

# TEXTURE PROPERTIES OF GELLAN GELS AS AFFECTED BY TEMPERATURE

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## ABSTRACT

*Gellan gels can be made very brittle, similar to agar gels, or very flexible, like gelatin gels. The entropy or enthalpy nature governing those gellan gel behaviors was studied by mechanical testing at temperatures varying from 2 to 62°C. Both failure stress and strain for 1% low acyl and low acyl/high acyl mixed gellan gels decreased with increasing temperature, indicating that the hydrogen bonding contributed significantly to the stabilization of gellan gels in addition to the polyanion-calcium-polyanion bonding. Hydrophobic interactions were less important. The initial Young's modulus for two mixed high and low acyl gellan gels containing 2 mM  $\text{Ca}^{++}$  increased with temperature from 2–42°C, indicating entropy elasticity. Average molecular weight between adjacent crosslinks for these two mixed gels was larger than  $10^4$ . For other gels, the entropy elasticity was not a dominant mechanism for elastic force because of molecular weights between crosslinks and from the observation of negative temperature dependence of the modulus.*

## INTRODUCTION

Gellan gum is produced by the microorganism *Sphingomonas elodea* (formerly *Pseudomonas elodea*) (Kang *et al.* 1982) and was approved by the

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FDA in 1992 for food use (Pszczola 1993). Because of its excellent gelling ability and potential in food applications, gellan gel has attracted extensive research in the past two decades.

Temperature is a very important parameter in food and biological processes. Many physical properties, such as firmness and strength, are temperature sensitive. Maintenance of near constant temperature is required to accurately determine those properties, to specify the grade of the product, and to compare the results from various researchers (Bourne 1982a,b, 1998; Bourne and Comstock 1986). The temperature dependence of the physical properties is also important to understanding the thermodynamic principles governing the characteristics of a gel system. The temperature dependence of the modulus of an elastomer can be used to determine the enthalpy or entropy nature of the elasticity (Mark 1993). The enthalpy elasticity is commonly observed in metals, as characterized by a decrease in modulus with increasing temperature. The entropy elasticity is frequently observed in polymer rubbers, as indicated by an increase of modulus with increasing temperature (Mark 1993). Experimental data revealing temperature dependence of the failure properties of gel systems can be used to understand the gel stabilization force which is composed primarily of covalent bonding, hydrogen bonding, and hydrophobic interaction (Howe *et al.* 1994; Case and Hamann 1994).

Published literature on the effects of temperature on physical properties of gellan gels has been concentrated on small deformation storage modulus and loss modulus as measured by dynamic mechanical tests (Moritaka *et al.* 1991; Morris *et al.* 1996; Miyoshi *et al.* 1994a, 1995a,b, 1996a,b; Nakamura *et al.* 1993, 1996; Nishinari *et al.* 1996; Watase and Nishinari 1993), or on the thermograms measured by DSC (Moritaka *et al.* 1995; Morris *et al.* 1996; Miyoshi *et al.* 1994b, 1995a,b, 1996a,b; Nishinari *et al.* 1996; Watase and Nishinari 1993). This information is useful for studying the sol-gel transition and the hysteresis of such inverse transition, but cannot be used to reveal the thermodynamic characteristics of the gel elasticity.

Large deformation failure properties of gellan gels with various polymer contents and cation concentrations have been studied at room temperature (Tang *et al.* 1994, 1995, 1996; Mao *et al.* 1999a). The effect of temperature on the failure properties of gellan gels have not been reported, except for the work by Papageorgiou *et al.* (1994), in which the rupture strength of gellan/gelatin mixed gels decreased with increasing testing temperature.

The temperature dependence of texture properties of several other food gels have been reported in the literature. Marti de Castro *et al.* (1997) observed that the strength, hardness, cohesiveness and elasticity were all more stable in sardine mince gels frozen at -40C. Perez-Mateos *et al.* (1997) observed that the breaking force, deformation, and cohesiveness were greater for blue whiting muscle protein gels at 3C than at 37-90C. Szczesniak (1975) observed that the

strength of gelatin gel and carrageenan gel decreased with increasing temperature. Bourne (1982a,b, 1998) investigated a number of fruits and vegetables and found the firmness almost always decreased with temperature.

The objectives of this study were to determine the effect of temperature on the failure properties and small deformation modulus of gellan gels in order to understand the stabilization forces for gellan gels and to reveal the thermodynamic nature of the elasticity. Depending on gellan polymer and cation concentrations, some gellan gels may be flexible as gelatin gels and some may be rigid like agar gels (Tang *et al.* 1994, 1995, 1996; Mao *et al.* 1999a). Our hypothesis is that flexible gels may be governed by entropy elasticity while rigid gels by enthalpy elasticity.

## MATERIALS AND METHODS

### Preparation of Gellan Gels

Low acyl gellan (L) (Kelcogel F) and high acyl gellan (H) (Kelcogel LT100) were provided by NutraSweet Kelco Company (San Diego, CA). The main counter ion to the carboxylate group is potassium cation but small amount of sodium, calcium and magnesium cations also exist in gellan powders (Tang *et al.* 1996; Mao *et al.* 1999b). Weighed gellan powders were dispersed in deionized distilled water at 22C. The mixtures were heated to 97-98C and held for 1 min. Calcium chloride was added to the gellan solutions to provide eight  $\text{Ca}^{++}$  concentrations between 2 and 60 mM for 1% low acyl gellan gels and four  $\text{Ca}^{++}$  concentrations between 2 and 60 mM for two mixed gels (0.5% L + 0.5% H, or 0.25% L + 0.75% H). From previous measurements conducted at room temperature (Tang *et al.* 1994, 1995; Mao *et al.* 1999a), these gels exhibited various deformabilities from rigid agar-like gels to flexible gelatin-like gels, with the true failure shear strains ranging from 0.4 to 2.2. The range of these deformabilities covers most common food gels.

The solutions were stirred for 1 min and poured into stainless steel tubes (inner diameter 21 mm), which were preheated to 85C to prevent partial gelling along the metal walls. The gels were set by cooling the tubes in running tap water at 15C for 10 min. The samples were held at 22C for 24 h before being removed from the tubes to be sliced for compression tests.

### Temperature Control

Gel temperature during tests was controlled by water temperature in a custom built cylindrical bath (Fig. 1). This temperature was maintained by circulating water within the jacket of bath, and the temperature of the circulating water was in turn controlled by a Model 1157 Programmable Refrigerated

Circulator (VWR Scientific Products, Niles, IL) with a temperature constancy of better than  $\pm 0.1^\circ\text{C}$ . The temperature fluctuation of the water surrounding the gel sample was within  $\pm 0.3^\circ\text{C}$  between  $2\text{--}42^\circ\text{C}$  and within  $\pm 0.5^\circ\text{C}$  at  $62^\circ\text{C}$ .

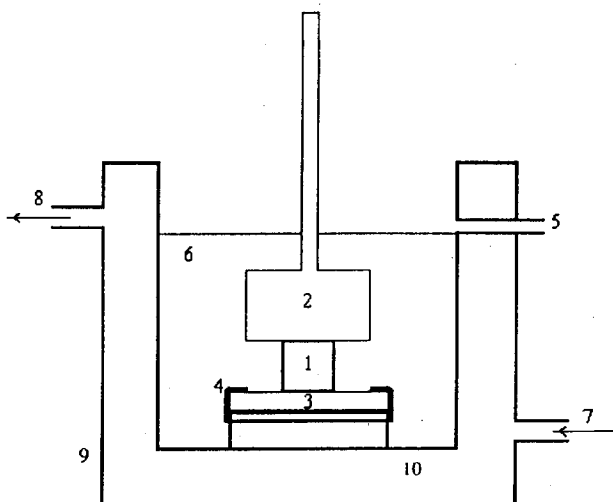


FIG. 1. SCHEMATIC DIAGRAM OF THE SAMPLE HOLDING BATH

1. Gel sample; 2. Teflon pellet; 3. Teflon platform; 4. Metal ring; 5. Water overflow outlet; 6. Sample holding solution; 7. Circulating water inlet; 8. Circulating water outlet; 9. Metal wall; 10. Jacket of the water bath

## Compression Tests

Cylindrical specimens of 21 mm diameter and 21 mm long were placed into the sample holding bath preset at 2, 22, 42, or  $62^\circ\text{C}$  for 10 min for all the specimens to reach the set temperature. The specimens with lubricated surfaces were then compressed between a Teflon pellet and a Teflon platform (Fig. 1). The Teflon pellet was connected to The TA.XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK). The Teflon platform was fitted inside the water bath by a metal ring, so that the gel sample would not slide off the platform. When calibrating the measurement of displacement of the probe, the metal ring was removed so that the two Teflon surfaces could come in contact with each other. The probe displacement calibration was conducted without water. The force calibration was conducted with a full bath of water and at the 21 mm distance between the two Teflon surfaces. The gels were deformed at a crosshead speed of  $0.3\text{ mm/s}$  until failure. All tests were repeated six times. The engineering strain ( $\epsilon_{\text{eng}} =$

reduction of length/original length) and stress ( $\sigma_{\text{eng}}$  = force/original cross-section area) at the failure point was obtained and converted to Hencky's strain ( $\epsilon_h$ ) and true stress ( $\sigma_t$ ) which take into account the enlarged cross-sectional area of the specimens by following equations (Tang *et al.* 1996):

$$\epsilon_h = -\ln (1 - \epsilon_{\text{eng}}) \quad (1)$$

$$\sigma_t = \sigma_{\text{eng}}(1 - \epsilon_{\text{eng}}) \quad (2)$$

The failure shear stress and strain are often used because they represent the true failure properties of gellan gels (Tang *et al.* 1994). The true failure shear strain ( $\gamma$ ) and true failure shear stress ( $\sigma$ ) were obtained from  $\epsilon_h$  and  $\sigma_t$  by following relations (Hamann 1983):

$$\gamma = (1 + \nu)\epsilon_h \quad (3)$$

$$\sigma = \frac{\sigma_t}{2} \quad (4)$$

Gellan gels contain about 99% water and can be reasonably assumed to be incompressible under these test conditions, which means that the Poisson's ratio ( $\nu$ ) in Eq. 3 is 0.5 (Juvinall 1967).

The initial Young's modulus (E) under small deformation was derived from the slope of the regression line of true normal stress ( $\sigma_t$ ) vs Hencky's normal strain ( $\epsilon_h$ ) for strain not exceeding 6%.

#### Texture-Temperature Coefficient (TTC)

The texture-temperature coefficient (TTC), defined as the percentage change of a texture property (stress, strain, etc.) per degree C (Bourne 1982a,b, 1998; Bourne and Comstock 1986), was calculated by following equation:

$$\text{TTC} = \frac{\text{texture at } T_2 - \text{texture at } T_1}{\text{texture at } T_1 \times (T_2 - T_1)} \times 100 \quad (5)$$

where  $T_1$  is the lowest testing temperature and  $T_2$  the highest testing temperature.

### Statistical Analysis

The ANOVA procedure of Microsoft Excel (Microsoft Corp. 1995) was used to determine differences between texture properties measured at different temperatures. A significance level of  $P < 0.05$  was chosen.

## RESULTS

### Failure Stress

The true failure shear stresses of 1% low acyl gellan gels or L and H mixed gellan gels measured at 2-62°C are shown in Fig. 2-4. For all gels, the failure stress decreased with increasing temperature. The texture-temperature coefficient (TTC) for failure stress of gellan gels varied between -0.59 to -1.35%/°C (Table 1), which is similar to that of fruits and vegetables (mostly between -0.4 and -1.0%/°C) and carrageenan gels (-1.4%/°C) but smaller than that of gelatin gels (-6%/°C) (Bourne 1982a, 1998; Bourne and Comstock 1986; Szczesniak 1975). At all tested temperatures, the failure stress of gellan gels increased with increasing calcium concentrations up to an optimum calcium concentration, then decreased with further increasing calcium concentrations. Similar patterns were observed at other gellan concentrations at room temperature. The optimum calcium concentration for failure stress at room temperature was about 6 mM for 1% low acyl gellan gels and about 30 mM for the mixed gellan gels (Tang *et al.* 1994, 1995, 1996; Mao *et al.* 1999a).

### Failure Strain

Similar to the changes in failure stress, the failure strains of 1% low acyl gellan gels and L & H mixed gels decreased significantly with increasing testing temperature at each calcium level (Fig. 5-7). The TTC for failure strains varied between -0.36 to -0.79%/°C (Table 1). At each testing temperature, the failure strain of the 1% low acyl gellan gels decreased with increasing calcium concentrations when calcium concentration did not exceed 8 mM, then the failure strain remained unchanged with further increasing calcium concentrations (Fig. 5). For the two low and high acyl mixed gellan gels, the failure strain at each testing temperature increased when calcium concentration increased from 2 to 8 mM, then remained unchanged with further increasing calcium concentrations (Fig. 6 and 7), similar to the corresponding mixed gellan gels measured at room temperature (Mao *et al.* 1999a).

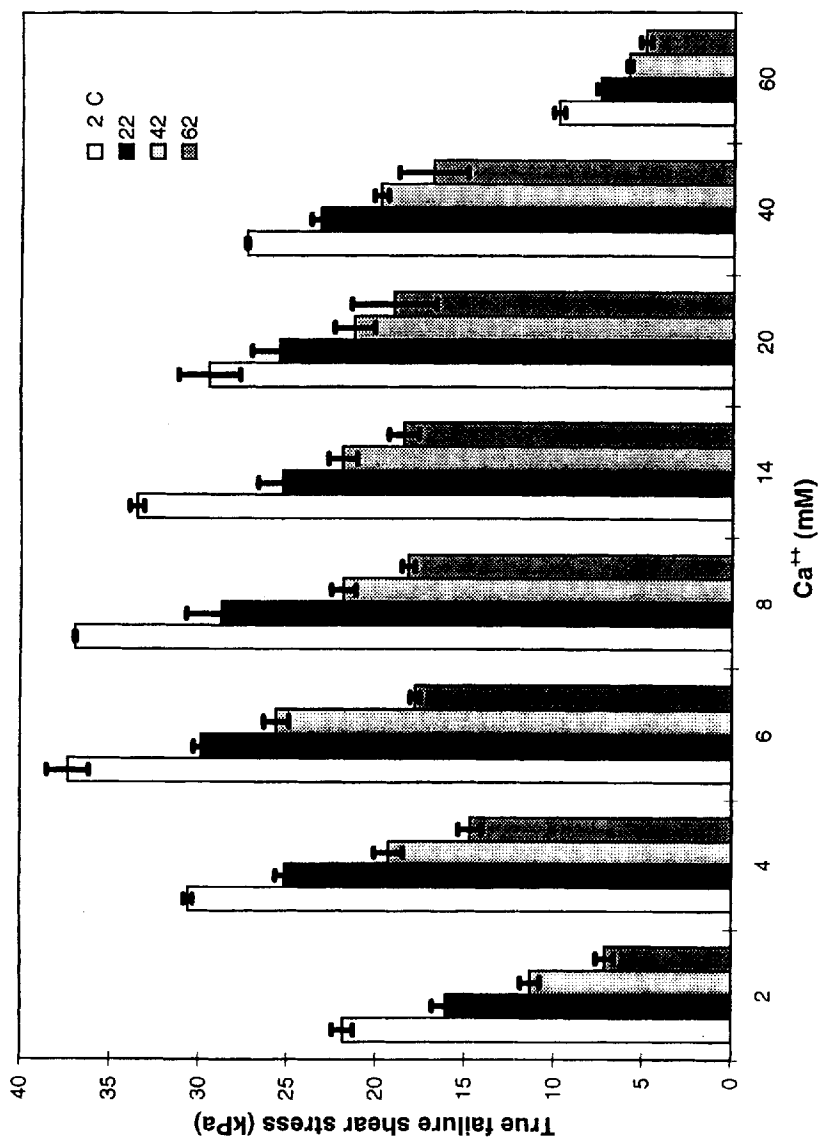


FIG. 2. TRUE FAILURE SHEAR STRESS OF 1% LOW ACYL GELLAN GELS AT 2, 22, 42, AND 62°C

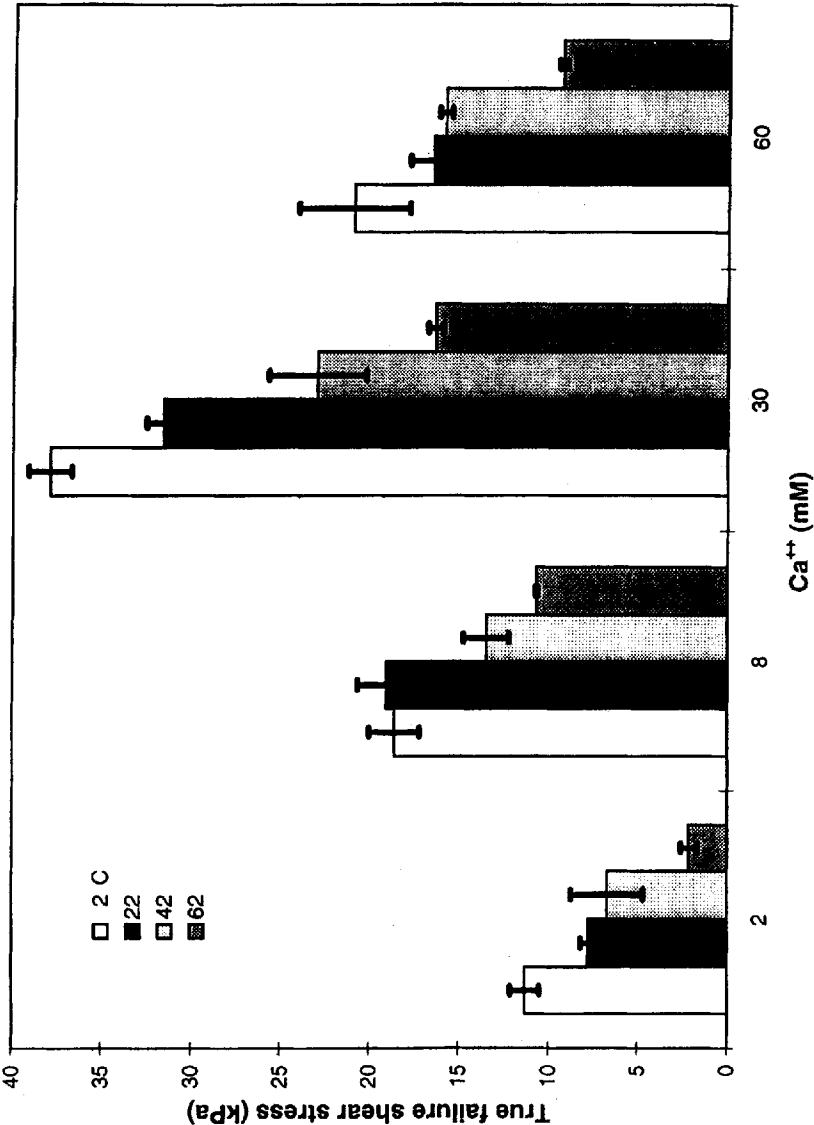


FIG. 3. TRUE FAILURE SHEAR STRESS OF 0.5% L + 0.5% H MIXED GELLAN GELS AT 2, 22, 42, AND 62C



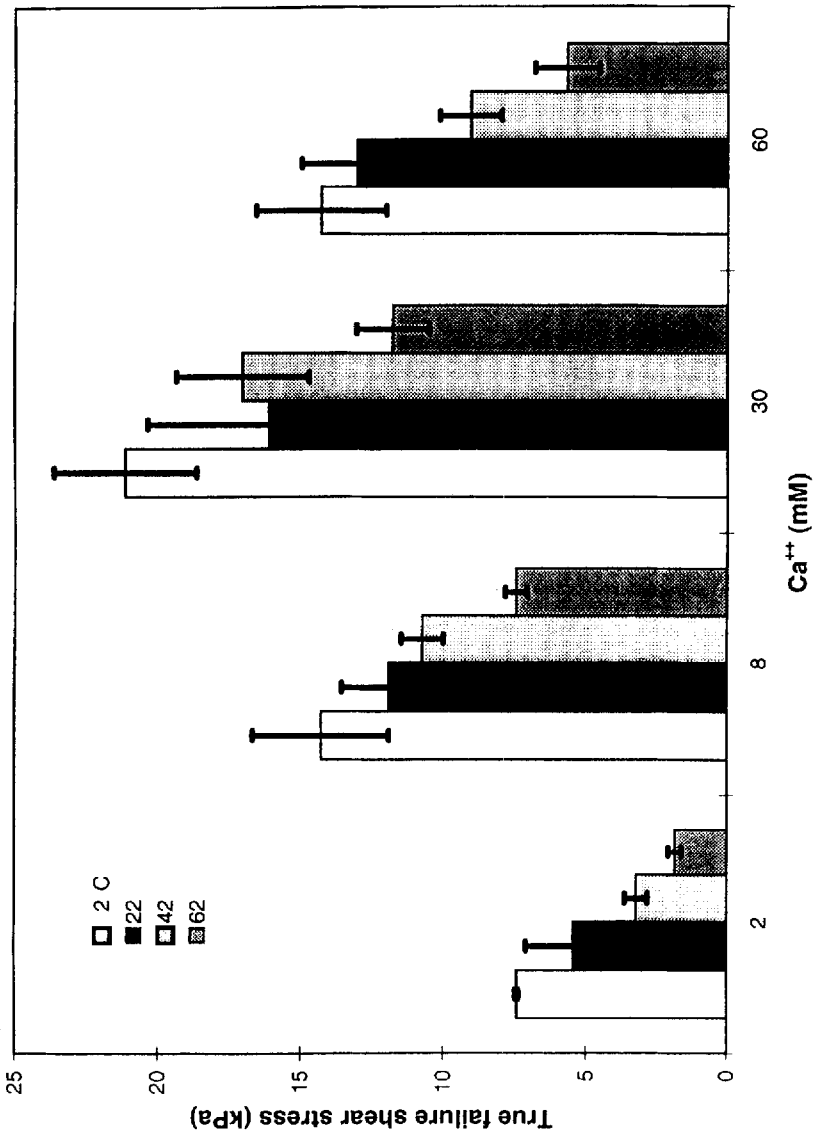


FIG. 4. TRUE FAILURE SHEAR STRESS OF 0.25% L + 0.75% H MIXED GELLAN GELS AT 2, 22, 42, AND 62°C

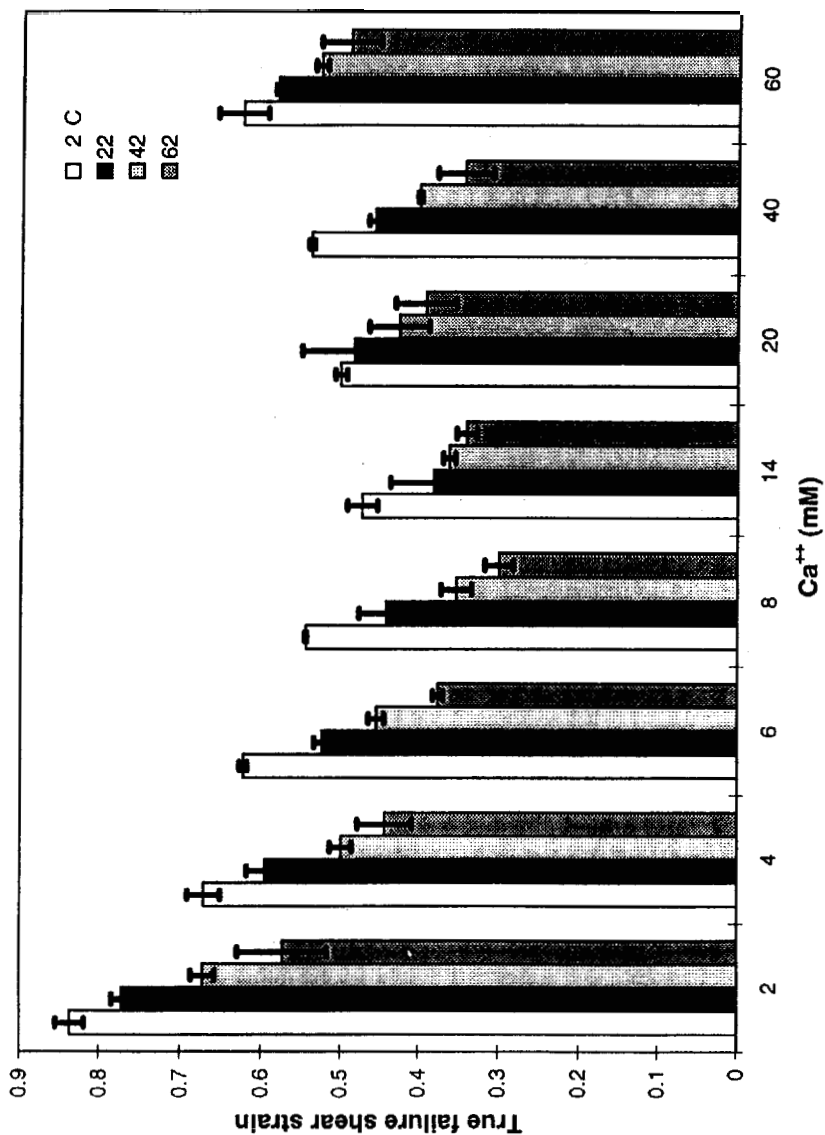


FIG. 5. TRUE FAILURE SHEAR STRAIN OF 1% LOW ACYL GELLAN GELS AT 2, 22, 42, AND 62°C

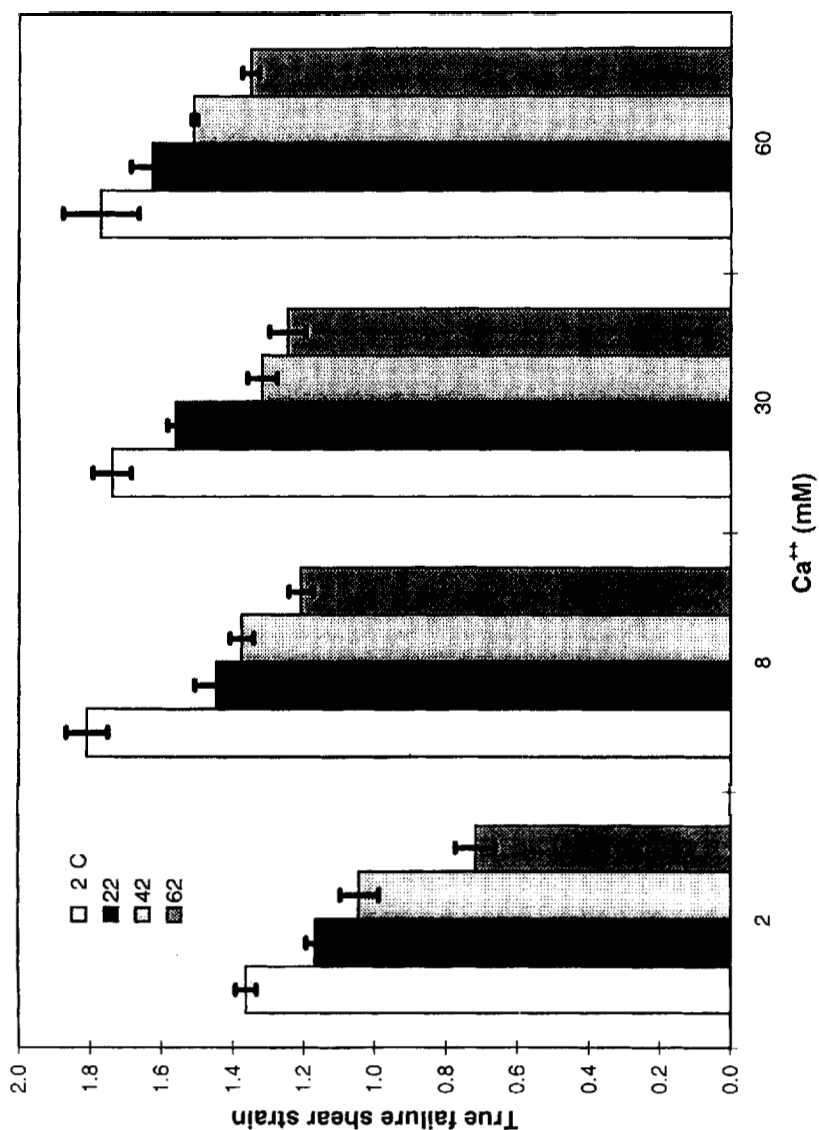


FIG. 6. TRUE FAILURE SHEAR STRAIN OF 0.5% L + 0.5% H MIXED GELLAN GELS AT 2, 22, 42, AND 62°C

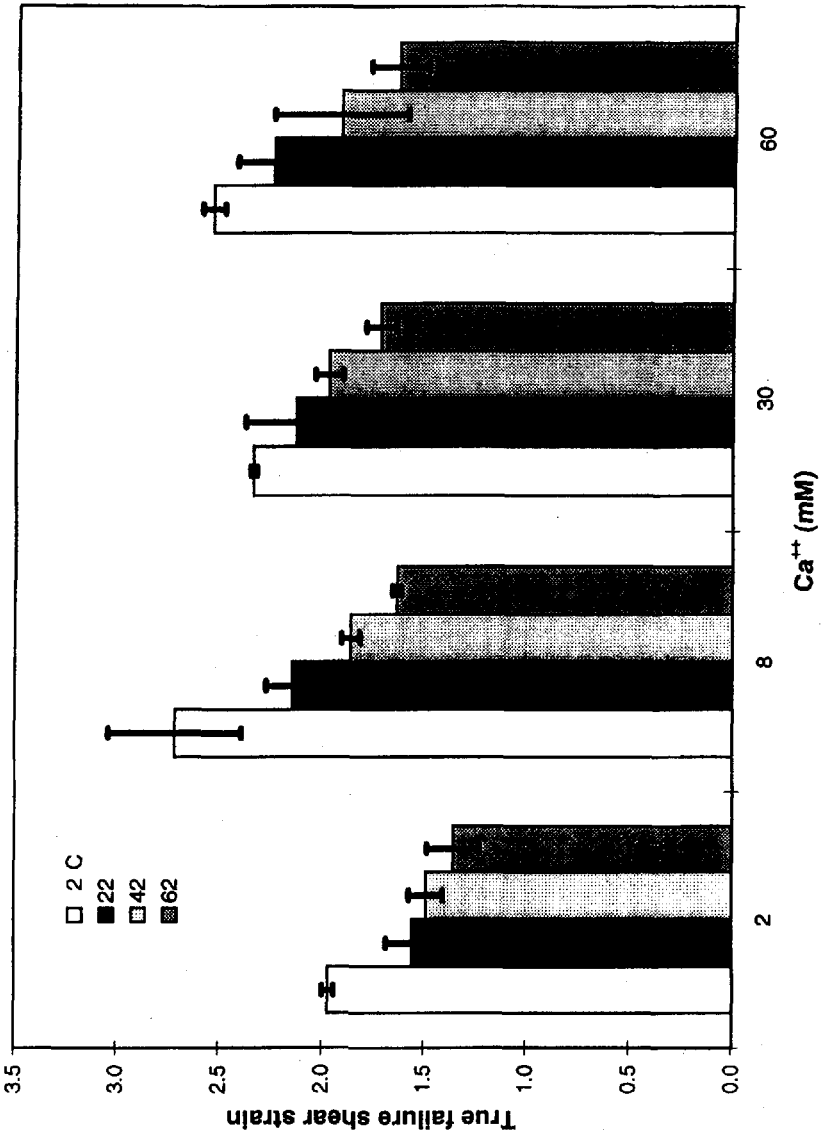


FIG. 7. TRUE FAILURE SHEAR STRAINS OF 0.25% L + 0.75% H MIXED GELLAN GELS AT 2, 22, 42, AND 62°C

TABLE 1.  
TEXTURE-TEMPERATURE COEFFICIENTS FOR TRUE FAILURE SHEAR STRESS  
AND STRAIN OF GELLAN GELS AT 2-62C

Gellan		Ca <sup>++</sup>	TTC for	TTC for
Low acyl	High acyl		failure stress	failure strain
(%)	(%)	(mM)	(%/°C)	(%/°C)
1	0	2	-1.12	-0.53
1	0	4	-0.86	-0.56
1	0	6	-0.87	-0.66
1	0	8	-0.84	-0.75
1	0	14	-0.75	-0.47
1	0	20	-0.59	-0.36
1	0	40	-0.64	-0.60
1	0	60	-0.83	-0.36
0.5	0.5	2	-1.35	-0.79
0.5	0.5	8	-0.71	-0.55
0.5	0.5	30	-0.95	-0.47
0.5	0.5	60	-0.93	-0.40
0.25	0.75	2	-1.25	-0.52
0.25	0.75	8	-0.80	-0.66
0.25	0.75	30	-0.74	-0.44
0.25	0.75	60	-1.01	-0.59

### Young's Modulus at Small Deformations

The initial Young's modulus of the low acyl gellan gels, and the low and high acyl mixed gellan gels measured at 2-62C, are shown in Fig. 8-10. At each

temperature, the initial Young's modulus followed a similar pattern of the failure stress to the corresponding gels. The maximum initial Young's modulus was observed at 14 mM  $\text{Ca}^{++}$  for 1 % low acyl gellan gels and at 8 mM  $\text{Ca}^{++}$  for the mixed gellan gels.

The temperature dependence of the initial Young's modulus was complicated and seemed not to follow a general trend. For 1% low acyl gellan gels, the initial Young's modulus did not change significantly with testing temperature when the calcium concentration was very low (2-4 mM) or very high (40-60 mM). At medium calcium concentration (6-20 mM), the initial Young's modulus decreased significantly with increasing testing temperature. For the low and high acyl mixed gellan gels, there did not seem to be an obvious temperature dependence for the initial Young's modulus, with the exception of gels with 2 mM  $\text{Ca}^{++}$ , in which the initial Young's modulus increased with testing temperature from 2 to 42C.

## DISCUSSION

### Gel Stabilization Forces

The negative temperature dependence of the failure strain observed in this study (Fig. 5-7) for gellan gels is similar to the behavior of polyacrylamide gels (Foegeding *et al.* 1994) and konjac mannan gels (Case and Hamann 1994). However, the negative temperature dependence of the failure stress (Fig. 2-4) is different from those two gels, which were temperature independent (Foegeding *et al.* 1994; Case and Hamann 1994). Polyacrylamide gels are believed to be stabilized primarily by relatively permanent covalent bonding. The mechanical behavior of polyacrylamide gels is generally regarded as governed by entropic elasticity (Oppermann *et al.* 1985). Konjac mannan gels do not contain covalent crosslinking, and the gel characteristics are not entropic. It was believed that the combined effects of hydrogen bonding, which was weakened with increasing temperature, and hydrophobic interaction, which was strengthened with increasing temperature up to about 60C, caused the invariance of the failure stress to testing temperature (Case and Hamann 1994). The different temperature dependence of the failure stress for gellan gels tested in this study suggested a different mechanism of gel stabilization from polyacrylamide gels and konjac mannan gels.

As a hydrogel, gellan gels may be stabilized by covalent bondings, hydrogen bondings, and hydrophobic interactions. In particular, calcium crosslinked gellan gels are believed to have direct polyanion-calcium-polyanion bonding between the carboxylate groups of adjacent double helices (Chandrasekaran *et al.* 1988a,b, 1992; Chandrasekaran and Thailambal 1990).

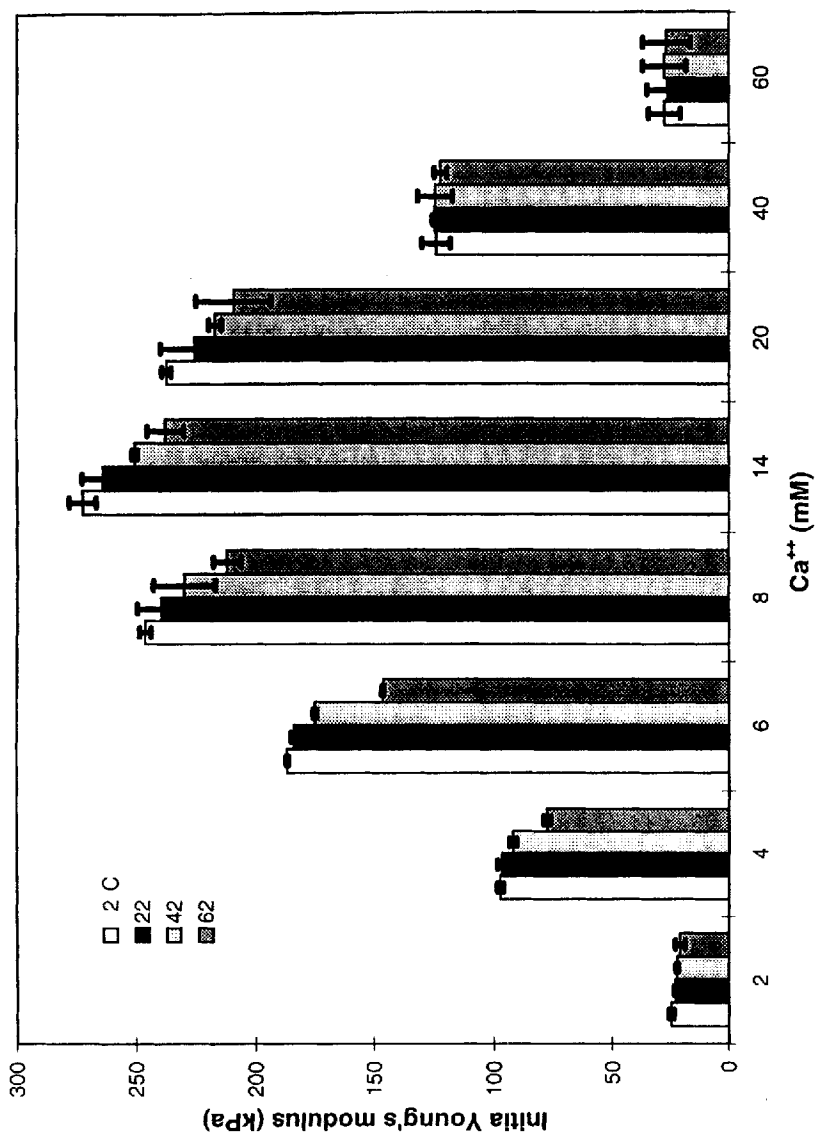


FIG. 8. INITIAL YOUNG'S MODULUS OF 1% LOW ACYL GELLAN GELS AT 2, 22, 42, AND 62°C

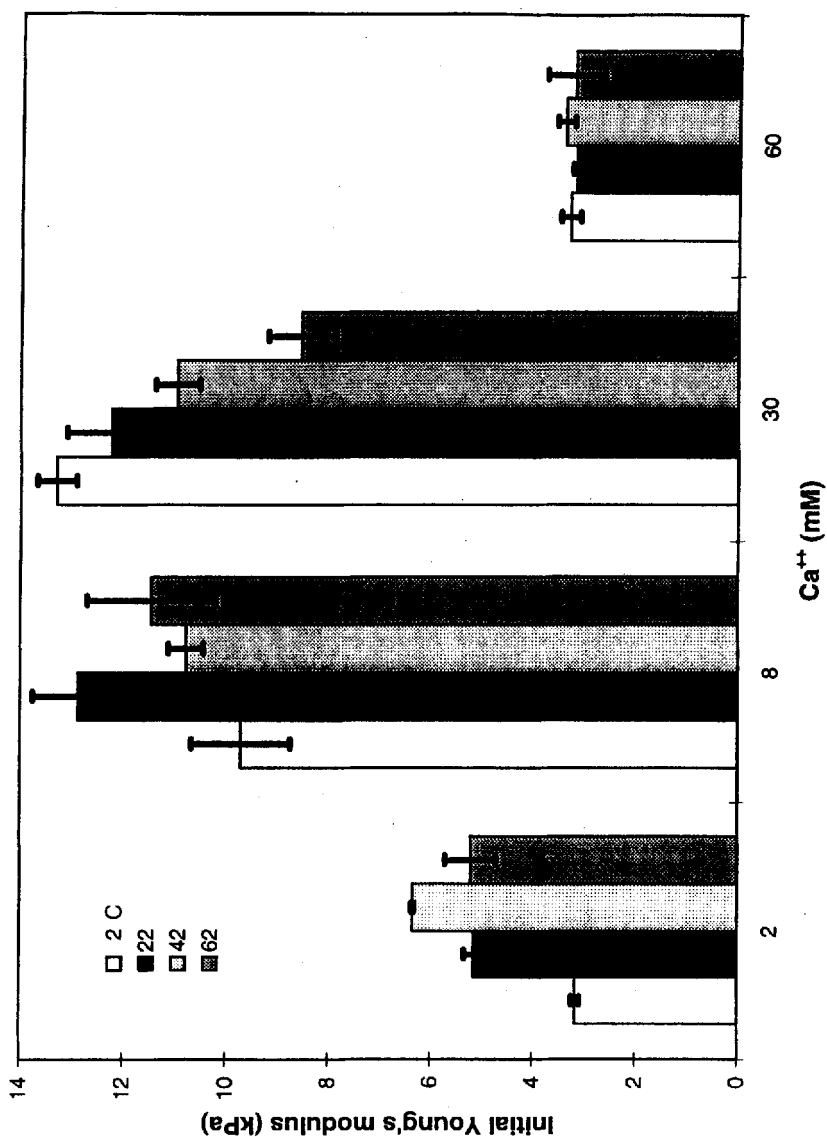


FIG. 9. INITIAL YOUNG'S MODULUS OF 0.5% L + 0.5% H MIXED GELLAN GELS AT 2, 22, 42, AND 62°C



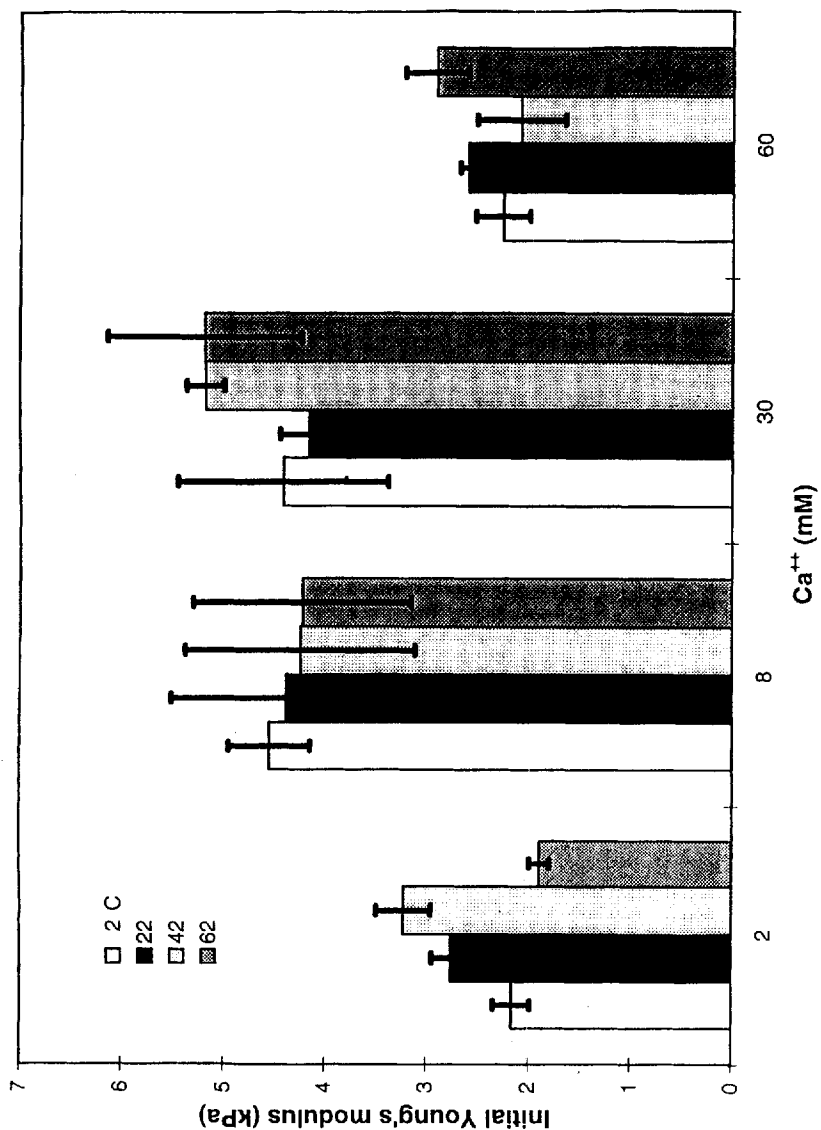


FIG. 10. INITIAL YOUNG'S MODULUS OF 0.25% L + 0.75% H MIXED GELLAN GELS AT 2, 22, 42, AND 62°C

The interchain hydrogen bonding also contributes to the stabilization of the double helix and the double helix packing because the abundant OH groups on gellan polymer chains (Chandrasekaran *et al.* 1988a,b). Thus, for low acyl gellan gels, the major stabilization forces are polyanion-calcium-polyanion bonding and hydrogen bonding. The polyanion-calcium-polyanion bondings are coordinate covalent bondings (Chandrasekaran and Thailambal 1990) and relatively stable with temperature. The strength of hydrogen bonding, however, decreases with temperature. At 2 mM  $\text{Ca}^{++}$ , the contribution of polyanion-calcium-polyanion bonding is the least, such that the TTC for stress has the greatest negative value (Table 1).

Because of the existence of the bulky acetyl and glyceryl groups in high acyl gellan chains, the double helices are more loosely packed in the high acyl gellan gels than in the low acyl gellan gels, and the interchain hydrogen bonding in high acyl gellan gels is weakened. The peripheral acetyl groups may produce hydrophobic interaction between different polymer chains (Chandrasekaran *et al.* 1992). Thus, low and high acyl mixed gellan gels should be stabilized primarily by polyanion-calcium-polyanion bonding, hydrogen bonding, and hydrophobic interactions. For the same reason as the low acyl gellan gels, the TTCs for stress at 2 mM  $\text{Ca}^{++}$  are the most negative (Table 1). In contrast to the hydrogen bonding, the strength of hydrophobic interaction increases with increasing temperature up to about 60°C (Howe *et al.* 1994; Case and Hamann 1994). The negative temperature dependence of the failure stress (Fig. 3 and 4) for the mixed gels suggested that the contribution of hydrophobic interaction was less important than the hydrogen bonding, even when the majority polymer was high acyl gellan.

### Thermodynamic Nature of Gel Elasticity

Polymer rubber theory (Flory 1953) is commonly used to study the elastic properties of the gels. For an ideal elastic rubber, the elasticity is produced purely through entropy change, and the modulus is proportional to the absolute temperature (Flory 1953; Mark 1993), such as in polyacrylamide gels (Foegeding *et al.* 1994). Flory stated that the necessary conditions for rubber elasticity (also called entropy elasticity) were: (1) the polymer must consist of long chain molecules with 100 or more single bonds between points of cross-linkage; (2) the system must possess sufficient internal mobility to allow the required rearrangements of chain configurations during deformation and during recovery; (3) a structure must be formed by sparsely spaced cross-linkages joining the chains into a space network of "infinite" extent. Similar requirements were expressed by Muller (1973) and Mark (1993).

The 100 or more single bond requirement, as stated by Flory, is applicable only to the free rotating bonds. In the polymer chain of polysaccharide, a sugar

unit provides two free rotational single bonds if not 1,6-linked, or three free rotational single bonds if 1,6-linked (Morris 1979). Thus for gellan gels, about 50 sugar units between two adjacent crosslinks were required to exhibit the entropy elasticity. Fifty sugar units are equivalent to an average molecular weight between crosslinks ( $M_c$ ) of 8,100, 8,780, and 9,120 for low acyl gellan gel, 0.5%L+0.5%H, and 0.25%L+0.75%H mixed gellan gels, respectively. From the rubber theory,  $M_c$  can be calculated by the following equation (Van Kleef *et al.* 1978):

$$G = \frac{c}{M_c} \left(1 - \frac{2M_c}{M_r}\right) (1 - w_s)RT \quad (6)$$

where  $G$  is the shear modulus,  $c$  is polymer concentration,  $M_r$  is the mean molecular weight of polymer before crosslinking ( $5 \times 10^5$  for gellan molecules),  $w_s$  is the sol fraction,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature. For polysaccharide gels,  $w_s$  was usually assumed as 0, and the term  $(1 - w_s)$  did not appear in the similar equations used by others (Ziegler and Rizvi 1989; Hsieh and Regenstein 1992; Case and Hamann 1994).

In order to study the entropy elastic nature of gellan gels, the experimentally obtained initial moduli of gellan gels at various temperatures were evaluated against Eq. 6. That is, we first assumed that Eq. 6 applied, and then used the calculated  $M_c$  to compare with the basic criteria for rubber theory; we also evaluated the trend of moduli vs temperature to see that if our assumption was correct. The  $M_c$  values for gellan gels tested in this study are listed in Tables 2 and 3. Table 2 indicates that all low acyl gellan gels did not satisfy the 50 sugar units requirement so no entropy elasticity behavior was exhibited in the test results. It is most likely that for low acyl gellan gels at medium to high concentration of calcium ( $\text{Ca}^{++} \geq 4\text{mM}$ ), both high polyanion-calcium-polyanion crosslinking density and a large amount of hydrogen bonding prevented the gels from exhibiting entropy elasticity. At the lowest calcium concentration (2 mM), on the other hand, the polyanion-calcium-polyanion crosslinking density may be small enough to satisfy the requirement of entropy elasticity, but the very large amount of interchain hydrogen bonding produced by the abundant OH groups still makes the effective crosslinking density too high for the gels to exhibit entropy elasticity. In contrast, most mixed gellan gels satisfied the 50 sugar units requirement and it is possible for these gels to exhibit entropy elasticity (Table 3).

Equation 6 also indicates that if a gel elasticity is purely an entropy characteristic, the shear modulus  $G$  will increase proportionally with absolute temperature (Mark 1993). For incompressible gels, the Young's modulus  $E$  is

three times the shear modulus  $G$  (Bourne 1982b). Therefore the initial Young's modulus  $E$  should also increase proportionally with the absolute temperature. In reality, both entropy and enthalpy elasticity may be present. In such a case, the positive or negative temperature dependence of the modulus can be used to determine which is the dominant factor. In sharp contrast to the entropy elasticity, the enthalpy elasticity decreases with temperature (Mark 1993). Figure 8 shows no positive temperature dependence of Young's modulus for all low acyl gellan gels. Thus, it can be concluded that for low acyl gellan gels, the entropy elasticity was not dominant. The small values  $M_c$  calculated by Eq. 6 (Table 2) also supported the conclusion that the entropy elasticity is either absent or a minor factor for low acyl gellan gels.

TABLE 2.  
THE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF 1% LOW ACYL  
GELLAN GELS AT VARIOUS TESTING TEMPERATURES

T(°C)	2	22	42	62
Ca <sup>++</sup> (mM)				
2	2,350±100	2,73±90	3,010±80	3,380±350
4	597±8	646±13	724±12	912±17
6	312±1	340±2	381±2	485±1
8	236±2	261±11	290±16	335±9
14	214±4	237±8	266±1	299±10
20	246±2	277±17	308±4	339±25
40	470±22	501±4	536±32	581±13
60	2,120±530	2,360±770	2,410±820	2,650±1020

TABLE 3.  
THE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF LOW AND HIGH ACYL  
MIXED GELLAN GELS AT VARIOUS TESTING TEMPERATURES

	T(°C)	2	22	42	62
	Ca <sup>++</sup> (mM)				
0.5% L	2	17,200±400	11,600±400	10,100±40	12,900±1,200
+0.5% H	8	5,860±580	4,770±330	6,040±190	6,050±660
	30	4,310±120	5,010±350	5,960±230	8,060±620
	60	16,600±1,000	18,200±400	18,300±900	20,300±3,500
0.25%L	2	24,300±2,000	20,800±1,400	19,100±1,600	32,600±1,700
+0.75%H	8	12,200±1,100	13,500±3,500	14,800±4,000	15,800±4,000
	30	12,500±2,900	12,200±1,000	12,300±400	13,000±2,400
	60	23,400±2,700	22,000±700	28,400±5,900	22,200±2,300

Due to the stereo hindrance of the bulky acyl groups, the interchain hydrogen bonding in the low and high acyl mixed gellan gels is weakened and the effective crosslinking density become smaller. Therefore, the molecular weight between crosslinks is, in most cases, large enough to satisfy the requirement for entropy elasticity (Table 3). However, the temperature dependence of the initial Young's modulus suggests that the entropy elasticity may be dominant only for gels with 2 mM Ca<sup>++</sup> for both mixed gels (Fig. 9 and 10). At 2 mM Ca<sup>++</sup> level, the initial Young's modulus increased significantly with testing temperature from 2 to 42C. At 62C, however, the gels are approaching their melting temperatures and some polyanion-calcium-polyanion bonding may be dissociated so that the modulus is decreased. Therefore, the elasticity of the mixed gellan gels with 2 mM Ca<sup>++</sup> is entropy dominant at 2-42C. For all other mixed gels entropy elasticity became less important and the modulus was not positively dependent on temperature (Fig. 9 and 10).

## CONCLUSION

The negative temperature dependence of the failure properties for all gels indicated that in addition to polyanion-calcium-polyanion bonding, hydrogen bonding is a major force for stabilizing gellan gels. The hydrophobic interaction was not an important factor, even for the mixed gels containing mostly high acyl gellan. The elasticity of mixed gellan gels crosslinked with 2mM  $\text{Ca}^{++}$  and containing 0.25% L + 0.75% H or 0.5% L + 0.5% H was entropy dominant, indicated by the positive temperature dependence of the initial Young's modulus between 2 and 42C and the large molecular weight between crosslinks. For all other gels, the entropy elasticity was not a dominant factor, based on the observations of the small molecular weight between crosslinks, the negative temperature dependence of the modulus, or both.

## ACKNOWLEDGMENTS

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