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Emako MIYOSHI

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Emako MIYOSHI

1. Introduction

Throughout the world there is a growing belief that natural foods are an integral part of a healthy life style. With increasing use of processed and simulated foods, health-conscious consumer needs reduced fat and enhanced fiber foods of all types, so that the food producers have sourced an increasing proportion the raw materials from nature itself. This objective can be achieved using natural type materials that have low calorific values, although foods containing such materials need to match the quality of the original product and without adverse dietary effects. It has been remarkably noted that most of polysaccharides used in the food industry, which are low calorie (except for starch), can interact with water to form new textures and perform specific functions (gelling and thickening agents, emulsion stabilizers, water absorption, fat replacer etc), moreover have further health benefits. Therefore, many nutritional scientists are now greatly interested in the physiological effects of such polysaccharides as health-functional materials.

Recently, with increasing of the global environmental problems, greater efforts have been made to develop the effective usage of traditional polysaccharides, because these polysacchrides are environmentally degradable and bioabsorbable. The biocompatibility of hydrocolloids can be used not only in the drug delivery system but also to supply wound dressings and replacements for human tissue. Therefore the medical applications have been rapidly advanced as a result of the basic research.

Especially, the new microbial polysaccharides are of growing commercial importance and are produced on a large scale by industrial fermentation. The microbial polysaccharides can be produced on demand and with consistent quality, so that availability and variability are not concerns (Sanderson, 1990). Gellan gum, is one of widely used fermentation materials, may offer a solution to many of problems encountered in the current gelling agents, because it can form a transparent gel in the presence of multivalent cations, which is resistant to heat and acid (Sanderson, 1990; Sworn, 2000). Since gellan gum can provide a wide-range of gel textures by careful control of added salts, these gels can give the same texture as other polysaccharide gels or create new textures. Therefore, gellan gum is one of the most intensively studies polysacchrides and expected for an appropriate model in order to study thermoreversible sol-gel transition.

It is important to compare the experimental results obtained on the same sample especially in the case of biopolymers such as gellan, because even a subtle difference in molecular structure and molecular weight can lead to significant differences in functional properties. It is well known in the history of the development of rheology that the distribution of NBS (National Bureau of Standards, USA) polyisobutyrene has played an important role. Using the same sample, various groups participating in the collaboration could compare their results, and thus made a great contribution to the establishment of a time-temperature superposition principle or a reduced variable method.

Based on the same idea, the research group on gellan gum was organized in the Research Group on Polymer Gels affiliated to the Society of Polymer Science, Japan, in 1989. The aim of this collaboration is to elucidate the conformation of gellan gum in solution and the gelation mechanism, and develop further industrial applications. Using the same sample, various laboratories participating in this collaboration have studied on gellan gum and compared these results. We frequently held some informal meetings in order to facilitate an active communication about the most recent findings on the common gellan gum sample. Our outcome has already been presented three times as a special issue of the international journal and this collaborative work has been advancing.

Therefore, the aim of this paper is to present the most recent findings on the functional properties of gellan gum comparing with some advanced references, and to show some useful results for various applications. Especially, our results investigating the rheological and thermal properties of gellan gum aqueous solutions（Miyoshi et al., 1994ab, 1995ab, 1996ab,; Miyoshi & Nishinari, 1999abc, 2000ab; Miyoshi, 1996, 2003, 2006, 2007）were obtained using rheology and differential scanning calorimetry (DSC), involving some theoretical approach, and were compared with other results by our coworkers with different methods.

2. Materials and Methods

2.1. Material

Purified sodium form gellan gum sample (the third common sample) kindly supplied by San-Ei Gen F.F.I. Inc., Osaka, Japan was used in the present work. The contents of the inorganic ions Na^+, K^+, Ca^{2+} and Mg^{2+} were determined as Na 2.59%, K 0.009%, Ca 0.02% and Mg 0.001%, respectively.

LiCl, NaCl, KCl, CsCl and $CaCl_2$ used in the present study were of the extra fine grade reagents (Wako Pure Chemical Industries Ltd., Osaka, Japan), and were used without further purification.

Glucose, fructose and sucrose used in the present study were of the extra fine grade reagents (Wako Pure Chemical Industries Ltd., Osaka, Japan), and were used without further purification. Trehalose, a newly developed disaccharide, was kindly supplied by

Hayashibara Biochemical Laboratories, Inc. (Okayama) and was used without further purification.

The gellan gum solutions were prepared in the same way as described previously (Miyoshi, 1996).

2.2. Rheological measurements

Mechanical spectra and thermal scanning rheological measurements were performed within a linear viscoelastic regime with a Dynamic Stress Rheometer DSR from Rheometrics Co.Ltd., NJ, USA, using a parallel plate geometry of 50mm diameter with radial grooves to avoid gel slippage. The details of rheological measurements have been described previously (Miyoshi, 1996).

2.3. DSC measurements

Differential scanning calorimetry (DSC) measurements were carried out using a Setaram micro DSC-III calorimeter, Caluire, France. The sample and reference pans were placed inside the calorimeter and heated to 110℃ and kept for 10min to make the mixture a homogeneous solution. Then the temperature was lowered to 5℃ at 0.5℃/min and raised again at the same rate up to 110℃. Finally, the temperature was scanned up and down at the same rate, and the enthalpy profiles were recorded. The details of DSC measurements have been described previously (Miyoshi, 1996).

3. Sol-Gel transition in Gellan Gum Aqueous Solution

Figures 1 (a),(b) show the temperature dependence of the storage modulus G' and the loss modulus G" during the cooling and heating processes for a 1% or 2% gellan gum solution at a frequency of 0.1rad/s and a scan rate of 0.5℃/min, and the temperature dependence of molar ellipticity at 202nm $[\theta]_{202}$ for a 1% gellan gum solution on cooling process at the same scan rate (Matsukawa et al., 1999). We have determined two transitions of gellan gum solutions (the coil-helix transition and the sol-gel transition) by the thermal scanning rheological measurement. The steepest change of G" was attributed to the coil-helix transition T_{ch}, because this transition temperature was in good agreement with the characteristic temperature observed by circular dichroism (CD) (Tanaka et al., 1996). It has been suggested (Crescenzi et al. 1988; Rinaudo, 1988) that the peak around 202nm in the CD spectrum reflects the optically active chemical structure of glucuronic acid unit in the random-coil gellan. When the optically active high ordered structure of gellan gum chain (double helical structure) is formed during cooling, the CD spectrum is changed to the superposition of the spectrum for the random-coil and that for the double-helix, so that the change of molar ellipticity at 202nm $[\theta]_{202}$ is proportional to the change of population of the random-coil.

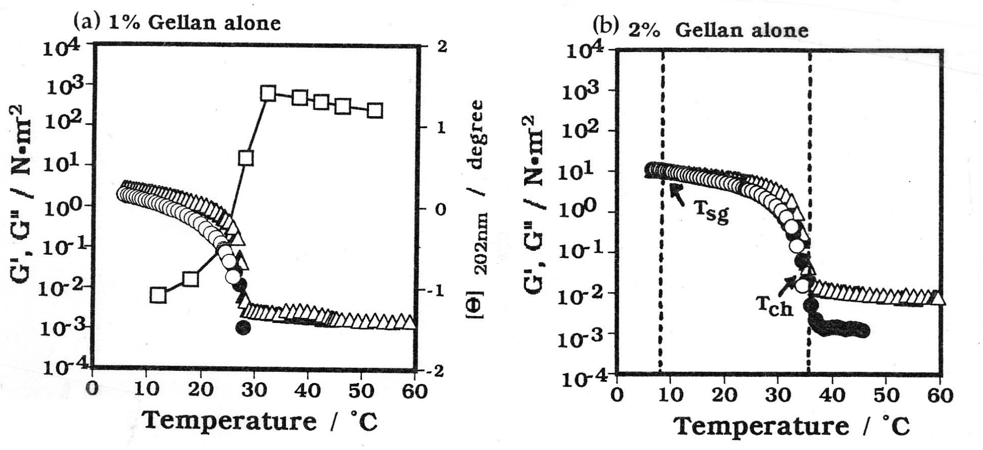


Figure 1

Temperature dependence of the storage modulus G' and the loss modulus G" during the cooling and heating processes for a 1% or 2% gellan gum solution at a frequency of 0.1rad/s and a scan rate of 0.5 °C/min, and the temperature dependence of molar ellipticity at 202nm $[\theta]_{202}$ for a 1% gellan gum solution on cooling process at the same scan rate. G'(○), G"(△), cooling; G"(●), G"(▲), heating; $[\theta]_{202}$ (□).

In ^{1}HNMR measurement which can investigate the hydrogen bonding behaviour of gellan gum (Matsukawa et al, 1999), for a 1% gellan gum solution, ^1HT_s of water slightly decreased with decreasing temperature down to 33°C because of showing of molecular motion of water, and then showed a steep change around T_{CD}. However, in the diffusion measurement, during the cooling process, it was observed that the translational motion of water molecule in gellan gum solution was much the same as that of pure water. From the standpoint of ^{1}HNMR measurement, three types of the hydrogen bond could be classified in the gellan gum system, thus the first one is formed between the hydroxyl group in gellan gum and water molecules, the second one is formed between gellan gum molecules (the intermolecular hydrogen bonds), and the third one is formed within gellan gum molecules (the intramolecular hydrogen bonds). Therefore, it has been suggested that the steepest decrease of ^1HT_s should be caused by the formation of hydrogen bonds within double helices of gellan gum induced by the conformational change.

For over 2% gellan gum solutions, the cross-over of G' and G" was observed on cooling, which was attributed to sol-gel transition T_{sg} (Figure 1(b)). The number of aggregated helices exceeded a critical value below a certain temperature in these concentrated solutions, so that at lower temperatures than the cross-over point, mechanical spectra changed to a weak gel behaviour with G'>G" throughout the accessible frequency range and both moduli are little frequency dependent.

The coil-helix transition (T_{ch}) and the sol-gel transition (T_{sg}) temperatures during cooling as a function of concentration of gellan gum determined by thermal scanning rheological measurements are shown in Figure 2. At lower concentrations of gellan gum (<2%), T_{sg} could not be observed even though the temperature was lowered to 0°C, in contrast, T_{ch} could be observed even at 0.2%. This indicated that the conformational transition from two singled-coiled chains to a double helix occurred even at fairly low concentrations of gellan gum, although T_{ch} was strongly concentration dependent in this concentration range (0~2%). The remarkable concentration dependence of the conformationnal transition temperature (T_{ch}) in the lower concentration range was also observed by viscometric measurement (Ogawa, 1999; Takigawa et al., 1999).

At concentrations higher than 2%, T_{sg} could be detected and shifted to significantly higher temperatures with increasing concentration of gellan gum. The difference between T_{ch} and T_{sg} gradually decreased with increasing concentration of gellan gum. Eventually, for a 3.5% gellan gum solution, the helix-coil transition and sol-gel transition occurred almost concurrently, which indicated that the number of helices formed on cooling was enough to prevail the whole space and form a three dimensional network. For further concentrated gellan gum solutions (>3.5%), both T_{ch} and T_{sg} observed at the same temperature became scarcely dependent on concentration.

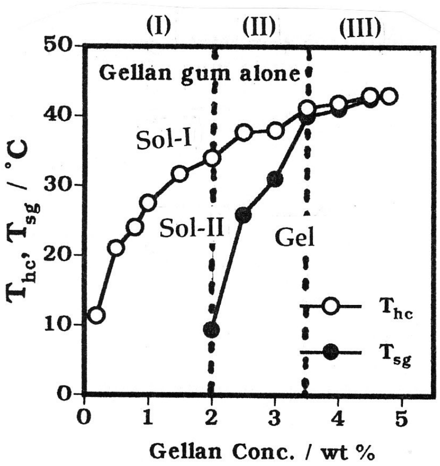


Figure 2

Temperature T_{ch} *(○) at which the loss modulus G" increased steeply, and the cross-over temperature of G' and G"* T_{sg} *(●) for gellan gum aqueous solutions during cooling as a function of concentration of gellan gum from 0 to 5%.*

As illustrated in Figure 2, states of gellan gum solutions are dependent on the temperature and concentration, and are classified into three; (1) Sol-I (gellan gum molecules take a single coil conformation); (2) Sol-II (gellan gum molecules take a helix conformation but the ordered structure could not lead to the gel); (3) Gel (the number of aggregates of helices exceeds a critical value on cooling and could form a gel). In both Sol-I and Sol-II states, the mechanical spectra showed a liquid-like behaviour, while those in Gel state tended toward that of a weak gel behaviour, as will be shown in Figure 3.

Whereas the relaxation time of gellan gum aqueous solution was almost same as that of pure water, the parameter of the symmetric distribution of relaxation time β deviated from unity throughout the accessible temperature range, as illustrated by the dielectric measurement (Shinyashiki et al., 1999). This indicates that gellan gum in water behaves as a hydrophilic polymer, so that many number of hydroxyl group in gellan gum molecules seem to cause the structural change of water surrounding gellan gum molecules. At higher temperatures where gellan gum molecules take a single coil conformation (Sol-I), β decreased with increasing temperature. This indicates that gellan gum molecules could strongly influence the structure of water, so that the variations of the local structure of water and the relaxation time of water are larger than those of pure water. This phenomenon may be induced by the fact that gellan gum molecules in the disordered state expand in solution (Takahashi et al., 1999).

In the temperature range between T_{ch} and T_{sg}, gellan gum molecules take a helix conformation but the ordered structure could not lead to the gel (Sol-II). β was closer to unity than that for a coiled conformation and this value did not change so much in this temperature range, therefore, the interaction between water and gellan gum molecules in the double helical conformation may be smaller than that in the coiled conformation.

At around T_{sg}, β showed a marked change, and then at lower temperatures where a gel was formed by the subsequent aggregation of double helices (Gel), β leveled off and this value was close to unity, which indicated that the subsequent aggregation seems to further reduce the interaction between water and gellan gum molecules. It has been concluded (Shinyashiki et al., 1999) that the interaction between water and gellan gum molecules is influenced significantly by the conformation of gellan gum molecules and this fact is reflected in the change of the parameter of the dielectric relaxation process of water (β).

The results observed by the dielectric measurement are consistent with the observation by ^{1}HNMR (Matsukawa et al, 1999). As previously mentioned in Figure 1, at higher temperatures where gellan gum molecules take a single coil conformation, ^1HT_s of water slightly decreased with decreasing temperature because of showing of molecular motion of water. ^1HT_s of water showed a steep change around T_{ch} and then at lower temperatures where gellan gum molecules take a helix conformation, this value leveled off with decreasing temperature. The ^{1}HNMR results also indicate that gellan gum molecules in the coiled conformation could more strongly influence the structure of water than those in the helix conformation because gellan gum molecules in the coiled state expand in solution and the interaction between gellan gum molecules in coiled state may be smaller than that in the helical state.

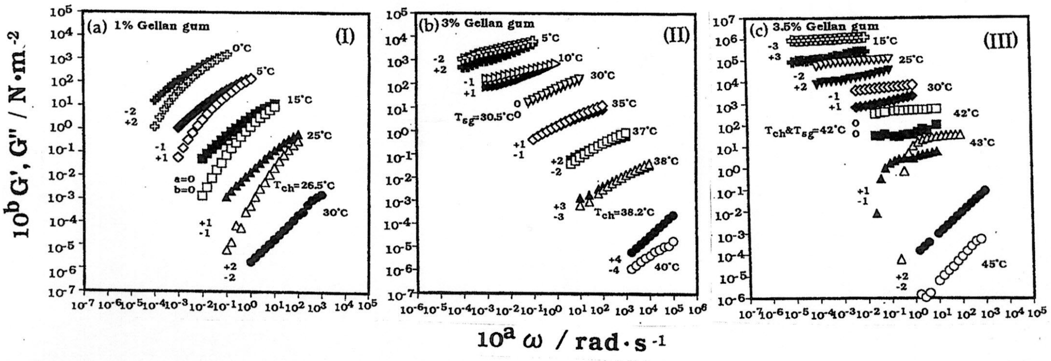


Figure 3

Frequency dependence of the storage modulus G' and the loss modulus G" for 1%, 3% and 3.5% gellan gum aqueous solutions at various temperatures. The data are shifted along both the horizontal and the vertical axes by shift factors a and b, respectively to avoid the overlapping Shift factor; a, b

Figures 3(a)-(c) show the frequency dependence of the storage modulus G' and the loss modulus G" for 1%, 3% 3.5% gellan gum aqueous solutions at various temperatures. The data are shifted along both the horizontal and the vertical axes by shift factors a and b, respectively to avoid any overlapping.

In all the cases, G' and G" at temperatures higher than T_{ch} were significantly small, however, both moduli markedly increased on cooling below T_{ch}, which seems to be satisfied with the results by the osmotic pressure (Ogawa, 1999), the light scattering measurement (Takahashi et al., 1999) and SAXS (Yuguchi et al., 1999) that the disordered structure was a single-coiled chain and the ordered structure was a double-helix.

For a 1% gellan gum solution belonging to the first type (I) (Figure 3(a)), the viscoelastic behaviour at any temperature on cooling below T_{ch} is typical of a dilute polymer solution with $G' < G"$ throughout the accessible frequency range and both moduli are strongly frequency dependent (Almdal, 1993). This indicated that a 1% gellan gum solution could not form a gel on cooling down even to 0°C. Frequency dependence of moduli for this solution at 25°C was very close to $G' \sim \omega^2$, $G" \sim \omega$, which is a characteristic feature of dilute polymer solutions (Strobl, 1996). However, for a 1% solution at 15, 5 or 0°C, the frequency dependence of both moduli of this solution slightly deviated from this behaviour (Winter & Chambon, 1986; Strobl, 1996).

Generally, for synthetic polymer such as polystyrene (random coil conformation), the characteristic feature of dilute polymer solutions, $G' \sim \omega^2$, $G'' \sim \omega$ is observed only for monodisperse polymers, and the frequency dependence of both moduli for samples might deviate from this behaviour with broader molecular weight distribution (Strobl, 1996). The steady-shear viscosity measurements indicated that gellan gum solutions showed a wide Newtonian plateau when gellan gum molecules took a coil conformation, and that the shear-thinning behaviour became more conspicuous with conformational change of gellan gum molecules from coil to helix, and the range of the Newtonian plateau became limited only to very shear rates (data not shown). Therefore, although the viscoelastic behaviour of a 1% gellan gum solution at any temperature on cooling below T_{ch} (Figure 3(a)) is typical of a dilute polymer solution, the frequency dependence of both moduli did not entirely obey $G' \sim \omega^2$, $G'' \sim \omega$ throughout the accessible frequency range because of helical conformation.

For a 3% gellan gum solution belonging to the second type (II) (Figure 3(b)), at temperature range from T_{ch} to T_{sg}, the mechanical spectra were typical of a concentrated polymer solution which showed a cross-over of both moduli at a certain frequency, and the cross-over point shifted to lower frequencies with decreasing temperature (Almdal, 1993). For a 3% solution at 30℃ ($=T_{ch}=T_{sg}$), G' and G" were equal over the accessible frequency range, and the slope of double logarithmic plots of both moduli against frequency was approximately 0.5, as would be expected for a critical gel (Winter & Chambon, 1986).

Winter and Chambon (1986) have found experimentally that the mechanical behaviour of crosslinking polymers could be described at the gel point by a power law relaxation shear modulus. Although this method has been developed for covalently cross-linked systems, te Nijenhuis and Winter have applied it to physical gels, and since then many investigations have been carried out to determine the gel point for physically crosslinking systems according to the Winter-Chambon method. However, different relaxation exponents (n) were found depending on stoichiometry, concentration and molecular weight of polymer, chain stiffness and thermal history.

As for our sample, the result obtained at T_{sg} for a 3% gellan gum solution at 30℃ are in good agreement with the critical gel (state at the gel point) in the Winter-Chambon model, which should satisfy the following relation; $G''/G'=\tan(\delta)=\tan(\pi n/2)$ which, for n=0.5, yields $G''/G'=\tan(\pi/4)=1$. Akutu et al. (1999) have reported that the power law relaxation exponent (n=0.5) was observed for the critical gel state between sol and gel in gellan gum systems, which coincided with our rheological results. For a 3% gellan gum solution at temperatures lower than T_{sg}, G' was larger than G" with little frequency-dependence throughout the accessible frequency range, which was classified rheologically as that of a weak gel (Almdal, 1993).

The gelation mechanism for a 3.5% gellan gum solution belonging to the third type (III) (Figure 3(c)) showed a complicated behaviour. As illustrated in Figure 2, T_{ch} and T_{sg} for a

3.5% gellan gum solution were observed at almost the same temperature (42℃), so that the mechanical spectra for this solution showed a drastic change around the transition temperature. This solution at temperatures slightly higher than the transition temperature showed a liquid-like behaviour. It behaved as a dilute polymer solution at 45℃, and it behaved as a concentrated polymer solution at 43℃. However, at 42℃, the behaviour became strikingly different; G' was much larger than G" throughout the experimentally-accessible frequency range and both moduli were essentially independent of frequency, as would be expected for an elastic gel as has been observed for agar gels (Nishinari, 1976), and for many other biopolymer gels (Morris, 1982). This behaviour seems to be close to that of an elastic gel or a true gel, so that the systems below 42℃ could be seen as almost perfect networks. Therefore, the critical state for a 3.5% gellan gum solution could not be observed around T_{sg}. As illustrated in Figure 3, the gel structures of the third type (III) seem to be obviously different from those of the second type (II).

4. Effects of Salts

4.1. Effects of monovalent cations

The order of effectiveness of the monovalent cations in promoting ordered structures ($Cs^+ > K^+ > Na^+ > Li^+$) was correlated with the dynamic hydration number (Shinyashiki et al., 1999). This order is also in good agreement with the effectiveness of the cation in increasing the cross-sectional radius of gyration R_{GC} estimated by SAXS (Yuguchi et al., 1999).

The dependence of the exothermic and endothermic peak temperatures for a 1% gellan gum solution on the salt concentration showed a common tendency. At lower concentration of salt, the differences between two transition temperatures were very small, so that the thermal hysteresis was almost negligible. However, upon addition of a certain concentration of salt, the heating DSC curves began to split into multiple peaks and the thermal hysteresis was observed, and then the thermal hysteresis was gradually modified with increasing concentration of the added salt.

Figure 4 shows the exothermic peak temperature T_s in the cooling DSC curves and endothermic peak temperature T_m in the heating DSC curves (a), and T_{ch} and T_{sg} determined by the thermal scanning rheological measurement (b) for 1% gellan gum solutions as a function of the concentration of the added CsCl. As illustrated in Figure 4, the comparison of the rheological results with the DSC results indicated that the onset of detectable splitting in heating DSC curves (the onset of observation of significant thermal hysteresis) was in good agreement with the onset of the observation of two transitions occurring at the same temperature by the rheological measurement.

As for 1% gellan gum solutions with monovalent cations as well as gellan gum solutions without salt, three types gellan gum systems (I, II, III in Figure 4(b)) can be classified rheologically depending on the concentration of gellan gum. Therefore, the thermal behaviours of gellan gum solutions with monovalent cations were more closely compared by rheology with DSC to give a better understanding as shown in Figure 5.

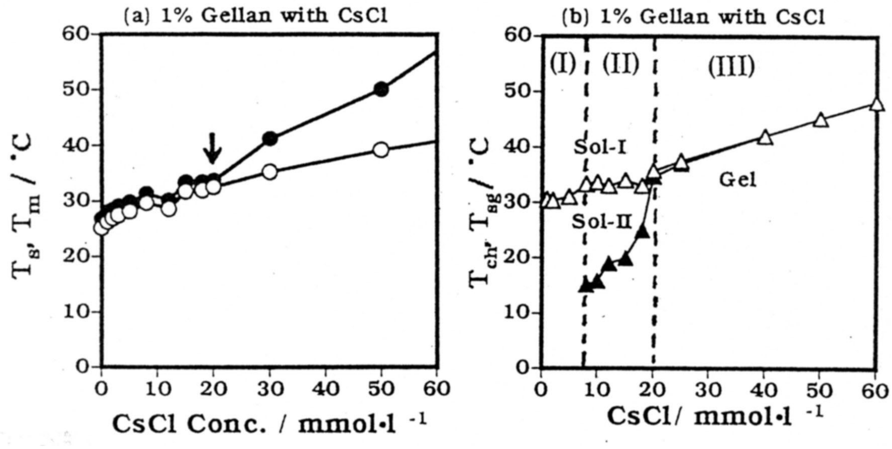


Figure 4

Exothermic peak temperature Ts (○) in the cooling DSC curves and endothermic peak temperature T_m *(●) in the heating DSC curves (a) and the temperature* T_{ch} *(△) at which G" increased steeply and the cross-over temperature of G' and G"* T_{sg} *(▲) during cooling for 1% gellan gum solutions as a function of the concentration of the added CsCl. Cooling and heating rate ; 0.5 ℃/min..*

Figures 5(a)~(f) show the temperature dependence of G' and G" during the cooling and heating processes for 1% gellan gum solutions containing CsCl of various concentrations, and cooling and heating DSC curves for these solutions. Upon addition of 5mM CsCl (Figures 5(a) and (d)), G" for a 1% gellan gum solution belonging to the first type (I) showed one step-like change during both cooling and heating, which was attributed to the coil-helix transition T_{ch}, as mentioned above. The cooling or heating DSC curve for this solution showed a single exothermic or endothermic peak, and this transition temperature almost coincided with T_{ch} in the thermal scanning rheology.

Upon addition of 10mM CsCl (Figures 5(b) and (e)), G" for a 1% solution belonging to the second type (II) showed two step-like changes, and the lower temperature process at which G' and G" showed a cross-over was attributed to the sol-gel transition T_{sg}, as mentioned above.

In the presence of 20mMCsCl (Figure 5(c)), T_{ch} and T_{sg} occurred concurrently, so that during the cooling process, a 1% solution belonging to the third type (III) showed one step-like change of G" and the single exothermic peak was observed (Figure 5(c)), which involved both the coil-helix transition and sol-gel transition. However, the thermal behaviour of this solution in the heating process was quite different from that of solutions with less CsCl; G" showed a two step-like change and the endothermic peaks split into two peaks, which would be expected for a significant thermal hysteresis (Figure 5(f)). The endothermic peak at lower temperature corresponded with the single exothermic peak in the cooling DSC curve, however, the other one in the heating DSC curve did not have any corresponding exothermic peak in the cooling process.

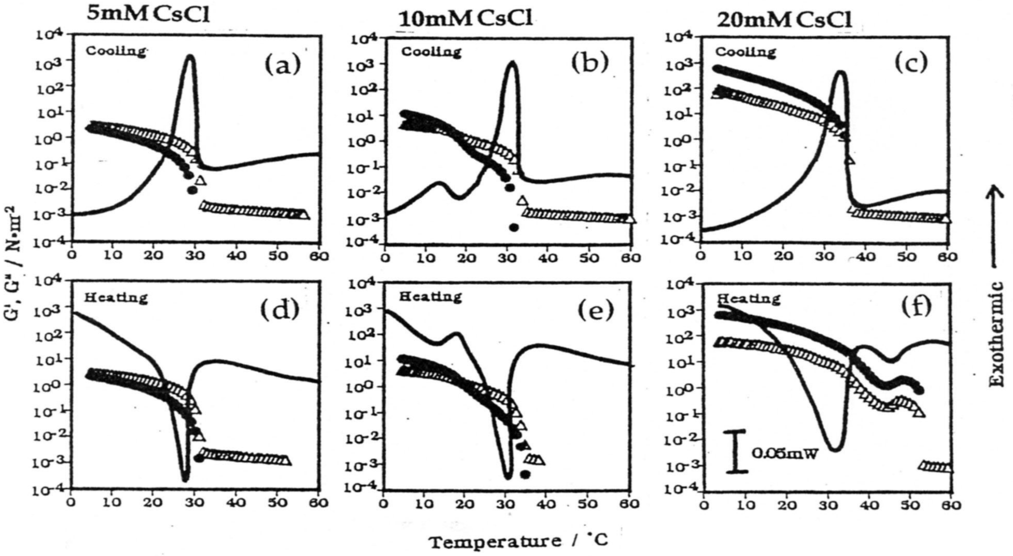


Figure 5

Temperature dependence of G' and G" during cooling and heating processes for 1% gellan gum solutions containing CsCl of various concentrations, and cooling and heating DSC curves for these solutions. (●)G', (△)G"; cooling and heating; rate; 0.5 ℃/min.

Judging from the rheological and DSC results, the gelation mechanism for gellan gum solutions could be schematically explained as shown in Figure 6. At higher temperatures, gellan gum molecules exist as a single coil (Sol-I). On cooling, gellan gum chains associate by the formation of double helices to form a certain ordered structure, which contributes to the most steep increase of G" in the thermal scanning rheology and the main exothermic peak observed in the cooling DSC curves. However, this ordered structure, in itself, does not lead to form a gel network (Sol-II)(I in Figure 6).

Gelation occurs with subsequent aggregation of these helices mediated by cations, so that the sol-gel transition appeared at temperatures lower than the coil-helix transition, which corresponds to the cross-over of G' and G" in thermal scanning rheology and the other small exothermic peak observed at a lower than the main exothermic peak in the cooling DSC curves. Gellan gum systems, in which two transitions occurred separately (Sol-I⇔Sol-II⇔Gel), do not show thermal hysteresis in cooling and heating processes (thermoreversible) (II in Figure 6). Thus, the temperature at which T_{ch} or T_{sg} is observed during the cooling process is almost the same as that during the heating process.

The difference between T_{ch} and T_{sg} decreased with increasing concentration of the added salt (or gellan gum). Eventually, for gellan gum in the presence of sufficient salt or in the sufficiently concentrated gellan gum solution, the individual helices are formed and immediately the aggregation of helices occurred in the cooling process so that T_{ch} and T_{sg} are observed at almost the same temperature (III in Figure 6). Moreover, in these systems, more than two kinds of junction zones with different thermal stabilities seem to be formed in at this transition temperature during cooling. Therefore, during heating, the non-aggregated double helices melt around 30°C (the main peak) and then thermally stable aggregated helices (mediated by specific binding of cations) melt at higher temperatures (Figure 5(f)), which would be expected for a significant thermal hysteresis (III in Figure 6).

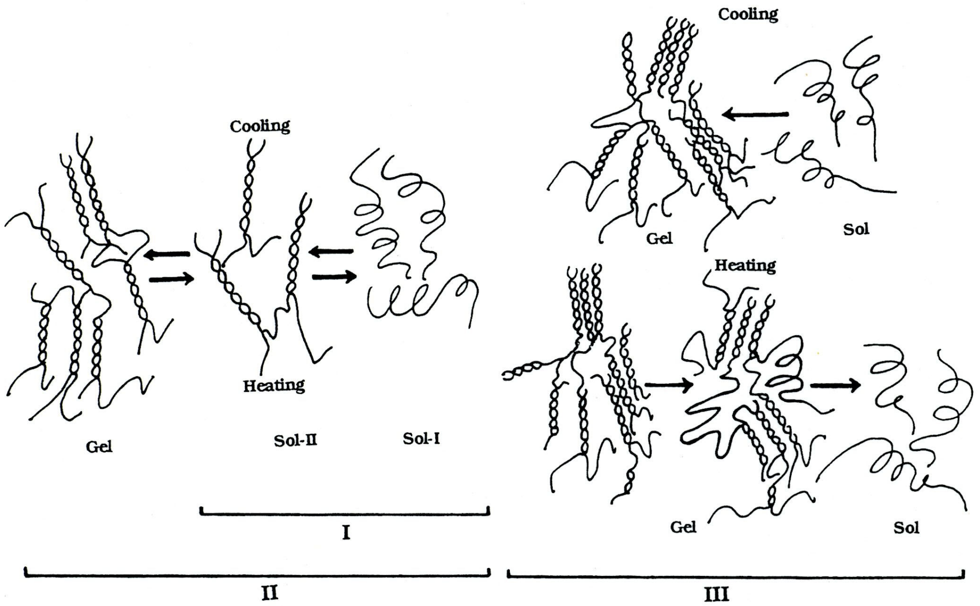


Figure 6

Schematic model to explain the gelation mechanism for gellan gum solutions with and without monovalent cations.

Using common sample, the observations by both ^{1}HNMR and CD （Matsukawa et al.,

1999) essentially coincided with our rheological results. Generally, the effects of salt on gelation could be explained that the introduction of cations can shield the electrostatic repulsion between carboxyl groups in gellan gum molecules, so that it permits tight binding and aggregation of helices at lower temperatures or leads to the reduction of coil dimensions at higher temperatures. The effect of salt on gelation is also explained that salt influences the conformation and association of polymers through their effects on the solvent properties of water, but potassium ions could directly promote association of carrageenan because potassium ions belong to the structure disordering ions (Uedaira & Ohsaka, 1990). Therefore, both specific and non-specific ion effects seem to influence the gelation of gellan gum, and especially in the presence of sufficient salt, the specific ion effect becomes more important.

Manning et al. (1992) have shown the schematic representation of model on the basis of DSC, optical rotation and rheological studies of gellan in the presence of sodium chloride, and a similar model has been suggested by V.J.Morris and Belton (1980). They have suggested that the lower temperature peak may be caused by the melting of unaggregated helices while the higher temperature peak may be caused by the melting of aggregated helices. Our interpretation may be essentially consistent with theirs, however, this interpretation must be inapplicable to the gelation mechanism of gellan gum in the presence of divalent cation, as will be discussed below.

4.2. Effects of divalent cations

Figures 7 (a)~(f) show the temperature dependence of G' and G" during cooling and heating processes for 1% gellan gum solutions containing $CaCl_2$ of various concentrations, and cooling and heating DSC curves for these solutions. The thermal behaviour in the presence of divalent cations was virtually different from that in the presence of monovalent cations.

On addition of $CaCl_2$ of a fairly low concentration (1mM), the cross-over of G' and G" was observed around 5℃ during cooling process (Figure 7 (a)), which indicated that this system could form a gel on cooling. However, the clear exothermic peak corresponding to the sol-gel transition could not be observed in the cooling DSC curve. During the heating process, the temperature at which a steep decrease of G" was observed was slightly higher than that of the main endothermic peak observed in the heating DSC curve, moreover, many small peaks were observed at higher temperatures than the main peak (Figure 7 (d)).

On addition of only 1.2mM$CaCl_2$ (Figure 7(b)), G" showed one step-like change around 35℃ on cooling, and then at the temperatures lower than this temperature, G' was significantly larger than G". On further addition of $CaCl_2$, both G' and G" drastically increased, which indicated that an elastic gel could be formed by the addition of sufficient divalent cations (Figures 7(c)). However, the height of exothermic peak in the cooling DSC curves gradually decreased with increasing concentration of $CaCl_2$ (Figures 7(a)~(c)), and this tendency was obviously different from that in the presence of monovalent cations.

Moreover, the behaviour of gellan gum solutions with $CaCl_2$ during the heating process became more complicated. Although the endothermic enthalpy estimated for a main peak gradually decreased with increasing concentration of $CaCl_2$, the endothermic peaks even with 2mM $CaCl_2$ were clearly recognized (Figure 7(e)). However, the thermal scanning rheological results showed that for gellan gum solutions containing more than 1.2mM $CaCl_2$ (Figures 7(e), (f)), no remarkable change of G' and G" was observed during heating up to 60°C.

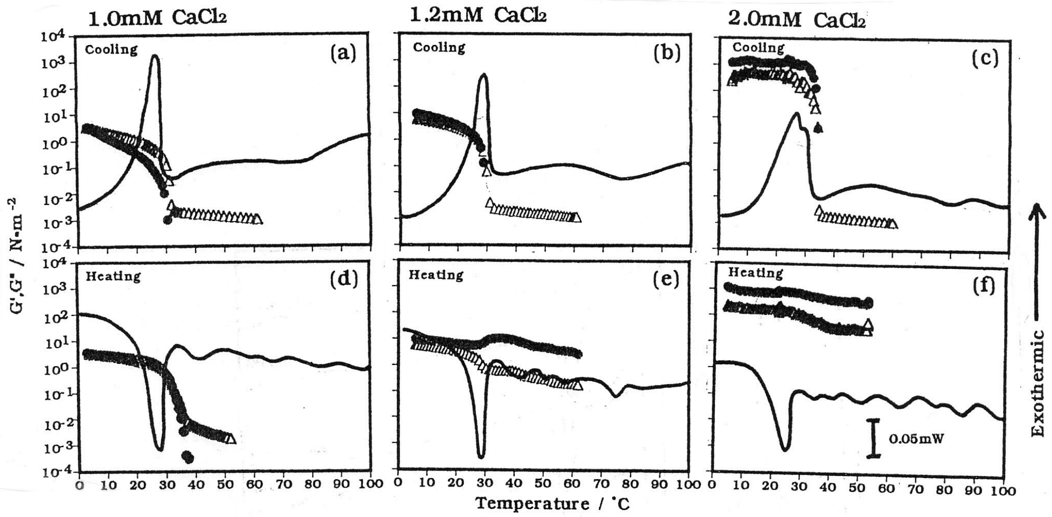


***Figure** 7*

Temperature dependence of G' and G" during cooling and heating processes for 1% gellan gum solutions containing $CaCl_2$ of various concentrations, and cooling and heating DSC curves for these solutions. (●)G', (△)G"; Cooling and heating rate; 0.5 ℃/min.

As for DSC curves of 1% gellan gum solution with $CaCl_2$, the concentration of $CaCl_2$ was represented stoichiometrically (mN). The concentration was also expressed as a percentage of the stoichiometric requirement of the carboxyl groups of gellan gum molecules. Endothermic enthalpy determined from heating DSC curves for 1% gellan solutions as a function of concentration of $CaCl_2$ is shown in Figure 8. The decrease of endothermic enthalpy with increasing concentration of Ca^{2+} was found to be linear, and the extrapolation to zero enthalpy approached the Ca^{2+} concentration of stoichiometric equivalence (100%).

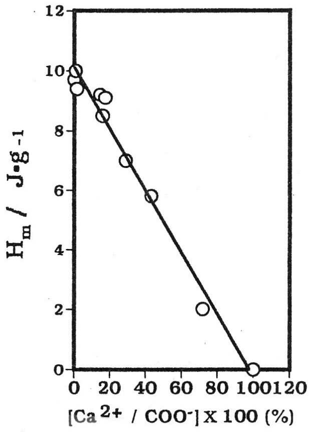


Figure 8

Endothermic enthalpy from heating DSC curves for 1% gellan solutions as a function of concentration of $CaCl_2$.

We propose the following interpretation of gelation mechanism of gellan gum in the presence of Ca^{2+} from the present data, as outlined schematically in Figure 9. During cooling process, calcium ions seem to be immediately associated with the gellan gum chains at temperatures higher than the conformational transition (the formation of double helices), which seems to be satisfied with the evidence that for gellan gum solutions containing $CaCl_2$ of low concentrations (3, 4, 6mN), the second exothermic peak began to develop at slightly higher temperature than the one corresponding with the coil-helix transition. This ordered structure, consisting of the interactions between gellan gum segments and calcium ions, could lead to form an elastic gel, rheologically (Figure 7).

On further addition of calcium ions, the ordered structures, which are specifically stabilized by calcium ions, stoichimetrically increase and become extremely thermally-stable. Therefore, with increasing concentration of $CaCl_2$, the endothermic enthalpy estimated for a main peak in heating DSC curves monotonically decreased and the other numerous endothermic peaks appeared especially at higher temperatures. During heating process up to 100°C, these heterogeneous zones involving the specific cation-polyanion interaction were gradually melted at various temperatures, and then calcium ions may stabilize gellan gum molecules even in the partially disordered helical conformation.

Therefore, this may explain the fact that in the presence of any concentration of $CaCl_2$, the total endothermic enthalpies in the heating DSC curves were essentially smaller than the total exothermic enthalpies in the cooling DSC curves. Consequently, divalent cations could form the electrostatic bonds where a metal ion bridged two anions at a temperature higher than T_{ch}, so that the ordered structures stabilised by divalent cations stoichiometrically increased.

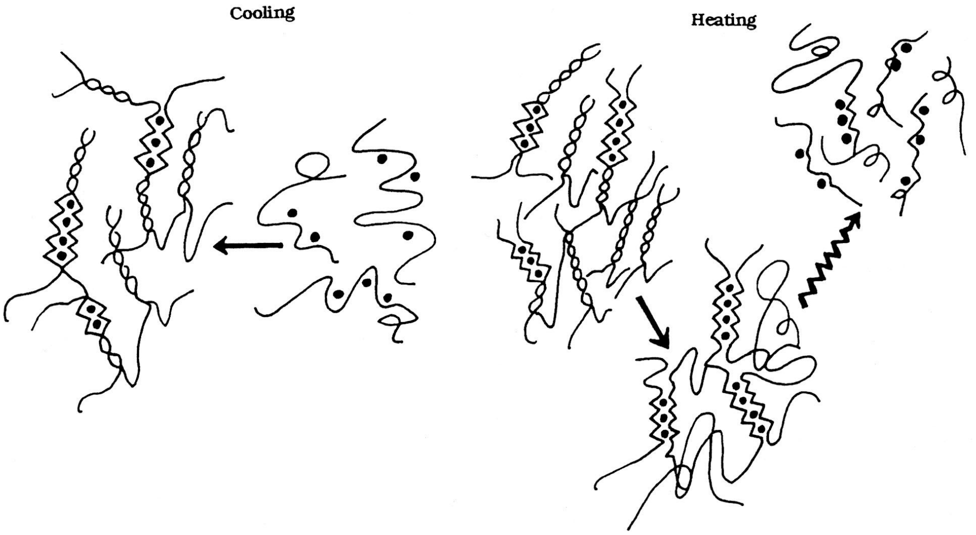


Figure 9

Schematic model to explain the gelation mechanism for gellan gum solutions in the presence of divalent cations (●).

The same phenomena were observed by both ^{1}HNMR and CD (Matukawa et al., 1999). In the presence of 5mM $CaCl_2$, both $[\theta]_{202}$ and $^1HT_2$ gradually decrease during the cooling process, however, both values didn't change so much during heating up to 70°C. This indicated that the specific ordered structures formed by the electrostatic bonds between carboxyl groups and a calcium ion increased with stoichimetrically increasing concentration of the added calcium ion.

It has been reported (Sime, 1990) that the gelation of alginates requires divalent cations such as Ca^{2+}, and the gels are not thermoreversible. E.R.Morris et al. (1978) have suggested that in the alginate gelation, the primary role of Ca^{2+} is to combine pairs of random-coil chain segments into ordered dimers, so that the specific metal ions are required for the formation of ordered structures of alginate. Gelation of low-methoxyl pectins is believed to be primarily a consequence of ionic cross-linkages through calcium bridges between arrays of carboxyl groups belonging to different chains (Rolin & Vries, 1990). It is well known that two mechanisms have been proposed to explain the gelation process of κ-carrageenan solutions, and consequently, it has been the subject of some controversy. E.R.Morris et al. (1980) have suggested that the crosslinks of carrageenan are formed by segments of a double helix, and then these segments are aggregated by ions such as K^+. Smidrod and Grasdalen (1981) have proposed the other mechanism that the single helices are formed, which are subsequently aggregated by K^+ to dimers, trimers etc.

The present work indicates that the gelation characteristics of gellan gum may depend on the nature of the added salt, especially, the gelation mechanism in the presence of divalent cations shows a more complicated nature compared to that in the presence of monovalent cations. From these results, the thermally stabilised structure in the presence of divalent cations was essentially different from that in the presence of monovalent cations. Here, we would like to especially emphasize that monovalent cations play a significant role to promote the subsequent aggregation of double helices at temperatures lower than the formation of double helices (T_{ch}), and that divalent cations directly interact with the gellan gum segments to form the ordered structures at slightly higher temperatures than the formation of double helices (T_{ch}).

Interpretation of the gelation mechanism of gellan gum in the presence of divalent cations is extremely difficult, especially because of the lack of information from visually microscopic methods. More investigations by means of different methods have still to be done to clarify it further. There is also an urgent need for purified gellan gums having different molecular weights with narrow molecular weight distribution to achieve a better understanding of the gelation mechanism.

5. Effects of Sugars

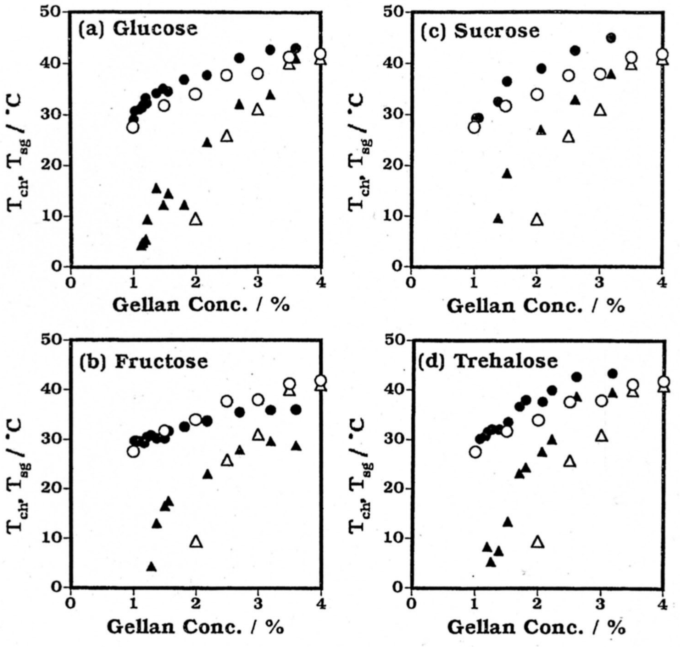
As illustrated in the previous studies, disaccharides were more effective than monosaccharides in promoting ordered structures observed by both rheology and DSC. Moreover, the influence of sugar was more remarkable for glucose than fructose, and for sucrose than trehalose. These differences would depend on the molecular weight and configuration of each sugar. The effectiveness of sugars in promoting ordered structures is as follows: sucrose ＞trehalose＞glucose＞fructose. This order is in good agreement with the dynamic hydration number [nDHN(sucrose)=25.2; nDHN(trehalose)=25.4; nDHN(glucose)=18.6; nDHN(fructose)=16.5] and the number of equatorially attached OH groups [n(e-OH)(sucrose)=6.3; n(e-OH)(trehalose)=7.2; n(e-OH)(glucose)=4.6; n(e-OH)(fructose)=3] (Uedaira and Ohshita, 1990), when it was considered that the differences of these values between sucrose and trehalose were little. The relationships between these nDHN or n(e-OH) in sugars and the effectiveness of sugars in promoting ordered structures of gellan gum will be discussed later.

Effects of a sugar on the helix-coil transition and sol-gel transition of gellan gum could be attributed to one of or both of the following factors; 1) the direct hydrogen bonding between hydroxyl groups in gellan gum molecules and in the sugar and/or 2) the structural change of water as a solvent. Sugar increases the number of elastically active network chains by forming hydrogen bonds or increases the effective concentration of gellan gum by immobilising water molecules or due to volume exclusion. On addition of 4M monosaccharide or 2M disaccharide, these gellan gum solutions contain 68.5% sugar, so that the amount of water, which is available for the dissolution of gellan gum in these systems, may be very small, compared to that in the absence of sugar. Therefore, the concentration of gellan gum was calibrated as a percentage of gellan gum in the system from which the amount of sugar was subtracted.

Figures 10 (a)~(d) show the transition temperature T_{ch} at which G" increased steeply, and the cross-over temperature of G' and G", T_{sg}, for a gellan gum system in the presence of sugar during cooling as a function of the calibrated concentration of gellan gum. As shown in Figure 10(a), in the presence of glucose, two transitions (the helix-coil and sol-gel transitions) did not change so much compared to those for gellan gum alone, however, the sol-gel transition for gellan gum solutions with glucose of fairly low concentration was obviously promoted, because gellan gum solutions (＜2%) could not form gels even on cooling down to 0℃. In the presence of disaccharide (sucrose or trehalose) (Figures 10(c) and (d)), both T_{ch} and T_{sg} for each system significantly shifted to higher temperatures compared to those for gellan gum alone or in the presence of monosaccharide.

As described above, disaccharides were more effective than monosaccharides in promoting ordered structures, however, this reason could not be explained only by the differences of the molecular weight. Because these behaviours in the presence of disaccharides were quite different from those in the presence of monosaccharides, regardless of considering the volume exclusion by the presence of sugar. This seems to be influenced by the volume of hydration of sugar in gellan gum gels. From the results in the presence of disaccharide and the fact that both sucrose and trehalose were non-reducing sugars, the first possibility of direct interaction between hydroxyl groups in polymers and in disaccharides might not be plausible.

As shown in Figure 10(b), in the presence of fructose of relatively low concentration, the helix-coil transition did not change so much compared to that for gellan gum alone. However, with increasing concentration of the added fructose (indicating the increase of the effective concentration of gellan gum), both T_{ch} and T_{sg} gradually shifted to lower temperatures compared to those for gellan gum alone. This indicated that both transitions were inhibited by the addition of sufficient fructose.



Figures 10

Temperature T_{ch} at which G" increased steeply, and the cross-over temperature of G' and G" T_{sg} for a gellan gum system in the presence of sugar during cooling as a function of the calibrated concentration of gellan gum.

(●)T_{ch}, with sugar; (○) T_{ch}, gellan gum alone, (▲)T_{sg}, with sugar; (△) T_{sg}, gellan gum alone

As discussed in the chapter 4, cations could stabilise the junction zones of gellan gum by the electrostatic interaction. Although sugar could stabilise the junction zones of gellan gum, the stabilisation by the addition of sugar should be essentially different from that by the addition of cations. The ability of sugar promoting the formation of gellan gum gels might be attributed to the effects of structural change of water as a solvent.

Water is both a hydrogen bond donor and a hydrogen bond acceptor, so that hydrogen bonds depend very much on the nature of water as a solvent. In the presence of sugar, the structure of water surrounding sugar would be changed and stabilised in gellan gum solutions, and as a result, sugar could create more hydrogen bonds through the water molecules with increasing concentration of the added sugar. Ohtsuka and Watanabe (1996) have found that the diffusional mobility of water in gellan gum gels is much the same as pure water, and this observation is consistent with the conclusion deduced from dielectric measurements by Mashimo et al. (1996). Mashimo et al. (1996) have concluded that most of water in gellan gum gels is free water, and that free water molecules construct a cluster consisting of 20-30 molecules. In the presence of sugar, free water molecules surrounding sugar were changed and stabilised, so that they tend to make a larger cluster than those for gellan gum solutions without sugar. Therefore, the thermal motion of stabilised water was deactivated than that for gellan gum solution without sugar, consequently, sugar indirectly could stabilise the junction zones of gellan gum molecules and promote the formation of gels.

To understand the effects of sugar on the structural change of water, the conformation of sugars, especially the number of equatorially attached OH n(e-OH) groups in sugar molecules should be taken into account. The effectiveness of sugar to stabilise the water in gellan gum gels seems to depend on n(e-OH) in sugar molecules, because sugar with larger n(e-OH) could stabilise the water structure much more. It is well known that there was a good correlation between the number of (e-OH) in saccharides and dynamic hydration number (Uedaira et al., 1990; Uedaira and Ohshita, 1990), therefore, the effectiveness of sugar to stabilise water in gellan gum gels also depends on the dynamic hydration number of sugar. This could explain the fact that sucrose or trehalose was more effective than glucose, not by the difference of molecular weights (Figure 10).

Two types of transition, the glass transition temperature T_g of the amorphous component and crystalline melting temperature T_m, are known for partially crystalline polymers. Sugar-water systems have been studied by DSC from this point of view, and it was found that the ratio $T_m/T_g=1.06$ for function was far lower than the ratio for glucose (1.42) or sucrose (1.43). indicating higher free volume and high mobility for fructose. This conclusion was also consistent with lower viscosity at T_g for fructose 10^{11}Pa•s with comparison to the typical value of 10^{14}Pa•s (Slade and Levine, 1998). This means that fructose is more instable in water than glucose and sucrose, and therefore, fructose is less effective to stabilise the ordered structure of gellan.

It is concluded that sugar indirectly influences the stabilisation of gellan gum gels due to the hydration and structural change of water surrounding sugar, so that the stabilities of gellan gum solutions gradually increase with increasing concentration of the added sugar.

6. Conclusion

The aim of this paper is to review our current knowledge of the gelation mechanism of gellan gum aqueous solutions, mainly using the dynamic viscoelatic measurement and differential scanning calorimetry (DSC) and to present the most recent findings on the common gellan gum sample in our collaborative research group on gellan gum. For the improvement of existing products and the development of new ones, the basic understanding of the gelation mechanism at the molecular level is required.

Advanced researches using Atomic Force Microscopy (AFM) for investigating the gelation mechanism of gellan gum have been reported (Gunning et al., 1996; Morris et al, 1999 & 2000). These results must give some new information for crosslinking domains of gellan gum, because the AFM studies can achieve submolecular resolution images of biopolymers in aqueous or gaseous environments. Therefore, the AFM observation of hydrated gellan films seems to be obviously different from the scanning tunneling microscopy (STM) observation of dried gellan gum films (Nakajima et al., 1996). These AFM studies have suggested that the gelation of gellan gum consists of a two-stage process; the first process means that the coil-helix transition results in the formation of filamentous structures, and the second process means that in the presence of gel-promoting cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, cation binding occurs throughout the entire structure so that the fibrous structures are formed by the additional side-by-side aggregation of these filaments.

Judging from the AMF observations, they have suggested that the gels have no separate junction zones and the interhelical binding is continuous throughout the entire fibrous network of the gels and that the elasticity of the gel arises by the stretching or bending of the fibres. Therefore, their model supported by the AMF results is essentially different from the conventional model for polysaccharide gels, which assumes the entropic rubber-like elasticity. The AMF methods have proved very useful for studying polysaccharide gels, however, their interpretation of gellan gum gels seems to be inapplicable to the peculiarity of the thermal behaviour with sufficient salt which was illustrated in Figure 7. Hence, the temperature dependence of G' for a 1% gellan gum solution with 1.2mM $CaCl_2$ (Figure 7(e)) showed a maximum at a certain temperature, however, on further addition of $CaCl_2$ (Figure 7(f)), G' for 1% gellan gum solutions decreased monotonically with increasing temperature. Therefore, some questions have still remained to achieve a universal model of gellan gum gels.

The importance of collaboration using same sample has been well demonstrated in the history of the development of rheology by the great contribution of NBS (National Bureau of Standards, USA) to the establishment of a time-temperature superposition principle or a reduced variable method. Our collaborative work has been advancing and we hope that the outcome of our further investigation has been contributing to the elucidation of some subjects with gelation mechanism of gellan gum and the development of further industrial applications.

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Our Recent Findings on the Functional Properties of Gellan Gum

Emako MIYOSHI

Recently, with increasing of the global environmental problems, greater efforts have been made to develop the effective usage of traditional polysaccharides, because these polysacchrides are environmentally degradable and bioabsorbable. Gellan gum is one of the most intensively studied polysaccharides and is expected for an appropriate model in order to study thermoreversible sol-gel transition, because it can form a transparent gel with outstanding flavour release, which is resistant to heat and its gel strength is less dependent on pH than many other polysaccharide gels.

The understanding of the physicochemical properties of gellan gum aqueous solutions has advanced remarkably by using the common gellan gum samples. The importance of collaboration using same sample has been well demonstrated in the history of the development of rheology by the great contribution of NBS (National Bureau of Standards, USA) to the establishment of a time-temperature superposition principle or reduced variable method.

Based on the same idea, the research group on gellan gum was organized in the Research Group on Polymer Gels affiliated to the Society of Polymer Science, Japan, in 1989. Using the same sample, various laboratories participating in this collaboration have studied on gellan gum and compared these results. Our outcome has already been presented three times as a special issue of the international journal and this collaborative work has been advancing.

The aim of present paper is to present the most recent findings on the functional properties of gellan gum, mainly using the dynamic viscoelatic measurement and differential scanning calorimetry (DSC), and were compared with other results by our coworkers with different methods.