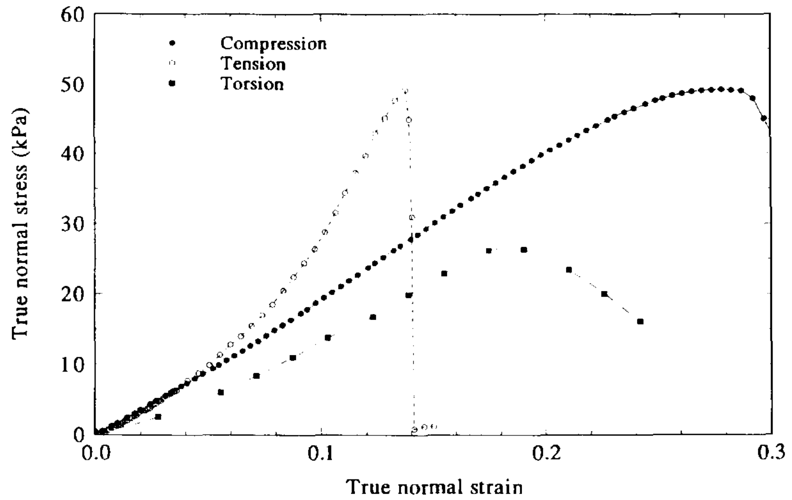

Fig. 1. True normal stress–strain relationships for gels containing 1·0% gellan polymer with 6 mM Ca^{++} in three testing modes.

calcium ion concentrations as shown by the values of initial shear modulus of elasticity $G[=E/2(1+\nu)$, E is the modulus of elasticity] in uniaxial tensile and compressive modes (Table 2). This phenomenon can be explained by the following analysis.

The stored energy function under uniaxial load can be written as:

$$W = W(\varepsilon) \tag{33}$$

where ε is the strain in the direction of the load, it is positive in tension and negative in compression. Given a small strain, $W(\varepsilon)$ can be expressed as a Taylor series:

$$W(\varepsilon) = W_o + \left(\frac{dW}{d\varepsilon}\right)_o \varepsilon + \frac{1}{2}\left(\frac{d^2W}{d\varepsilon^2}\right)_o \varepsilon^2 \tag{34}$$

where W_o is the stored-energy at $\varepsilon = 0$, and the derivatives are evaluated at $\varepsilon = 0$. Equation (34) was simplified by neglecting all the terms with higher than second order of the strain. Assuming a negligible effect of gravity, the stored-energy of a specimen under no load assumes a minimum value of zero. Therefore, the energy function W and its first derivative at $\varepsilon = 0$ are equal to zero, and eqn (34) becomes:

$$W(\varepsilon) = \frac{1}{2}\left(\frac{d^2W}{d\varepsilon^2}\right)_o \varepsilon^2 \tag{35}$$

From the above equation, and eqns (4) and (10), we have:

$$\sigma = \left(\frac{d^2 W}{d\varepsilon^2} \right)_0 \varepsilon \tag{36}$$

which reveals a linear relationship between stress and strain in small deformations. The corresponding modulus of elasticity is the second derivative of the energy function at $\varepsilon = 0$. According to eqn (5), the second derivative of the energy function for incompressible food gels is continuous. Therefore, from eqn (36), the modulus of elasticity of gellan gels in small deformation should be the same in both tension ($\varepsilon > 0$) and compression ($\varepsilon < 0$). As the strain increased (Fig. 1), the stress–strain relationships deviated from the linear response. Gellan gels became increasingly

TABLE 2
Shear Moduli of Gellan Gels from Compression, Tension and Torsion

		Shear modulus, G (kPa)					
		Tension		*Compression*		*Torsion*	
Gellan (%, w/v)	*Ca^{++} (mM)*	*Initial*	*Max.*	*Initial*	*Max.*	*Initial*	*Max.*
0·6	1·5	1·13	6·47	1·12	3·20	1·09	2·96
	3·0	8·10	23·32	8·04	15·45	7·65	16·06
	4·5	11·17	59·32	11·53	29·14	10·23	28·85
	6·0	31·13	79·00	31·49	37·18	30·92	38·07
	24·0	26·46	64·68	26·17	30·48	27·24	30·93
	42·0	21·19	46·09	21·46	25·28	20·97	24·96
	60·0	6·14	23·94	6·04	11·60	5·98	11·44
1·0	1·5	3·63	15·49	3·44	7·68	2·91	7·26
	3·0	13·62	75·82	13·92	36·29	14·57	35·45
	4·5	40·77	106·23	40·87	57·30	41·18	56·29
	6·0	61·03	165·33	62·82	75·59	58·51	71·53
	24·0	75·53	213·05	76·18	106·76	72·73	101·86
	42·0	32·60	147·03	34·65	73·14	30·34	71·89
	60·0	13·64	95·16	12·95	43·12	12·62	44·00
1·4	1·5	3·10	27·80		3·30	19·04	3·0417·35
	3·0	29·30	90·84	28·88	46·65	28·91	44·33
	4·5	49·03	115·74	49·39	62·58	48·25	60·88
	6·0	107·71	197·18	106·58	119·91	104·57	116·29
	24·0	157·32	269·04	156·18	167·17	158·49	164·26
	42·0	82·06	160·65	81·70	94·02	80·22	91·64
	60·0	31·13	141·72	32·54	66·80	35·53	67·10
1·8	1·5	6·17	39·69	6·11	26·49	5·23	24·93
	3·0	35·51	99·41	35·08	52·92	33·50	50·22
	4·5	64·94	174·66	66·97	102·33	63·64	103·02
	6·0	143·45	256·95	145·12	158·15	140·02	155·96
	24·0	219·95	375·79	217·47	277·27	212·43	280·96
	42·0	136·53	311·64	135·40	174·56	140·38	178·94
	60·0	93·18	204·17	91·02	145·13	90·55	147·77

rigid in tension, but the trend was less dramatic in compression. This is consistent for different polymer and calcium concentrations, as indicated by the values of initial and maximum transient moduli in tension and compression (Table 2).

To demonstrate the general mechanical response of gellan gels under uniaxial loads, the tensile and compressive stress–strain profiles for specimens at a given gel and calcium concentration were combined by assigning negative signs to stress and strain in compression and positive signs to those in tension. As a typical example, the true normal stress–strain relationships for 6 mM Ca^{++} gels with varying gellan polymer content under uniaxial stresses are presented in Fig. 2. These curves reveal that the mechanical behavior of gellan gels in small deformations was continuous when the stress changed from tension to compression. They also show that gellan gels become more rigid at larger strains when in tension than in compression. The moduli of elasticity in both tension and compression increased with gel concentration; whereas, the failure strain was essentially the same at all gel concentrations, except for the 1·8% gellan gel. Tang *et al.* (1994) observed that when there were more divalent cations than the critical level of 0·5 present per repeat gellan polymer unit, the failure strains of the gels remained the same regardless of polymer concentrations. This critical cation level is equivalent to 2·9, 4·8, 6·7, and 8·6 mM added Ca^{++} for 0·6, 1·0, 1·4 and 1·8% gellan gels, respectively.

When the cations were less than the critical level as was the case with 1·8% gellan and 6 mM Ca^{2+}, the strain at failure increased in proportion to a decrease in the logarithm of calcium concentration.

Stress–strain relations in torsion

The true normal stress–strain curve in the principal axis of a surface element at the narrowest location of a torsion specimen is also included in Fig. 1. The principal

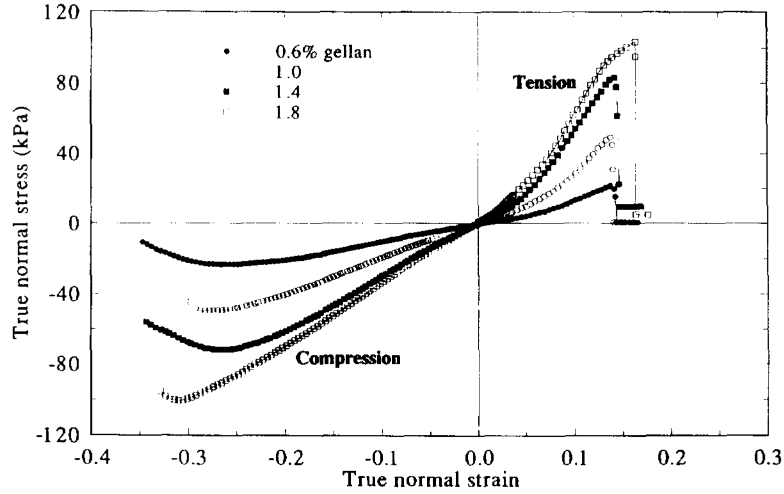

Fig. 2. True normal stress–strain relationships for gels containing 0·6, 1·0, 1·4 and 1·8% gellan polymer with 6 mM Ca^{++} in tension and compression.

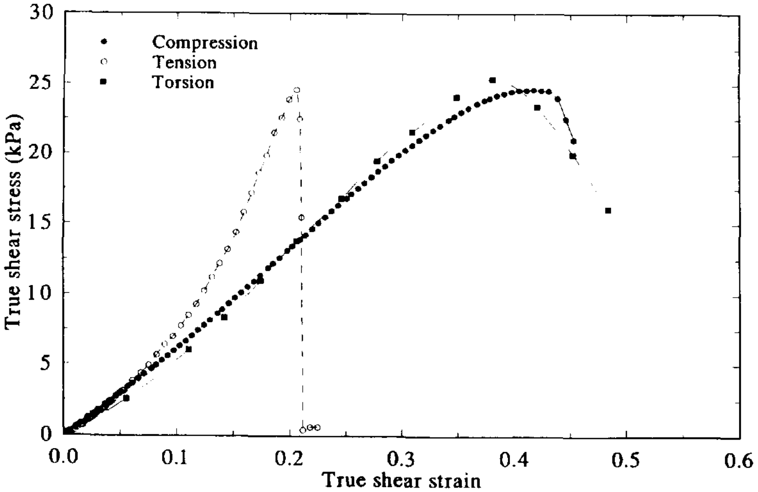

Fig. 3. True shear stress–strain relationships for gels containing 1·0% gellan polymer with 6 mM Ca^{++} in three testing modes.

normal stress from torsion tests was lower than that in tension and compression tests. This is because in the torsion test the strain along the principal axis was the result of not only the normal stress in this axis, but also of the normal stress perpendicular to it via the Poisson's ratio. Therefore, it may be more appropriate to compare the results from torsion tests with those from compression and tension tests using the maximum true shear stress–strain relations (Fig. 3). The relationships in Fig. 3 indicate essentially the same shear moduli at small strains in the three test modes. Similar results were found at other conditions of polymer and calcium concentrations (Table 2). The implication of this finding is that the three test methods yield identical linear shear stress–strain profiles when the strain is small ($\varepsilon < 0{\cdot}04$).

It is of interest to note that in large deformations, the compression and torsion modes yielded very similar maximum true shear stress–strain relationships. Gellan gel specimens failed at comparable values of shear stress (Fig. 3) in all three test modes. This indicates that failure in gellan gels occurred when the maximum shear stress reached a certain value, regardless of testing method. The failure shear stresses in tension tests were about half those in compression and torsion tests.

Constitutive equations

Energy functions in eqns (12), (15) and (18) were evaluated with the experimental data obtained using uniaxial tension and compression as well as torsional loading modes. A preliminary screening was performed based on R.M.S. values [eqn (32)] and visual examination of curve fitting to the data. The five best energy functions, in terms of goodness of fit and simplicity of the function form, were selected for discussion. They are the Mooney energy function [eqn (12)], and three forms of eqn (15) as follows:

$$W = C_1(I_1-3)+C_2(I_2-3)+C_3(I_2-3)^2 \tag{37}$$

$$W = C_1(I_1-3)+C_2(I_2-3)+C_3(I_1-3)^2 \tag{38}$$

$$W = C_1(I_1-3)+C_2(I_2-3)+C_3(I_1-3)(I_2-3) \tag{39}$$

and an additional three-term equation:

$$W = C_1(I_1-3)+C_2(I_2-3)^2+C_3(I_1-3)(I_2-3) \tag{40}$$

The constitutive equations corresponding to eqn (40) are:

$$\sigma = 2\left(\lambda - \frac{1}{\lambda^2}\right)\left\{C_1+2C_2(I_1-3)+C_3\left[\frac{(I_1-3)}{\lambda}+(I_2-3)\right]\right\} \tag{41}$$

$$\tau = 2\{C_1+2C_2(I_1-3)+C_3[(I_1-3)+(I_2-3)]\}\gamma \tag{42}$$

The values of R.M.S. for these five equations are shown in Table 3 for three gellan samples. Overall, R.M.S. for three-term energy functions were smaller than that of the two-term Mooney equation. This seems to be logical, since the additional term gives one more degree of freedom to the equation, and thus, improves the fit. However, in many cases this improvement may well be offset by the added complexity in the constitutive equation. Among possible forms of eqn (15), eqn (37) was found to be better than the other two [eqns (38) and (39)], judging from the R.M.S. values for uniaxial tensile and compressive as well as torsional modes. No single function was found to provide satisfactory fit to the experimental stress–strain relationships in all three testing modes. Some models provided an accurate fit for stress–strain relationships in the uniaxial modes, but did less well in torsion, the opposite was true with the other models. As a typical example, the value of R.M.S. for eqn (40) was small in the uniaxial modes, but large for the torsional mode (Table 3).

The predictive curves based on eqns (12), (37) and (40) are presented in Figs 4 and 5 for 1% gellan gels at 3 mM calcium concentration in uniaxial and torsional

TABLE 3

Comparison of Goodness of Fit Among Developed Energy Functions and the Mooney–Rivlin Equations for Stress–strain Relationships in Uniaxial (Tension and Compression) and Torsion Modes

		Relative Mean Square Error									
		Mooney		*eqn (37)*		*eqn (38)*		*eqn (39)*		*eqn (40)*	
Gellan (%,w/v)	*Ca^{2+} (mM)*	*U*	*T*	*U*	*T*	*U*	*T*	*U*	*T*	*U*	*T*
1·0	3	0·42	0·28	0·34	0·14	0·33	0·30	0·34	0·20	0·08	0·47
	6	0·26	0·14	0·24	0·08	0·23	0·13	0·23	0·11	0·14	0·28
	42	0·43	0·28	0·36	0·07	0·32	0·28	0·58	0·24	0·18	0·48

U: Uniaxial compression and tension modes.
T: Torsion mode.

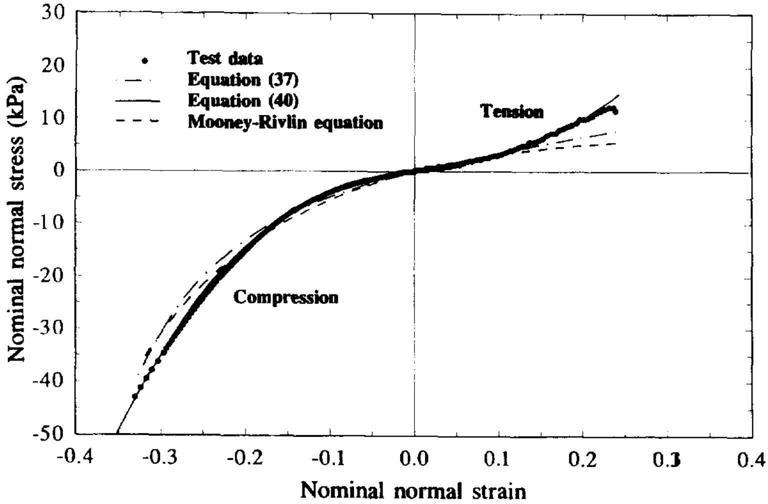

Fig. 4. Experimental and predicted nominal normal stress–strain behavior of 1·0% gellan gels with 3 mM Ca^{++} in uniaxial tensile and compressive modes.

modes, respectively. Similar curves are presented in Figs 6 and 7 for 1% gellan polymer and 6 mM calcium gels. The corresponding material constants for these equations are listed in Table 4. As expected based on its R.M.S. values, eqn (40) provided an almost perfect fit to the experimental data under uniaxial tension and compression modes at both calcium levels; however, its curves deviated dramatically

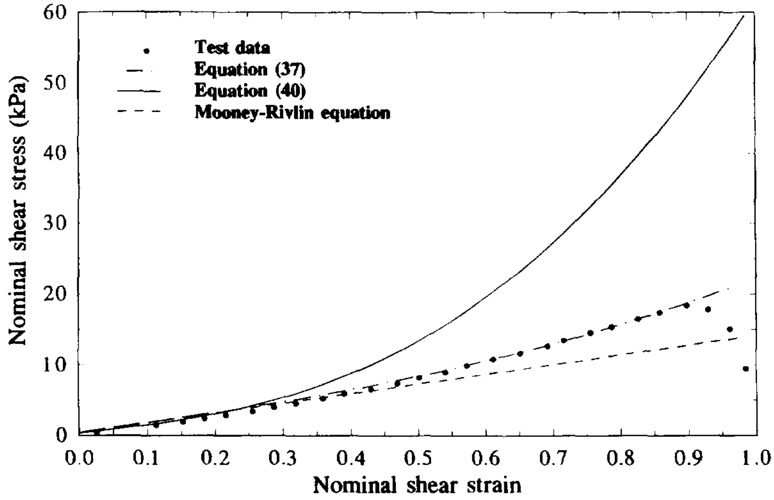

Fig. 5. Experimental and predicted nominal shear stress–strain behavior of 1·0% gellan gels with 3 mM Ca^{++} in torsional mode.

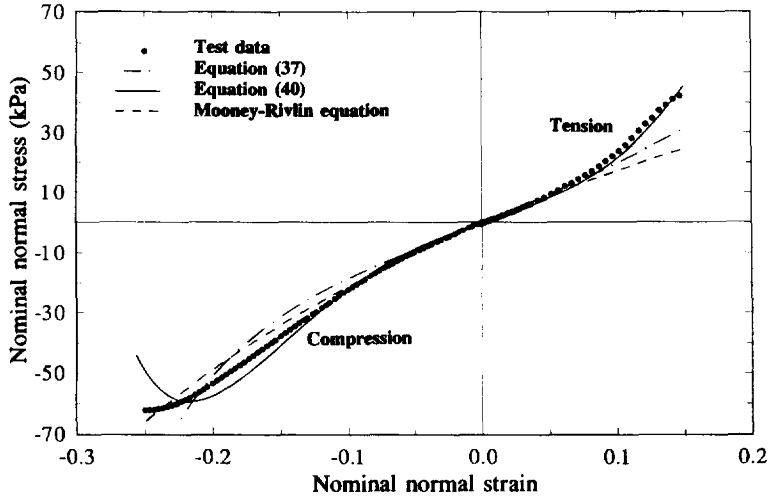

Fig. 6. Experimental and predicted nominal normal stress–strain behavior of 1·0% gellan gels with 6 mM Ca^{++} in uniaxial tensile and compressive modes.

from the data at large deformation in torsional mode. The constitutive equations based on eqn (37) and the Mooney function fitted the experimental results well over a certain strain range in uniaxial testing modes. These curves deviated from the data at large deformations under both tensile and compressive loads. Nevertheless, the constitutive relation from eqn (37) followed the pattern of the experimental stress–

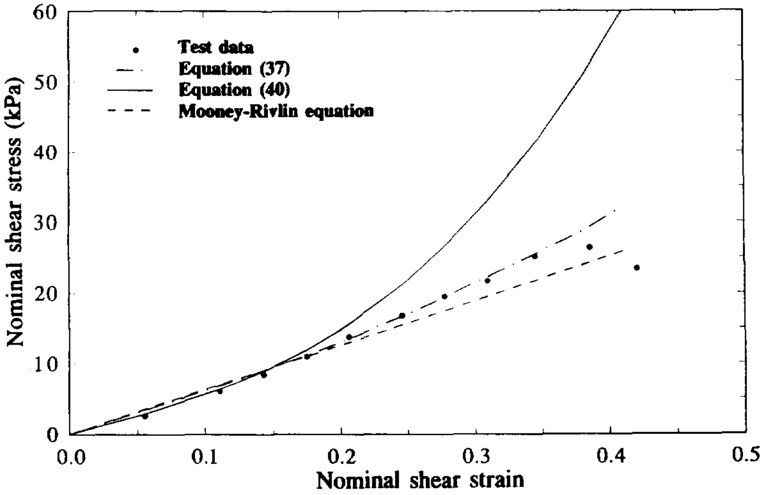

Fig. 7. Experimental and predicted nominal shear stress–strain behavior of 1·0% gellan gels with 6 mM Ca^{++} in torsional mode.

TABLE 4
The Parameters for the Mooney–Rivlin Equation and Eqns (37) and (40) for Stress–strain Relationships in 1·0% Gellan Gels in Tensile and Compressive Testing Modes

Equation	Ca^{2+} *(mM)*	C_1 *(kPa)*	C_2 *(kPa)*	C_3 *(kPa)*
eqn (12)	3	−4·05	10·94	
	6	28·81	2·65	
	42	20·26	−0·54	
eqn (37)	3	3·58	3·11	2·78
	6	75·85	−45·81	36·59
	42	117·77	−98·55	45·56
eqn (40)	3	5·38	42·88	−23·59
	6	24·97	899·18	−708·25
	42	14·80	1555·60	−1252·15

strain relationships in torsion; whereas, the Mooney–Rivlin equation described only the linear portion of the curves (Figs 5 and 7).

The physical interpretation of the constants in eqns (37) and (40) can be demonstrated by considering responses in small deformations. In this case, the second order terms were negligible and eqn (37) was reduced to the Mooney equation, and eqn (40) to the Gaussian equation (McCrum *et al.*, 1988). Therefore, eqn (37) can be considered as an extension of Mooney's energy function. Thus, $2(C_1+C_2)$ represents the shear modulus of the material in small deformation as shown in eqn (14). Equation (40) can be regarded as an extension of Gaussian Network theory with $2C_1$ representing the initial shear modulus. Table 5 provides a comparison of the related constants in eqns (12), (37) and (40) with the initial shear modulus of three modes. Indeed, the values for $2(C_1+C_2)$ in both eqn (12) and eqn (37) were close to that of initial shear modulus determined experimentally in three test modes. The values for $2C_1$ in eqn (40) were smaller than the experimentally determined initial shear moduli.

It may be concluded that the Mooney–Rivlin equation can be used effectively in describing the stress–strain relationships for gellan gels in a certain strain range. Equation (37) is applicable for uniaxial test modes in small strain ranges, and for torsional mode in large deformations. Equation (40) describes successfully the relationships for uniaxial loading modes over a large deformation range. However, no single energy function was found applicable for all test modes over the entire strain

TABLE 5
Comparison of Related Constants in Stored-energy Functions with Initial Shear Modulus for 1·0% Gellan Gels

	eqn (12)	*eqn (37)*	*eqn (40)*	*Initial Shear Modulus, kPa*		
Ca^{2+} *(mM)*	$2(C_1+C_2)$	$2(C_1+C_2)$	$2C_1$	*Tension*	*Compression*	*Torsion*
3	13·78	13·38	10·76	13·62	13·92	14·57
6	62·92	60·08	49·94	61·03	62·82	58·51
42	39·44	38·44	29·60	32·60	34·65	30·34

range. Although the above discussion was made with reference to a limited number of gel samples, the same general observations applied for gellan gels at other gel and calcium concentrations tested in the present study.

CONCLUSIONS

In this study, the stress–strain relationships of gellan gels exhibiting a wide range of mechanical properties were obtained in tensile, compressive and torsional testing modes. Gellan gels followed linear stress–strain relationships in small strain ($\varepsilon < 0{\cdot}04$). The modulus of elasticity in this strain range was the same regardless of the mode of loading. In large deformations, gellan polymer gels were more rigid in tension than in compression and torsion; however, they failed at the same maximum shear stress, regardless of the testing method. The compressive and torsional tests provided similar true shear–strain relationships. If this relationship was the main concern, the two methods could be used interchangeably. The Mooney–Rivlin constitutive equations based on a two-term energy function could be used to describe the stress–strain relationships up to medium strain. Three-term energy functions were more applicable to large deformation in specific testing modes. However, no single three-term energy equation was found which could be used satisfactorily for all loading conditions.

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