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Helix-Forming Polysaccharide and Konjac Glucomannan*

Emako MIYOSHI

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*Synergistic Interaction between Helix-Forming Polysaccharide
and Konjac Glucomannan*

Emako MIYOSHI

1. Introduction

Many polysaccharides have found widespread applications in the food industry because they form viscous solutions and gels, which are extremely useful in the texturing of foodstuffs. Often the mixed systems of two polysaccharides are employed to manipulate rheological properties, since the properties of mixtures are superior to those of either component alone. For example, such mixed systems give stronger gels than either of the individual polymers or give the same gel strength at a lower total concentration, which provides effective savings in production costs (Morris, E. R., 1990). Extensive studies on gelation mechanism of such mixtures have been carried out since the 1970s, and still gives rise to considerable controversy.

Cairns et al. (1987) have classified the mixture gels into four different types and these are illustrated in Figure 1. Structure (a) shows the case with only one of the polysaccharides contributes to the gel network and the second polymer is simply entrapped within the matrix.

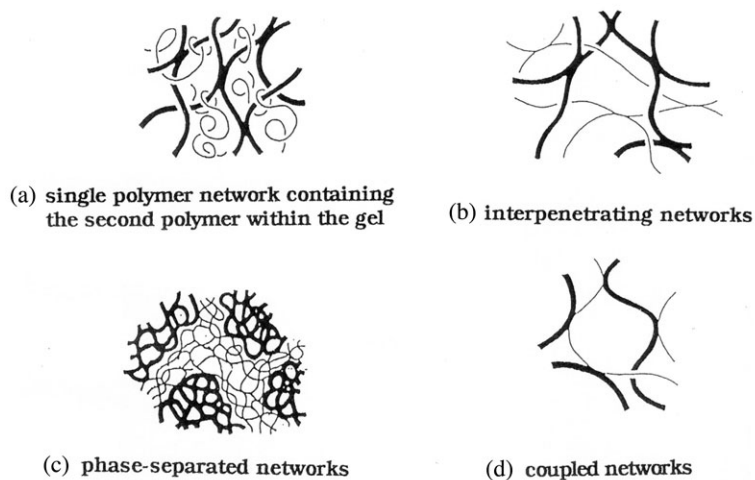


Fig.1
Various types of network structures for binary polysaccharide gels.

If both polysaccharides contribute to the network, the following three cases are possible: (b) separate polymer networks which interlace and form interpenetrating networks; (c) a phase-separated network; (d) one polysaccharide binds to the other to form a coupled network defined by specific junction zones.

The most familiar and widely explored mixed gels of food hydrocolloids are probably those involving galactomannans in combination with κ -carrageenan, furcellaran, agar or xanthan, which forms ordered structures. The addition of galactomannan to these polysaccharides (like agarose or κ -carrageenan) is known to improve mechanical properties and reduce brittleness or syneresis of the polysaccharide gel (Morris, V. J., 1986). It is known that when more than two polymers are mixed, the properties of mixtures are superior to those of either component, or they change qualitatively; this phenomenon is described as 'Synergism'. The synergistic effects between galactomannan and these polysaccharides impart increased elasticity and strength to the gel under conditions at which the pure components would not gel. More spectacularly, galactomannan and xanthan also form gels despite the fact that they neither form a gel independently at neutral pH. The mechanism of gelation of these mixtures has been the subject of much interest since early studies (Dea and Morrison, 1975; Dea, 1979) and is a matter of debate and several models have been proposed (Cairns et al., 1986; Cairns et al., 1987; Brownsey et al., 1988; Tako and Nakamura, 1986; Fernandes et al., 1991 and 1992; Rochas et al., 1990; Williams et al., 1991, 1993 and 1994; Cheetham and Mashimba, 1988 and 1991; Shatwell et al., 1991; Turquois et al., 1992; Kohyama et al., 1993; Miyoshi et al., 1996a-d, 1997, 1998; Nishinari et al., 1995ab, 1996; Oakenfull et al., 1999, 2000). Morris, V. J. (1986), Morris, E. R. (1990b, 2000), Williams (1994), and Miyoshi (1998, 2001) have reviewed the mechanism of gel formation and characterization of physical properties in mixed polysaccharide gels.

Konjac glucomannan (KGM) is a glucomannan obtained from the tuber of *Amorphophallus konjac* K.Koch, and forms a thermally stable gel on addition of alkaline coagulant. KGM is solubilised by a very low level of acetate substitution (about 1 acetyl group per 19 sugars), and removal of these substituents (by exposure to alkali) allows the polymer chains to associate and form a gel network. This gel has long been used in Japanese traditional foods (Nishinari, 1988). Although KGM is not a permitted food additive in the West, it has long history of food industrial use in Japan, which might facilitate approval by the United States Food & Drug Administration and the European Community (Morris, E. R., 1990b). KGM has also attracted much attention from a point of nutritional effects, because it could play a role as a dietary fiber.

KGM is a β -D-1,4 linked glucomannan and contains 1-3 linked branches occurring at the C3 position of glucose and mannose residues, however, the physicochemical properties of KGM have not been clarified sufficiently, because KGM is insoluble in water so that it is difficult to

obtain well-fractionated konjac glucomannan samples. The interaction of KGM with other hydrocolloids such as xanthan, and κ -carrageenan has been studied (Dea, 1979; Cairns et al., 1986; Cairns et al., 1987; Brownsey et al., 1988; Williams et al., 1991 and 1993; Kohyama et al.; 1993; Annable, 1994a). KGM interacts with non-gelling concentrations of both agarose and κ -carrageenan to give gels similar in rheological properties and melting point to those obtained with galactomannan. By mixing with xanthan gum, KGM forms gels at unusually low concentration and with unusually high melting points compared to those using galactomannan. In Japan, mixed gels of carrageenan with konjac glucomannan, are called 'konnyaku jelly', and used as low-calorie dessert jellies, much liked for their special texture.

KGM is virtually a neutral polysaccharide as it has few acetyl groups. Thus, gelation of KGM is not affected so much by ions as by molecular weight of the KGM. Kohyama et al. (1993) carried out rheological and DSC studies on the gelation of KGM/carrageenan mixtures using three KGM fractions with different molecular weights. The elastic modulus at small deformation, the breaking stress and breaking strain of the mixed gels increased with increasing molecular weight of KGM, however, the gel-sol transition temperatures were not influenced so much by molecular weight of KGM. From these results, another new model was proposed: the main network of the mixture is formed by carrageenan molecules, and KGM molecules interact with carrageenan molecules and form weak junction zones which contribute to the elasticity but not so much to thermal stability.

Gellan gum (GELL), an anionic polysaccharide produced by *Pseudomonas elodea*, has a complex tetrasaccharide repeating sequence of β -D-glucose, β -D-glucuronic acid, β -D-glucose, α -L-rhamnose, and it has a carboxyl side group. Since GELL is a helix-forming polysaccharide, analogous to carrageenans, it seemed likely that synergism might be observed in GELL/KGM mixtures, similar to that in carrageenan/KGM mixtures. However, there is less information available about GELL and KGM mixtures.

In this study, we investigate the rheological and thermal properties of GELL/KGM mixtures by dynamic viscoelastic measurement and differential scanning calorimetry and the results are reviewed. In particular, the effects of molecular weight of the KGM on these properties are discussed, and the effects of monovalent and divalent cations on the interaction between GELL and KGM are also described in order to elucidate the mechanism of interaction.

2. Materials and Methods

Purified sodium form GELL 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.

The non-degraded native KGM (NKGM) and two fractions of KGM with different molecular weights (KGM1 and KGM2), prepared by enzymatic degradation, were kindly supplied by Shimizu Chemical Co., Hiroshima, Japan. The molecular weights of the sample fractions determined by the same method in the previous work (Kohyama et al., 1993) were 1.17×10^6 (NKGM), 9.5×10^5 (KGM1) and 2.51×10^5 (KGM2). Man/Glc ratio estimated from the peak area detected by refractive index did not depend so much on the molecular weight of KGM, and was about 2.0. In the presence of salts, a fraction of KGM with medium molecular weight (KGM1), prepared by enzymatic degradation, was chosen among three KGM samples used in this study.

Salts, NaCl, KCl, CaCl₂ and MgCl₂ used in this study were of the extra fine grade reagents (Wako Pure Chemical Industries Ltd., Osaka, Japan), and were used without further purification.

Solutions of GELL /KGM at various ratios were prepared by mixing the appropriate amounts of each powder and dispersed by stirring to swell at 40 °C overnight.

As for the effects of molecular weight of the KGM, the total polysaccharide concentration was fixed at 1.6% (w/w) and the mixing ratio of GELL/KGM was changed. In the presence of salts, the total polysaccharide concentration was fixed at 0.8% and mixing ratio of GELL/KGM (KGM 1)=0.3/0.5 was chosen in the present work because the synergistic interaction was found at this ratio. For samples containing salts, the concentration of NaCl or KCl in solutions varied from 10 to 75mM and that of CaCl₂ or MgCl₂ ranged from 0.85 to 6.4mM, and each salt was added to solutions of GELL/KGM during stirring to swell before heating. Methods of rheological and DSC measurements were described in the previous study (Miyoshi, 1996).

3. Effects of Molecular Weight of Konjac Glucomannan on the Interaction

In this study, three fractions of KGM with different molecular weights (NKGM, KGM1, KGM2) were used in order to investigate the interaction between GELL and KGM by dynamic viscoelastic measurements and differential scanning calorimetry (DSC). Mechanical spectra showed that 1.6% solutions of GELL alone and of KGM2 alone behaved like a dilute polymer solution while 1.6% solutions of NKGM alone and KGM1 alone behaved like a concentrated polymer solution where molecular entanglements play an important role. Thermal scanning rheological measurements showed a step-like change in the loss modulus, which is attributed to the helix-coil transition, and subsequent aggregation of helices, and an exothermic and endothermic peak appeared in cooling and heating DSC curves respectively at the same temperature of transition. The transition temperature shifted to lower temperatures, and the transition enthalpy decreased with increasing KGM content in the mixture. The elasticity of

mixtures originates mainly from aggregated helices of GELL molecules for GELL/KGM2 systems while the contribution from KGM is more important for GELL/KGM1 and GELL/NKGM systems. Although the storage modulus of GELL/KGM1 and GELL/KGM2 as a function of mixing ratio showed a maximum, it is concluded that KGM inhibits the formation of the ordered structure of GELL.

The difference in behaviours of 1.6% solutions of KGM with different molecular weights is induced by a difference in the entanglement which is often observed for flexible macromolecules such as poly(methyl methacrylate) (Masuda et al. 1970) and polystyrene (Onogi et al. 1970). The cross-over frequency shifted to lower frequencies with increasing molecular weight of KGM as in poly (methyl methacrylate) or polystyrene molecules, although these macromolecules are slightly more flexible than KGM.

Figure 2 (a)~(c) shows the storage modulus G' for GELL/NKGM mixtures, GELL/KGM1 mixtures, GELL/KGM2 mixtures (total polysaccharide concentration 1.6%) as a function of mixing ratio at 0.1rad/s and at various temperatures. Although the highest molecular weight fraction NKGM seems to inhibit the helix formation of GELL more, the storage modulus of GELL/NKGM mixtures as a function of NKGM content increases with increasing NKGM content. This is simply because G' of a solution of NKGM alone is far larger (more than two decades!) than that of GELL alone. The inhibition seems to be most important at a mixing ratio of GELL/NKGM=0.8/0.8. Since NKGM inhibits most the helix formation of GELL, no synergistic interaction was observed in these mixtures.

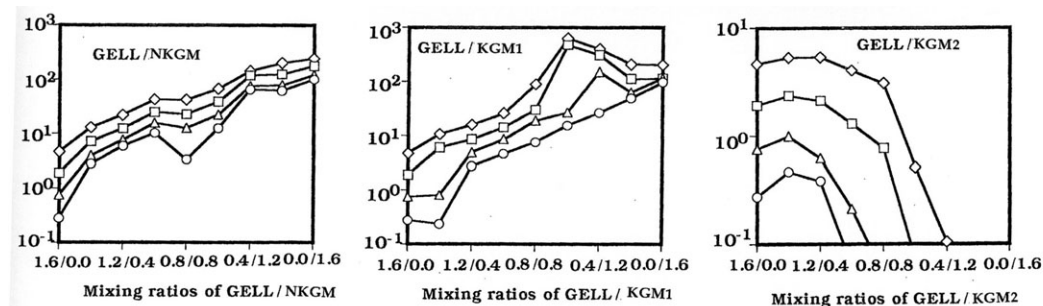


Fig.2

Storage modulus G' for GELL/NKGM mixtures, GELL/KGM1 mixtures, GELL/KGM2 mixtures (total polysaccharide concentration 1.6%) as a function of mixing ratio at 0.1rad/s and at various temperatures.
 () 30 , () 25 , () 15 , (◇) 0 ; Freq. =1.0rad/s

The findings that G' of GELL/KGM1 mixtures as a function of mixing ratio showed a maximum only below 25 suggest that the synergistic interaction occurs only between GELL molecules in helix conformation and KGM because GELL molecules take a helical conformation

at lower temperatures.

The synergistic interaction occurs only at lower temperatures around GELL/KGM1 ratio 0.6/1.0~0.4/1.2, and at wider temperature range for GELL/KGM2 around the mixing ratio 1.4/0.2~1.2/0.4. The reason why GELL/KGM2 mixtures show the synergistic interaction over a wider temperature range as well as a wider mixing ratio may be attributed to the least inhibition of helix formation of GELL molecules by KGM of the lowest molecular weight. If molecular association occurs between GELL and KGM, the increase in G' should be more prominent in a mixture with higher molecular weight KGM, however, this was not the case. Since the synergism between GELL gum and KGM does not seem to contribute so much to the increase of G' , the first or the second possibility is more plausible.

The fact that a cooling DSC curve shows two exothermic peaks while a heating DSC curve shows only one endothermic peak has been observed for a thermo-reversible gel system (Williams et al., 1993). The higher temperature exothermic peak in the cooling DSC curves for GELL/KGM mixtures may be attributed to the formation of ordered structure by the presence of small amount of calcium ions. As was shown in the previous studies (Miyoshi et al., 1994ab, 1995ab, 1996; Miyoshi & Nishinari, 1999ab, 2000ab, Miyoshi, 1996, 2003, 2006), an exothermic peak in cooling DSC curves splits into multiple peaks in the presence of excessive cations. It is improbable that helix-coil transition of GELL molecules shifted to such a higher temperature on addition of KGM.

It was suggested that the interaction between KGM and κ -carrageenan is weaker than that between κ -carrageenan and κ -carrageenan, but strong enough to produce another elastically active chains (Kohyama et al., 1993). It is difficult to understand why GELL /KGM does not show the similar synergism observed in κ -carrageenan/KGM although GELL and κ -carrageenan show quite a similar gelling behavior. The relation between the structure of polysaccharides and the synergistic interaction should be explored in the future, using various methods.

4. Effects of Monovalent and Divalent Cations on the Synergism

In the presence of salts, KGM with intermediate molecular weight (KGM1), and mixing ratio of GELL/KGM=0.3/0.5 was chosen, which is observed the synergistic interaction. Therefore, KGM sample with intermediate molecular weight will be called KGM hereafter.

Figure 3 shows the storage modulus G' for GELL/KGM mixtures (total polysaccharide concentration 0.8%) as a function of mixing ratio at 0.1rad/s and at various temperatures. G' at 0 showed a maximum at a mixing ratio GELL/KGM=0.3/0.5, although G' at any temperature > 0 increased monotonically with increasing concentration of KGM content.

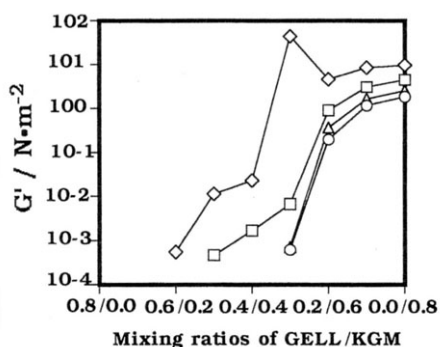


Fig.3

Storage modulus G' for GELL/KGM mixtures (total polysaccharide concentration 0.8%) as a function of mixing ratio at 0.1rad/s and at various temperatures.

(○) 30 , (□) 25 , (△) 15 , (◇) 0 ; Freq. =1.0rad/s

Frequency dependence of G' and the loss modulus G'' for a mixture with GELL/KGM=0.3/0.5 at 0 showed a typical behavior of a weak gel, G' was larger than G'' and both moduli were little frequency-dependent throughout the accessible frequency range, whereas this mixture behaved as a dilute polymer solution at higher temperatures than 0 (Figure 4). Therefore, the synergism would occur at low temperatures, where individual helices in GELL molecules aggregated and formed a certain ordered structure. As shown in Figure 3 and 4, the synergism occurred only at 0 at a certain mixing ratio, thus, the following experiments to study the effects of salts were performed using mixtures of this mixing ratio (GELL/KGM=0.3/0.5).

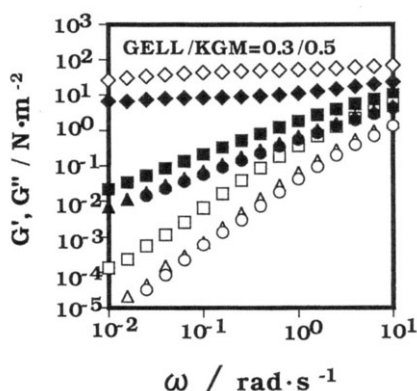


Fig.4

Frequency dependence of storage modulus G' and the loss modulus G'' for a mixture with GELL/KGM=0.3/0.5 in the absence of cations at various temperatures.

(○) G' , (△) G'' , 30 ; (□) G' , (◇) G'' , 25 ; (△) G' , (◇) G'' , 15 ; (◇) G' , (◆) G'' , 0

Figure 5 show the temperature dependence of G' and G'' for a mixture without salt (a) and mixtures containing 50mM NaCl (b), 75mM NaCl (c), 20mM KCl (d), 60mM KCl (e), 1.7mM CaCl_2 (f), 3.06mM CaCl_2 (g), 2.4mM MgCl_2 (h) or 3.4mM MgCl_2 (i) at 0.1rad/s during cooling or heating at a scan rate of 0.5 /min. As described in the previous study (Nishinari et al, 1995ab, 1996), the transition where G'' changed most steeply was attributed to the coil-helix transition in GELL molecules, and the transition where G' and G'' showed a crossover was attributed to the sol-gel transition. Therefore, these transition temperatures will be called T_{ch} and T_{sg} hereafter. There is a remarkable difference between thermal behaviors of mixtures with monovalent cations and with divalent cations. With progressive addition of monovalent cations, both moduli for mixtures increased, and T_{ch} significantly shifted to higher temperatures (Figure 5(b) and (d)) compared with a mixture without salt (Figure 5(a)). On adding more monovalent cations (Figure 5(c) and (e)), during the cooling process, T_{ch} and T_{sg} were observed at the same temperature and these transition temperatures significantly shifted to higher temperatures, moreover the mixture with sufficient monovalent cations formed an elastic gel with a large thermal hysteresis. In the presence of divalent cations lower than 1.7mM CaCl_2 (Figure 5(f)), or 2.4mM MgCl_2 (Figure 5(h)), both moduli for mixtures markedly increased and T_{ch} shifted to higher temperatures, moreover progressive addition of divalent cations, both moduli significantly decreased (3.06mM CaCl_2 (Figure 5(g)) or 3.4mM MgCl_2 (Figure 5(i))).

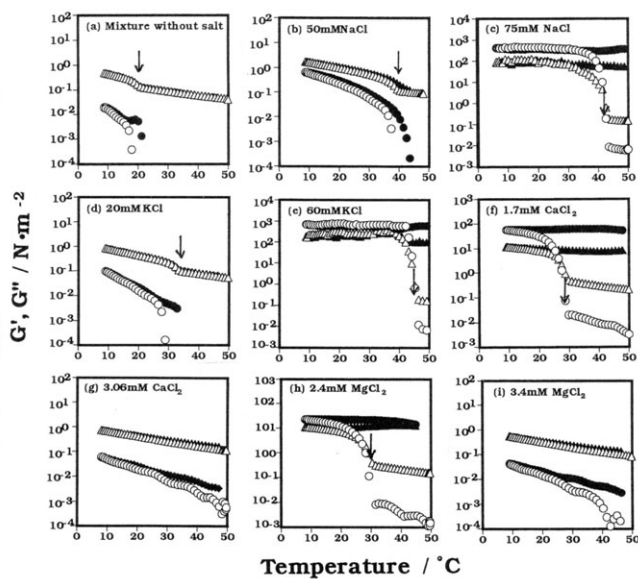


Fig.5

Temperature dependence of G' and G'' for a mixture without salt (a) and mixtures containing 50mM NaCl (b), 75mM NaCl (c), 20mM KCl (d), 60mM KCl (e), 1.7mM CaCl_2 (f), 3.06mM CaCl_2 (g), 2.4mM MgCl_2 (h) or 3.4mM MgCl_2 (i) at 0.1rad/s during cooling or heating at a scan rate of 0.5 /min.

Figure 6 shows the frequency dependence of G' and G'' for a mixture containing 75mM NaCl (a), 1.7mM CaCl_2 (b) or 3.4mM CaCl_2 (c). In the presence of 75mM NaCl (Figure 6(a)), the mixture behaved as an elastic gel even at a higher temperature such as 30 °C. Upon more progressive addition of NaCl, mixtures formed firm gels (Data not shown). In the absence of KGM, a 0.3% GELL alone could not form gels even upon addition of sufficient NaCl. Therefore, at lower concentration of GELL, the number of helices formed on cooling is not sufficient to prevail the whole space and to form a three dimensional network. The addition of 0.5% KGM was necessary for a 0.3% GELL solution to reach a gel state at 0 °C (Figure 4), and the sufficient NaCl promotes not only the formation and aggregation of helices in GELL molecules but also the synergistic interaction between GELL and KGM.

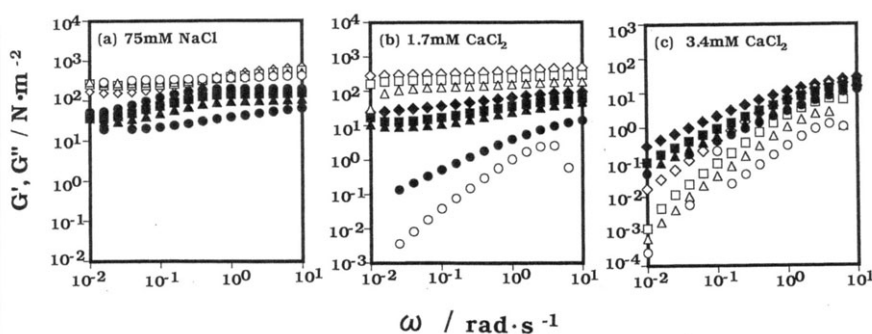


Fig.6

Frequency dependence of G' and G'' for a mixture containing 75mM NaCl (a), 1.7mM CaCl_2 (b) or 3.4mM CaCl_2 (c). (○) G' , (●) G'' , 30 °C; (△) G' , (▽) G'' , 25 °C; (□) G' , (◇) G'' , 15 °C; (◇) G' , (◆) G'' , 0 °C

As illustrated in Figure 5 (c), the temperature dependence of both moduli for a mixture with 75mM NaCl showed the monotone decreasing behavior with increasing temperature. The experimental findings that G' is larger and $\tan \delta$ is smaller at a higher temperature (30 °C) than at lower temperatures (Figure 6(a)) suggest that a 1% GELL solution in the presence of 75mM NaCl tends to a more solid-like behavior at a higher temperature. The experimental findings that G' is larger and $\tan \delta$ is smaller at a higher temperature (30 °C) than at lower temperatures (Figure 6(a)) suggest that a 1% GELL solution in the presence of 75mM NaCl tends to a more solid-like behavior at a higher temperature.

Moreover, G'' showed a slight dip at 30 °C, which is often observed in true gels. This behavior was not observed in solutions of GELL alone even in the presence of sufficient salt. According to the reel-chain model (Nishinari et al., 1985), the bonding energy of segments and/or the upper limit of the number of segments which can be liberated from junction zones before gel-to-sol transition occurs and/or the mean end-to-end distance of flexible chains which connect junction zones should increase by the addition of 75mM NaCl.

In the presence of 1.7mM CaCl_2 , the viscoelastic behavior for a mixture at a temperature 25 tended towards that of a weak gel (Figure 6 (b)), which was similar to that with 75mM NaCl. However, in the presence of excessive CaCl_2 (3.4mM) (Figure 6 (c)), the mechanical spectra showed a liquid-like behavior. It was, thus, suggested that upon addition of CaCl_2 , the sol-gel transition temperature for mixtures significantly shifted to higher temperatures up to a certain concentration of CaCl_2 , however, in the presence of excessive CaCl_2 , the synergistic interaction between GELL and KGM was inhibited. The reason will be discussed later in relation to DSC results. The effects of KCl on the mechanical spectra of mixtures were similar to those of NaCl, and those of MgCl_2 were similar to those of CaCl_2 .

Figure 7 shows cooling and heating DSC curves for a 0.8% GELL alone, a 0.8% KGM alone and mixtures with GELL/KGM=0.2/0.6, 0.3/0.5 and 0.6/0.2 in the absence of cations. For GELL alone and mixtures, the cooling or heating DSC curves showed an exothermic or an endothermic peak around 15~25 . Williams et al. (1993) have reported that in the mixtures of κ -carrageenan and KGM, when KGM content was in excess, a single exothermic peak was observed at a temperature significantly higher than the transition temperature observed for κ -carrageenan alone, however, when κ -carrageenan was in excess, the cooling curves showed two exothermic peaks and a second transition appeared at the normal transition temperature of κ -carrageenan alone.

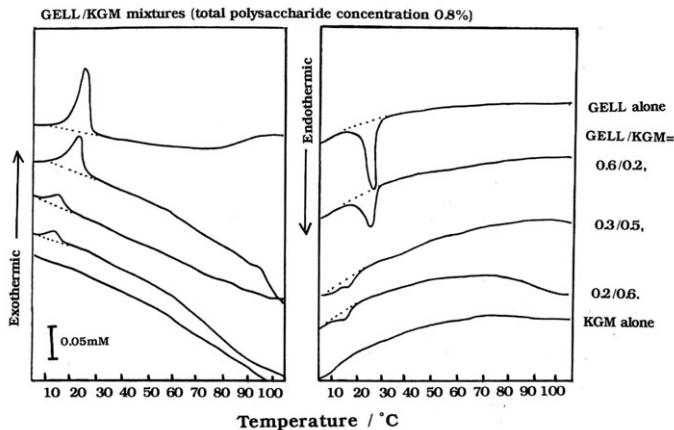


Fig. 7

Cooling and heating DSC curves for a 0.8% gellan gum alone, a 0.8% KGM alone and mixtures with GELL/KGM=0.2/0.6, 0.3/0.5 and 0.6/0.2 in the absence of cations. Cooling and heating rate: 0.5 /min.

It was suggested that under the condition of excessive κ -carrageenan, the coil-helix transition of κ -carrageenan molecules in mixture with KGM occurred in two separate transition steps each involving a fraction of the κ -carrageenan molecules, thus, a high temperature

transition was affected by the presence of KGM, and a transition at a slightly lower temperature GELL/KGM mixtures described in the present study, each cooling DSC curve showed a single exothermic peak, whether GELL was in excess or KGM was in excess. KGM does not seem to show any conformational changes as shown in this figure since both cooling and heating curves for KGM alone no peaks. The transition temperature shifted to lower temperatures and the exo- and endothermic enthalpies decreased monotonically with decreasing GELL content, in other words, the transition temperatures in GELL molecules little changed by the presence of KGM (Data of GELL alone not shown), so that KGM does not seem to interact synergistically with GELL but rather prevent the structural ordering of GELL.

Figure 8 (a)~(b) shows cooling and heating DSC curves for 0.3% GELL alone and mixture containing KCl and $MgCl_2$ of various concentrations. It has been reported (Williams

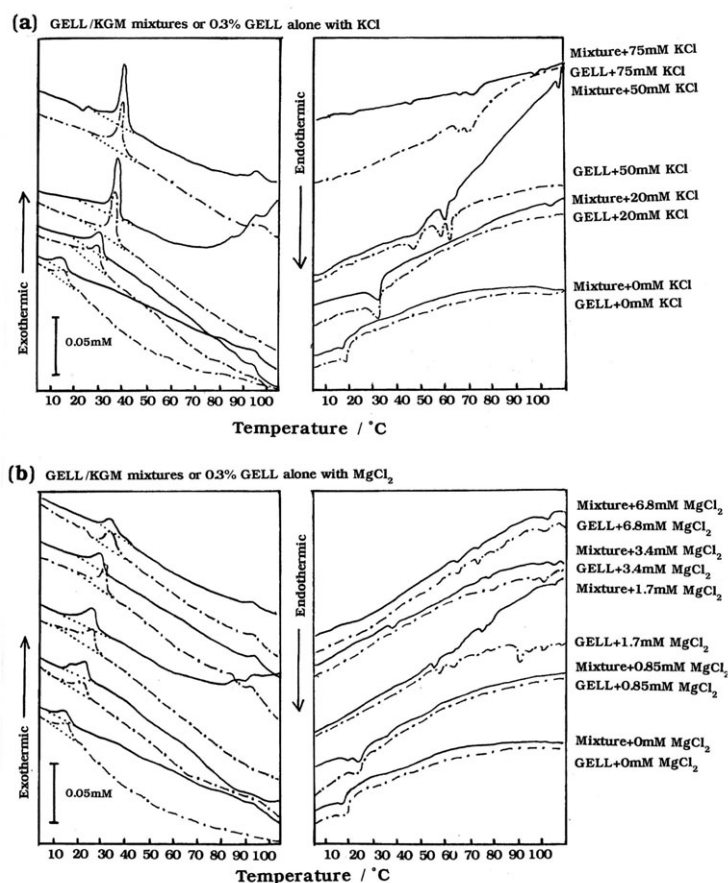


Fig.8

Cooling and heating DSC curves for 0.3% gellan gum alone and mixture containing KCl and $MgCl_2$ of various concentrations.

Cooling and heating rate: 0.5 /min.

et al., 1991) for the xanthan/KGM mixtures that whereas in the absence of cations, the cooling DSC curves showed a single exothermic peak at a temperature slightly above the order-disorder transition expected for xanthan alone, in the presence of monovalent cations, another transition peak appeared at a temperature significantly lower than the normal transition temperature of xanthan alone.

As shown in this figure, for GELL/KGM mixtures in the presence of KCl, each cooling curve showed a single exothermic peak, however, it was clear that the presence of KGM markedly influenced the disorder-order transition of GELL molecules, because at each concentration of added KCl, the shapes of these peaks for mixtures containing 0.3% GELL were quite different from those for 0.3% GELL alone. In the presence of KCl (Figure 8 (a)), in all cases, the DSC cooling curves for GELL alone and mixtures showed a main endothermic peak with the setting temperatures T_s shifting to progressively higher temperatures with increasing concentration of KCl, however, T_s for mixtures was significantly higher than that for 0.3% GELL alone at each concentration of KCl, especially, the exothermic peak for a mixture with 50mM or 75mM KCl became much sharper and the enthalpy significantly increased compared to that for a 0.3% GELL alone with 50mM or 75mM KCl. This indicated that KGM promotes the formation and aggregation of GELL molecules in the presence of KCl during the cooling process.

In the heating DSC curves, T_m for mixtures, as well as T_s , was significantly higher than that for GELL alone in the presence of KCl of the same concentration, moreover, the main endothermic peak for a mixture with 75mM KCl was observed around 75 °C, which was markedly higher than that for 0.3% GELL with 75mM KCl. Since during heating process, KGM, which attached to large aggregates of GELL helices could retard the helix-coil transition in GELL molecules, the melting temperature shifted to higher temperatures, hence, a larger thermal hysteresis was observed for a mixture with sufficient monovalent cations (Figure 5 (c), (e)). Therefore, it was suggested that in the presence of sufficient monovalent cations, KGM could shift the helix-coil transition temperature in GELL molecules to higher temperatures, and could contribute to the formation of thermally stable gels.

In the presence of $MgCl_2$, for both GELL alone and mixtures, the exothermic enthalpies in the cooling DSC curves showed a maximum at 1.7mM $MgCl_2$ and then decreased with increasing concentration of added $MgCl_2$. In the presence of sufficient $MgCl_2$ (Figure 8 (b)), the cooling DSC curve for a mixture became much broader and the exothermic enthalpy significantly decreased compared to that of GELL alone with 6.8mM $MgCl_2$, which corresponded well to the rheological results; the mixture with sufficient divalent cations could not form gels even at 0 °C (Figure 6 (c)).

Upon addition of 0.85mM $MgCl_2$, the heating DSC curves for both a mixture and a 0.3%

GELL showed a main endothermic peak around 25 °C, however, the endothermic enthalpy for this mixture was larger than that for a GELL alone. With more progressive addition of MgCl₂, the heating DSC curves for both mixtures and GELL alone became broader, however, many small peaks were observed and the main endothermic peak was observed at much higher temperature such as 102 °C (not shown in the figure). Therefore, since GELL sufficient divalent cations formed various junction zones with different thermal stabilities, for a mixtures under this condition, the synergistic interaction between GELL and KGM molecules may be inhibited. Therefore, in the presence of sufficient divalent cations, many self-aggregates of GELL helices were formed, however, the size of each aggregates of GELL helices became smaller, so that the probability of the interaction of KGM with GELL aggregates decreased.

G' for mixtures with sufficient divalent cations (Figure 5 (g), (h)) also decreased rather than that for mixtures without salts (Figure 4) but showed a larger values than that for 0.3% GELL solutions with and without divalent cations (data not shown) because G' for KGM alone was far larger than that for GELL alone (Figure 3).

As described in Figure 2 (total polysaccharide concentration 1.6%), the frequency dependence showed a gel-like behavior below 15 rad/s at a mixing ratio of GELL/KGM=0.6/1.0. As for samples of total polysaccharide concentration 0.8%, the synergistic interaction occurred only at 0 rad/s at the same mixing ratio of GELL/KGM=0.3/0.5. It has been generally accepted that in the cooling process, the individual helices of GELL molecules were formed at a certain temperature, and then these helices gradually aggregated with increasing temperature, and as result, a certain ordered structure was formed. As illustrated in this study, the synergism of GELL and KGM would occur at much lower temperatures than the coil-helix transition temperature, where individual helices of GELL molecules were formed at a certain ordered structure which provided evidence that KGM chains should interact with self-aggregates of GELL helices, rather than individual GELL helices. This is similar to the results reported by Piculell et al. (1994) that the synergistic interaction disappeared in mixtures of KGM and κ-carrageenan in the present of iodide ions, which inhibit the self-aggregation of κ-carrageenan helices. Therefore, we suggest that the mixed aggregates of GELL/KGM consist of a core of aggregates of GELL helices with KGM chains attached to the surface. In other words, the main ordered structure for mixtures was formed by aggregates of GELL helices, and KGM attached to these aggregates and forming 'weak' junction zones as in mixtures of KGM and κ-carrageenan (Kohyama et al., 1993). The DSC observations, that no peak of a specific interaction between the ordered GELL and KGM was observed (Figure 7 and 8), supported this suggestion.

Many workers have reported that cations can promote the aggregation of helices in GELL molecules by a screening effect, thus, the coil-helix transition temperature in GELL

molecules shifted to higher temperatures and the self-aggregates of GELL helices became gradually larger with increasing concentration of cations. Thus, the introduction of cations to mixtures of GELL and KGM should permit KGM chains attached to larger aggregates of GELL helices at higher temperatures compared to those in the absence of cations, which explains that the gel-like behavior for a mixture with 75mM NaCl (Figure 6 (a)) or 1.7mM CaCl₂ (Figure 6 (b)) was observed at significantly higher temperatures compared to that for a mixture without salt (Figure 4).

In the previous studies (Miyoshi et al., 1994ab, 1995ab, 1996; Miyoshi & Nishinari, 1999ab, 2000ab, Miyoshi, 1996, 2003, 2006), we suggested that in the presence of sufficient divalent cations, GELL could form various junction zones with different thermal stabilities. Since many self-aggregates of GELL helices in mixtures were formed in the presence of excessive divalent cations but the size of each aggregates of GELL helices became smaller, mixtures could not form gels in the presence of excessive divalent cations, as described above.

Frequency dependence of both moduli for mixtures containing 1.7mM or 6.8mM MgCl₂ at 30 °C (the temperature was lowered from 60 °C to 30 °C at a cooling rate of 0.5 °C/min), 30 °C after a cooling and heating cycle between 30 °C and 0 °C was shown in Figure 9 (a) and (b) respectively. Triangle symbols showed that the mixtures with salts were cooled from 30 °C to 0 °C and reheated up to 30 °C at a constant scanning rate (0.5 °C/min), and then frequency dependence of both moduli was observed at 30 °C. In the presence of 1.7mM MgCl₂ (Figure 9 (a)), the viscoelastic behavior at 30 °C was typical of a dilute polymer solution, however, it changed to that of a weak gel at 30 °C after cooling and heating cycle. This also illustrated that the synergistic interaction between GELL and KGM would occur at lower temperatures where the

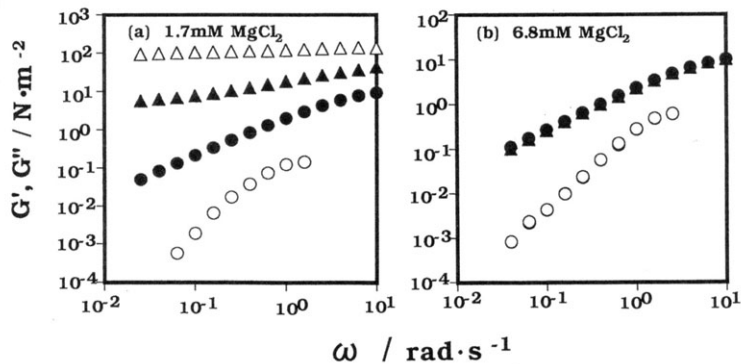


Fig.9

Frequency dependence of both moduli for mixtures with GELL/KGM=0.3/0.5 containing 1.7mM or 6.8mM MgCl₂ at 30 °C (the temperature was lowered from 60 °C to 30 °C at a cooling rate of 0.5 °C/min), 30 °C after a cooling and heating cycle between 30 °C and 0 °C. Cooling and heating rate: 0.5 °C/min.

helices of GELL molecules aggregated sufficiently, and that KGM molecules which are attached to larger aggregates of GELL helices could retard the helix-coil transition in GELL molecules. If KGM interacts with the disordered GELL molecules, synergism would be inhibited, because the electrostatic shield leads to the reduction of coil dimensions (Miyoshi et al., 1994a; Piculell et al., 1994) and then the overlap between GELL coils and KGM chains should decrease. However, as also shown in Figure 5 (c), (e), (f), (h), by addition of cations, the elastic moduli for mixtures significantly increased and the gel like behavior was observed at higher temperatures compared to that without salt (Figure 4), thus, this possibility should be excluded.

In the presence of 6.8mM $MgCl_2$ (Figure 7(b)), this mixture could not form a gel after the cooling and heating cycle. Therefore, it seems that the degree of mixed aggregates is governed by the degree of self-aggregated GELL helices, as well as by the mixing ratio of GELL/KGM.

5. Mechanism of the Interaction of Gellan Gum and Konjac Glucomannan

It has been studied in many hydrocolloid mixed systems that in ternary systems containing two polymers in a common solvent, the polymers may or may not associate, as described in the introduction. Association is usually described to explain the synergistic effects observed in some of mixtures, e.g. whey proteins and carboxymethyl cellulose (Hidalgo and Hansen, 1971) or xanthan and KGM (E.R.Morris et al., 1990b; Williams et al., 1991), whereas the segregation is thought of as a micro-phase separation, driven by an incompatibility of the two polymers (Annable et al., 1994b; Piculell et al., 1994).

The reason for the increase of G' by the addition of KGM may be ascribed to the following three possibilities: 1) An increase of effective concentration of GELL due to volume exclusion. 2) Segregation due to thermodynamic incompatibility. 3) Association of GELL and KGM. If molecular association occurs between GELL and KGM, the increase in G' should be more prominent in a mixture with higher molecular weight KGM. However, as illustrated above, no synergistic interaction was observed in mixtures of GELL and KGM with the highest molecular weight (NKGM), while mixtures of GELL and KGM with the lowest molecular weight (KGM2) show the synergistic interaction over a wider temperature range as well as over a wider mixing ratio. The elastic moduli of GELL/NKGM mixtures as a function of NKGM content increase with increasing NKGM content simply because G' of NKGM alone is far larger than that of gellan alone, so that synergism between GELL and NKGM should not contribute so much to the increase of G' . Therefore, in the case of GELL/ NKGM mixtures, the first or second possibility seems to be more plausible.

However, in the case of GELL/KGM with intermediate molecular weight, G' as a function

of mixing ratio showed a maximum only below 15 at a mixing ratio of GELL/KGM=0.6:1.0 (total polysaccharide concentration 1.6%). As for mixtures of total polysaccharide concentration 0.8%, the synergistic interaction occurs only at 0 around GELL/KGM ratio 0.3/0.5, which was in good agreement with the result of 1.6% mixtures of GELL/KGM. In the present study, solutions of 0.3% GELL alone could not form gels even if monovalent or divalent cations were present, however, a gel was formed on addition of 0.5% KGM at 0. This fact indicated that gel-like behavior was observed when the polymers are mixed at low concentrations, where exclusion effects are likely to be negligible. It is suggested that mixed aggregates of GELL/KGM consist of a core of aggregates of GELL helices with KGM chains attached to the surface, as described later. A similar conclusion was reached in recent studies on gels of κ -carrageenan mixed with galactomannan or glucomannan (Williams et al., 1993; E.R.Morris, 1990b, Piculell and Lindman, 1992, Piculell et al., 1994).

In this work, it seems that KGM chains attach to self-aggregates of GELL helices, rather than individual g GELL helices. This reason could be explained as follows. In the cooling process, the individual helices of GELL molecules were formed at a certain temperature, corresponding to the coil-helix transition temperature, and then these helices gradually aggregated with decreasing temperature, and as result, a certain ordered structure was formed whether it could lead to the gel formation or not. As shown in our studies, the synergism of GELL and KGM occurred at much lower temperatures than the coil-helix transition temperature. Therefore, it was suggested that the synergism should occur at low temperatures, where individual helices in GELL molecules sufficiently aggregated. This is similar to the results by Piculell et al. (1994) that the synergistic interaction disappeared in mixtures of KGM and κ -carrageenan in the presence of iodide ions, which inhibit the self-aggregation of κ -carrageenan helices.

In the presence of sufficient divalent cations, since GELL in mixtures could form various junction zones with different thermal stabilities, as described in the previous studies (Miyoshi et al., 1994ab, 1995ab, 1996; Miyoshi & Nishinari, 1999ab, 2000ab, Miyoshi, 1996, 2003, 2006). Thus, in the presence of sufficient divalent cations, many self-aggregates of GELL helices were formed and then KGM chains could attach to each surface of its aggregate. However, since the size of each aggregate of GELL helices became smaller, the size of mixed aggregates became smaller. This may explain the fact that the cooling DSC curve for mixtures with sufficient divalent cations became much broader compared to that for solutions of 0.3% GELL alone with the same concentration of divalent cations or mixtures with lower concentration of divalent cations. G' for mixtures with sufficient divalent cations also decreased rather than that for mixtures without divalent cations but showed a larger value than that for 0.3% GELL solutions with and without divalent cations (data not shown) because G' for KGM alone was far larger than

that for GELL alone. This may indicate that polymer segregation, which leads to weaker ordered structures, occurs. This explanation is favored by the possibility that the intermolecular binding complexes between GELL and KGM molecules could not form.

It was interesting that mixtures with low concentration of divalent or monovalent cations could not form gels even at 0 , although a mixture without salt could form weak gel only at 0 . If KGM interacts with GELL in coil conformation, since the electrostatic shield leads to the reduction of coil dimensions, the overlap between GELL coils and KGM chains should decrease in the presence of salts, and hence synergistic interaction between GELL and KGM would decrease. However, since with more progressive addition of salt, the elastic moduli for mixtures significantly increased and a gel formation was observed, this possibility should be excluded. Although KGM was uncharged, cations changed water structures around KGM molecules or GELL molecules, so that the chances that KGM chains attach to the self-aggregated GELL helices may decrease. This simply may relate to the low total polysaccharide concentration, however, it seems to be difficult to explain this phenomenon by a single factor.

Annable et al. (1994b) have studied for mixed potato maltodextrin (PMD)/hydrocolloid systems, and have reported that in the case of mixed PMD/carboxymethyl cellulose (CMC), phase separation could not be observed at all in the absence of electrolyte for the compositions investigated but was observed when electrolyte was present. They have also found that in the case of mixed PMD/gum arabic(GA), phase separation was observed without added electrolyte but only at very high polymer concentration. Both high polymer concentration and addition of salt to such mixtures (one of polymers in the mixture carried an ionic charge) should generally result in an increase of segregation. If the concentration of GELL increases, where GELL itself could form gel whether cations are present or not, the segregation due to thermodynamic incompatibility was promoted, so that no synergistic interaction may be observed in such high polymer concentration mixtures.

We have concluded that KGM is adsorbed onto the surface of large aggregates of GELL helices, and the synergistic interaction is promoted with increasing concentration of cations, however, in the presence of excessive divalent cations, the phase-separation in mixtures is promoted. However, the present data were obtained only from rheological and thermal measurements, indeed, more detailed studies based on other methods to describe the phenomena at the molecular level are required.

References

- Annable, P., Williams, P. A. and Nishinari, K. (1994a), Interaction in xanthan-glucomannan mixtures and the influence of electrolyte. *Macromolecules*, 27, 4204-4211.
- Annable, P., Fitton, M. G., Harris, B., Phillips, G. O. and Williams, P. A. (1994b), Phase

- behaviour and rheology of mixed polymer systems containing starch. *Food Hydrocoll.*, 8, 351-359.
- Brownsey, G. J., Cairns, P., Miles, M. J. and Morris, V. J. (1988), Evidence for intermolecular binding between xanthan and the glucomannan konjac mannan. *Carbohydr.Res.*, 176, 329-334.
- Cairns, P., Morris, V. J., Miles, M. J. and Brownsey, G. J. (1986), Effect of the molecular fine structure of galactomannans on their interaction properties. *Food Hydrocoll.*, 1, 89-93.
- Cairns, P., Miles, M. J., Morris, V. J. and Brownsey, G. J. (1987), X-ray fibre diffraction studies of synergistic, binary polysaccharide gel. *Carbohydr.Res.*, 160, 411-423.
- Cheetham, N. W. H. and Mashimba, E. N. M. (1988), Conformational aspects of xanthan-galactomannan. *Carbohydr.Polym.*, 9, 195-212.
- Cheetham, N. W. H. and Mashimba, E. N. M. (1991), Conformational aspects of xanthan-galactomannan gelation. Further evidence from optical-rotation studies. *Carbohydr.Polym.*, 14, 17-21.
- Dea, I. C. M. and Morrison, A. (1975) Chemistry and interactions seed galactomannans. *Adv. Carbohydr. Chem. Biochem.*, 31, 241-312.
- Dea, I. C. M. (1979), Interactions of ordered polysaccharide structures-synergism and freeze-thaw phenomena. In Blanshard, J. M.V. and Mitchell, J. R. (Eds.), *Polysaccharides in Food*, (p.p.229-247) Butterworths, London.
- Fernandes, P. B., Goncalves, M. P. and Doublier, J. L. (1991), A rheological characterization of kappa-carrageenan/galactomannan mixed gels: a comparison of locust bean gum samples. *Carbohydr.Polym.*, 16, 253-274.
- Fernandes, P. B., Goncalves, M. P. and Doublier, J. L. (1992), Effect of galactomannan Addition on the Thermal Behaviour of κ -Carrageenan Gels. *Carbohydr.Polym.*, 19, 261-269.
- Hidalgo, J. and Hansen, P. M.T. (1971), *J.Dairy Sci.*, 59, 1270-1274.
- Kohyama, K., Iida, H. and Nishinari, K. (1993), A mixed system composed of different molecular weights konjac glucomannan and kappa carrageenan: Large deformation and dynamic viscoelastic study. *Food Hydrocoll.*, 7, 213-226.
- Miyoshi, E., Takaya, T. and Nishinari, K. (1994a), Gel-sol transition on gellan gum aqueous solutions. I. Rheological studies on the effects of salts. *Food Hydrocoll.*, 8, 505-527.
- Miyoshi, E., Takaya, T. and Nishinari, K. (1994b), Gel-sol transition on gellan gum aqueous solutions. II. DSC studies on the effects of salts. *Food Hydrocoll.*, 8, 529-542.
- Miyoshi, E., Takaya, T. and Nishinari, K. (1995a), Gel-sol transition in gellan gum aqueous solutions. *Makromol.Symp.*, 99, 83-91.
- Miyoshi, E., Takaya, T. and Nishinari, K. (1995b) Effects of salts on the gel-sol transition of gellan gum by differential scanning calorimetry and thermal scanning rheology. *Thermochim.Acta*, 267, 269-287.

- Miyoshi, E. (1996), *Rheological and thermal studies on the sol-gel transition of gellan gum and mixed polysaccharides*. PhD Thesis, Faculty of Human Life Science, Osaka City University.
- Miyoshi, E., Takaya, T. and Nishinari, K., (1996a), Gel-sol transition on gellan gum aqueous solutions. I. Rheological studies on the effects of salts. *Carbohydr.Polym*, 36, 109-120.
- Miyoshi, E., Takaya, T. and Nishinari, K., (1996b), Effects of Glucose, Mannose and Konjac Glucomannan on the Gel-Sol Transition in Gellan Gum Aqueous Solutions by Rheology and DSC., *Polymer Gels & Networks*, 6, 273-290.
- Miyoshi, E., Takaya, T., Williams, P. A. and Nishinari, K. (1996c), Effects of Sodium Chloride and Calcium Chloride on the Interaction between Gellan Gum and Konjac Glucomannan., *J.Agric.Food Chem.*, 44, 2486-2495.
- Miyoshi, E., Takaya, T., Williams, P. A. and Nishinari, K. (1996d), Effects of Salts on the Interaction between Gellan Gum and Konjac Glucomannan., *Reports on Progress in Polymer Physics in Japan*, 39, 217-220.
- Miyoshi, E., Takaya, T., Williams, P. A. and Nishinari, K. (1997) Rheological and DSC Studies on Mixtures of Gellan Gum and Konjac Glucomannan., *Macromol.Symp.*, 120, 271-280.
- Miyoshi, E. (1998), Biopolymer-co-gels.(In Japanese), *The Japanese Society for Food Science and Technology*, 45, 73-82.
- Miyoshi, E., Takaya, T. and Nishinari, K. (1998), Effects of Glucose, Mannose and Konjac Glucomannan on the Gel-Sol Transition in Gellan Gum Aqueous Solutions by Rheology and DSC., *Polymer Gels & Networks*, 6, 273-290.
- Miyoshi, E. and Nishinari, K. (1999a), Non-newtonian flow behaviour of gellan gum aqueous solutions. *Colloid Polym.Sci.*, 277, 727-734.
- Miyoshi, E. and Nishinari, K. (1999b), Rheological and thermal properties near the sol-gel transition of gellan gum aqueous solutions. *Progr.Colloid .Polym.Sci.*, 114, 68-82.
- Miyoshi, E. and Nishinari, K. (2000a), In Phillips, G.O., Wedlock, D.J. and Williams, P.A. (Eds.), *Gums and Stabilisers for the Food Industry (Vol.10)* (pp.111-128), The Royal Society of Chemistry, Cambridge.
- Miyoshi, E. and Nishinari, K. (2000b), Physicochemical Properties of Gellan Gum Aqueous Solutions. *Reports on Progress in Polymer Physics in Japan*, Special Issue, 43, 665-688.
- Miyoshi, E. (2001), What is Gel?, *Development and Environment*, 2, 19-39.
- Miyoshi, E. (2003), Some Theoretical Approach to the Sol-Gel Transition of Gellan Gum. *Development and Environment*, 4, 3-33.
- Miyoshi, E. (2006), A Study on the Structural Changes of Aqueous Environment Surrounding Gellan Gum Molecules. *Development and Environment*, 6, 5-22.
- Morris, V., J. (1986), In Phillips, G.O., Wedlock, D.J. and Williams, P.A. (Eds.) *Gums and Stabilisers for the Food Industry (Vol.3)*, (p.p.87-99) Elsevier Applied Science Publishers,

London and New York.

- Morris, E. R. (1990), Mixed polymer gels. In Harris, P. (Ed.) *Food Gels*, Elsevier Applied Science (p.p.291-359), London.
- Morris, E. R. (2000), Rheology of biopolymer co-gels. In Nishinari, K. (Ed.) *Hydrocolloids Part 2: Fundamentals and Applications in Food, Biology (p.p.135-146), and Medicine*, Elsevier, The Netherlands.
- Nishinari, K., Koide, S. and Ogino, K. (1985), On the temperature dependence of elasticity of thermoreversible gels., *J. Phys. France*, 46, 793-797.
- Nishinari, K., Miyoshi, E., Takaya, T. and William, P. A. (1995a), Mixtures of Gellan Gum and Konjac Glucomannan I. Rheological Study., *Reports on Progress in Polymer Physics in Japan*, 38, 651-654.
- Nishinari, K., Miyoshi, E., Takaya, T. and William, P. A. (1995b), Mixtures of Gellan Gum and Konjac Glucomannan II. DSC Study, *Reports on Progress in Polymer Physics in Japan*, 38, 655-656.
- Nishinari, K., Miyoshi, E., Takaya, T. and William, P. A. (1996), Rheological and DSC Studies on the Interaction between Gellan Gum and Konjac Glucomannan., *Carbohydr. Polym.*, 36, 193-208.
- Oakenfull, D., Miyoshi, E., K. Nishinari and Scott, A. (1999), Rheological and Thermal Properties of Milk Gels Formed with κ -Carrageenan. I. Sodium Caseinate., *Food Hydrocoll.*, 13, 525-533.
- Oakenfull, D., Nishinari, K. and Miyoshi, E. (2000), A Comparative Study of Milk Gels Formed with κ -Carrageenan or Low-Methoxy Pectin., In Nishinari, K. (ed.) *Hydrocolloids Part 2: Fundamentals and Applications in Food, Biology, and Medicine* (p.p.153-163) Elsevier.
- Piculell, L. and Lindman, B. (1992) Association and segregation in aqueous polymer/polymer, polymer/surfactant, and surfactant/surfactant mixtures: similarities and differences. *Adv. Coll. Interf. Sci.*, 41, 149-178.
- Piculell, L., Illiopoulos, I., Linse, P., Nilsson, S., Turquois, T., Viebke, C. and Zhang, W. (1994) Association and segregation in ternary polymer solutions and gels. in Phillips, G. O., Wedlock, D. J. and Williams, P. A. (Eds.) *Gums and Stabilisers for the Food Industry, Vol. 6*, (p.p.309-322), Oxford University Press, Oxford.
- Rochas, C., Taravel, F. R. and Turquois, T. (1990), N.M.R. studies of synergistic kappa-carrageenan/carob galactomannan gels. *Int. J. Biol. Macromolecules*, 12, 353-358.
- Shatwell, K. P., Sutherland, I. W., Ross-Murphy, S. B. and Dea, I. C. M. (1991), Influence of the acetyl substituent on the interaction of xanthan with plant polysaccharides-III. Xanthan-konjac mannan systems. *Carbohydr. Polym.*, 14, 29-51, 115-130, 131-147.
- Tako, M and Nakamura, S (1986) Synergistic interaction between kappa-carrageenan and locust-bean gum in aqueous media. *Agric. Biol. Chem.*, 50, 2817-2822.

- Turquois, T., Rochas, C. and Tareel, F.R. (1992) Rheological studies of synergistic kappa carrageenan-carob galactomannan gels. *Carbohydr. Polym.*, 17, 263-268.
- Williams, P.A., Day, D.A., Langdon, M.J., Phillips, O.G. and Nishinari, K. (1991) Synergistic interaction of xanthan gum with glucomannans and galactomannans. *Food Hydrocoll.*, 6, 489-493.
- Williams, P. A., Clegg, S. M., Langdon, M. J., Nishinari, K and Piculell, L. (1993) Investigation of the gelation mechanism in κ -carrageenan/konjac mannan mixtures using differential scanning calorimetry and electron spin resonance spectroscopy. *Macromolecules*, 26, 5441-5446.
- Williams, P.A., Annable, P., Phillips, O.G. and Nishinari, K. (1994) Mixed Polysaccharides Gels Formed between Xanthan Gum and Glucomannan. In Nishinari, K (Ed.) *Food Hydrocolloids: Structures, Properties and Functions* (p.p.435-449) Plenum Press, New York.

Synergistic Interaction between Helix-Forming Polysaccharide and Konjac Glucomannan

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It is known that when more than two polymers are mixed, the properties of mixtures are superior to those of either component polymer or they change qualitatively; this phenomenon is described as 'Synergism'. The synergistic effects between galactomannan and these polysaccharides impart increased elasticity and strength to the gel under conditions at which the pure components would not gel.

Konjac glucomannan (KGM) interacts with non-gelling concentrations of helix-forming polysaccharides to produce gels whose rheological properties and melting point are similar to those of gel obtained with galactomannan. Since gellan gum (GELL) is a helix-forming polysaccharide, analogous to carrageenans, it is expected that synergism might be observed in GELL/KGM mixtures, similar to that in carrageenan/KGM mixtures.

In this study, we investigate the rheological and thermal properties of GELL/KGM mixtures by dynamic viscoelastic measurement and differential scanning calorimetry are reviewed. In particular, the effects of molecular weight of the KGM on these properties and the results are discussed, and the effects of monovalent and divalent cations on the interaction between GELL and KGM are also described in order to elucidate the mechanism of interaction.

Three fractions of KGM with different molecular weights (NKGM, KGM1, KGM2) are used in order to investigate the interaction between GELL and KGM. In the case of GELL/KGM with an intermediate molecular weight, the synergistic interaction occurs only at lower temperatures around GELL/KGM ratio 0.3/0.5.

We have concluded that KGM is adsorbed onto the surface of large aggregates of GELL helices. Further the synergistic interaction is promoted with increasing concentration of cations, however, in the presence of excessive divalent cations, phase-separation is promoted in mixtures.