

New Application of Konjac Glucomannan as a Texture Modifier

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Abstract

In addition to being used as a material for the preparation of traditional alkaline gel, konjac glucomannan (KGM) can be utilized as a texture modifier under neutral or acidic conditions. Rheological and thermal properties of KGM with different molecular weights were studied under neutral conditions to promote further utilization. KGM molecules showed a coil overlap and entanglements even at a low concentration (0.01%). The mixed gels of KGM and κ -carrageenan (CAR) were considered to involve 2 crystalline regions: one consisting only of CAR molecules and the other consisting of the interaction between CAR and KGM. Upon heating, the latter region was disintegrated at a lower temperature and the former melted at a higher temperature. Gels containing KGM with a higher molecular weight or a higher KGM content have a stronger tendency to make junction zones formed by CAR and KGM.

Discipline: Food

Additional key words: differential scanning calorimetry, gel, viscoelasticity, Viscosity

Introduction

Konjac glucomannan (KGM) is a major component of the tuber of *Amorphophallus konjac* K. Koch, which grows in Southeast Asia⁷⁾. Its main chain is composed of β -1, 4-linked D-mannose and D-glucose, and it forms a highly viscous solution. KGM forms a thermo-irreversible gel, which is known as “konnyaku”, a Japanese traditional food, under alkaline conditions (pH = 11–12). KGM is not consumed in other countries. However, it has recently attracted a great deal of attention as a texture modifier which controls the rheological properties of food. The new utilizations of KGM include the improvement of viscosity of a food system, stabilization of a dispersion or an emulsion, gelling agent under neutral or acidic pH, holding of water, etc. For such new applications, one of the basic properties, high viscosity, seems to be especially important, and the molecular weight, which strongly affects the viscosity, is a key parameter.

A mixture of KGM and κ -carrageenan (CAR) gives rise to thermo-reversible gels under neutral or acidic conditions. This konjac jelly has become one

of the most appreciated dessert products in Japan today. Cairns et al.¹⁾ observed the lack of interaction between CAR and KGM based on X-ray fiber diffraction patterns, and proposed a model involving a CAR network containing KGM for the mixed gel. However, Williams et al. observed some interaction between the 2 polysaccharides by differential scanning calorimetry (DSC) and electron spin resonance⁸⁾. We proposed a new model involving 2 kinds of junction zones^{4,5)}. Some of them are formed by the CAR molecules alone, while KGM molecules interact with CAR and make weaker junction zones than those formed by CAR alone. Influences of total gum content, CAR/KGM ratio, and molecular weight of KGM on the gel properties are discussed in the present paper.

Materials and methods

1) Materials

Commercially available κ -carrageenan given by San-Ei Gen F. F. I., Inc. (Osaka), and powdered KGM from konjac tuber and fractions of KGM with different molecular weights, prepared by enzymatic degradation, supplied by Shimizu Chemical Co.

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(Hiroshima) were used. Intrinsic viscosity ($[\eta]$), Huggins coefficient (k') and molecular weight (M_w) of the samples are shown in Table 1. A fractionation based on KGM solubility in a mixed solvent composed of water and methanol was also performed for viscometry.

Table 1. Molecular weight of CAR and various KGM samples

Sample	$[\eta]^{a)}$ (dL/g)	$k'^{a)}$	$M_w^{b)}/10^3$
CAR	-	-	493
LM1	1.98	0.38	256
LM2	2.63	0.31	438
LM3	-	-	444
LM4	3.50	0.41	596
ND	3.91	0.48	689

a): With Ubbelohde viscometer at 25°C in cadoxen²⁾.

b): By gel permeation chromatography at 60°C in 50 mM NaNO₃ for CAR and at 23°C in cadoxen for KGM.

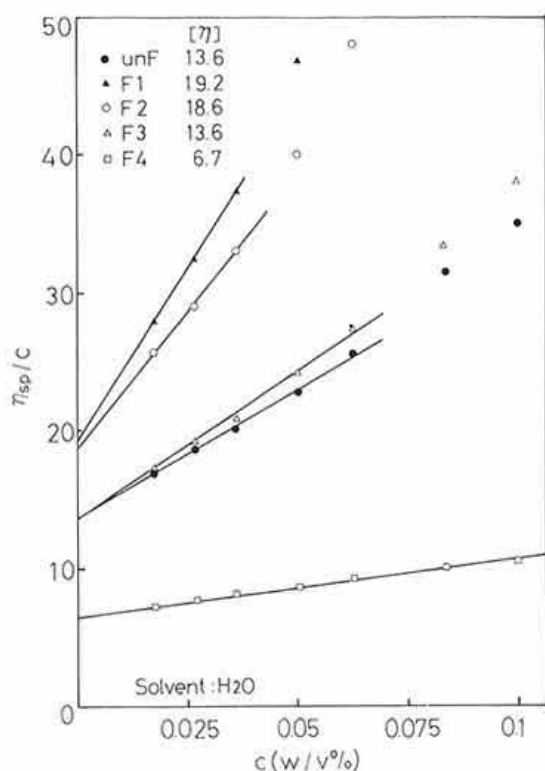


Fig. 1. Reduced viscosity as a function of the concentration of konjac glucomannan in water at 25.4°C

Symbols represent unfractionated material, fractions 1, 2, 3, and 4 from above. Fraction number indicates the order of molecular weight. $[\eta]$ is the intrinsic viscosity (Y-intercept) in dL/g.

2) Rheological measurement

Intrinsic viscosity was determined using Ubbelohde viscometers at 25°C. The flow times for solvents were approximately 240 s. The viscosity of aqueous KGM solutions was also observed using a low shear rate viscometer³⁾ at 25°C. The storage and loss moduli (G' and G'') were measured with a Rheograph Sol (Toyoseiki Seisakusho, Tokyo) as previously reported^{4,5)}.

3) Differential scanning calorimetry (DSC)

Measurements were carried out using a Micro-DSC III (Setaram, Caluire) as described in a previous report⁵⁾.

Results and discussion

1) Viscosity of KGM solutions

The plots of reduced viscosity (η_{sp}/c) against KGM concentration (c) in water and 4 M urea solution are shown in Figs. 1 and 2, respectively. Fractions with higher molecular weight showed a deviation from linearity in the plot of reduced

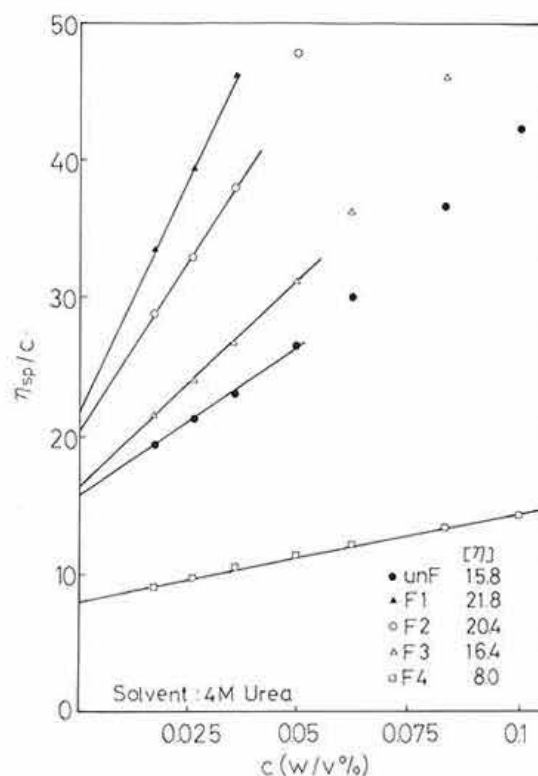


Fig. 2. Reduced viscosity as a function of the concentration of konjac glucomannan in 4M urea solution at 25.4°C

Symbols are the same as in Fig. 1.

viscosity against concentration at lower concentrations in both solvents compared with the fractions with a lower molecular weight. Each fraction in 4 M urea had a higher value for the intrinsic viscosity ($[\eta]$) than that in water, presumably due to the effects of urea, which breaks hydrogen bonds between hydroxyl groups in KGM molecules leading to a more expanded conformation of KGM molecules.

The relationships between the logarithm of the zero shear specific viscosity (η_{sp0}) and the logarithm of KGM concentration (c) are shown in Fig. 3. $\log \eta_{sp0}$ increased linearly with increasing $\log c$ when the value of $\log \eta_{sp0}$ was less than about 1. The double logarithmic plots of the zero shear specific viscosity η_{sp0} against the coil overlap parameter ($c[\eta]$) are shown in Fig. 4. For dilute solutions, slopes of the plots were close to 1.4 for all the fractions as observed for many polysaccharide solutions⁶⁾. It was not possible to obtain a clear inflection point⁶⁾ of the curves in Fig. 4, because the low solubility of konjac glucomannan made it difficult to prepare solutions which exhibited large $c[\eta]$ values. However the inclination of the slope of the curves increased gradually with increasing $\log c[\eta]$, suggesting that significant coil overlap and entanglement had already

started when $c[\eta] > 1$. The onset of coil overlap occurs at lower concentrations for KGM molecules than for other polysaccharides⁶⁾.

2) Thermal scanning rheological measurements of KGM/CAR mixtures

Fig. 5 shows the storage and loss moduli for CAR and CAR/KGM mixtures in the cooling process. At higher temperatures, all the samples tested were sols and the loss modulus was slightly larger than the storage modulus. A sol containing higher molecular weight KGM showed higher moduli. KGM alone did not gel. Below the sol-gel transition temperature (T_{gel}), the storage modulus became far larger than the loss modulus for all the samples.

As shown in Fig. 6, when the gel state mixture was heated, the values of storage and loss moduli decreased with temperature. However the values were larger than those observed during cooling at the same temperature in the temperature range of 20–60°C. Samples showed similar values of storage and loss moduli both in the heating and cooling processes at a temperature above the melting temperature or gel-sol transition temperature (T_{sol}). All the mixed systems exhibited T_{gel} and T_{sol} values between those

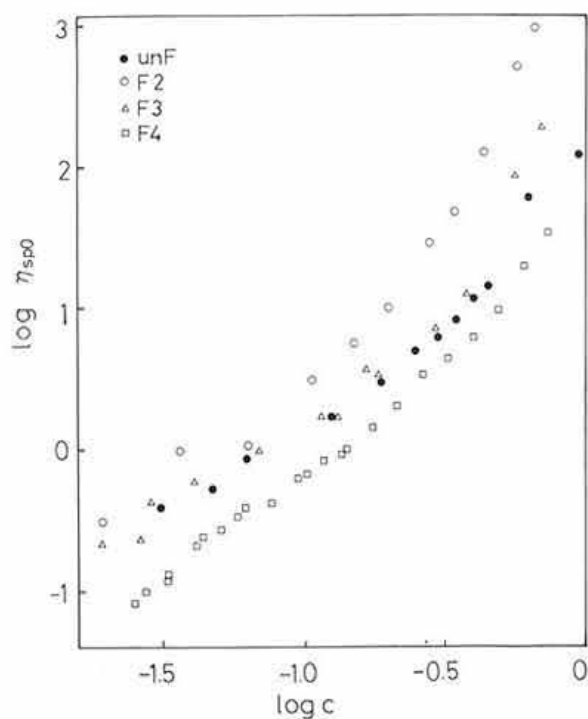


Fig. 3. Concentration dependence of the zero shear specific viscosity η_{sp0} for konjac glucomannan solution

Symbols are the same as in Fig. 1.

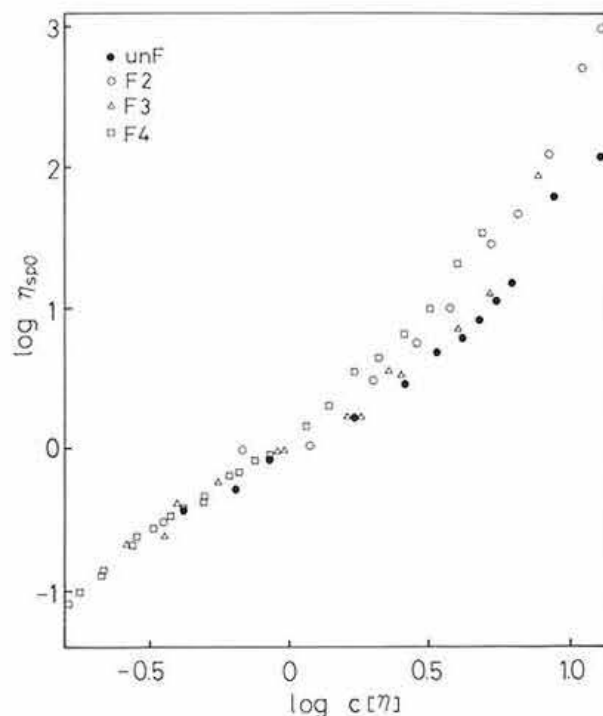


Fig. 4. Dependence of the zero shear specific viscosity η_{sp0} of konjac glucomannan on the coil overlap parameter $c[\eta]$

Symbols are the same as in Fig. 1.

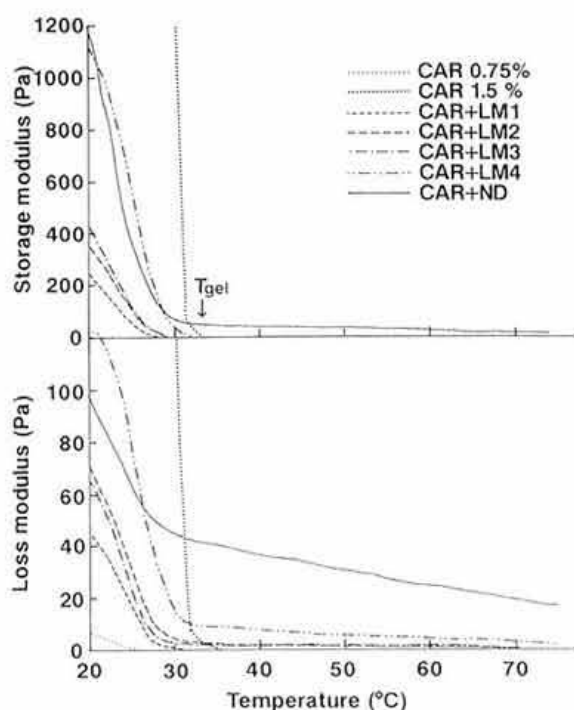


Fig. 5. Temperature dependence of storage and loss moduli for CAR and KGM mixtures (1.5w/w%) in the cooling process. Cooling rate: 1.0°C/min. The arrow indicates the sol-gel transition temperature (T_{gel}) for the 1.5w/w% CAR sample.

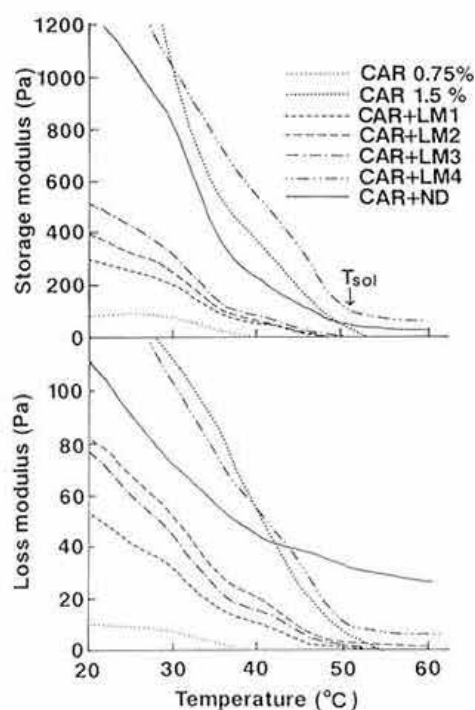


Fig. 6. Temperature dependence of storage and loss moduli for CAR and KGM mixtures (1.5w/w%) in the heating process. Heating rate: 1.0°C/min. The arrow indicates the gel-sol transition temperature (T_{sol}) for the 1.5w/w% CAR sample.

of 1.5w/w% and 0.75w/w% CAR.

3) Thermal properties of KGM/CAR mixtures determined by DSC

An exothermic peak corresponding to the sol-gel transition in the DSC curves of the cooling process and an endothermic peak indicating the gel-sol transition in DSC curves of the heating process were observed for CAR alone systems (Fig. 7). Both peaks shifted to higher temperatures with increasing CAR concentrations. KGM alone did not show any peak in either the cooling or the heating processes.

As shown in Fig. 8 (left), DSC peaks shifted to lower temperatures and the peak area decreased with decreasing CAR content in the 1.5w/w% mixture. The mixtures with excess CAR (>0.7) clearly showed a second exothermic peak at a lower temperature in the DSC curves of the cooling process. Although all the 5/5 mixed systems showed similar DSC curves for the cooling process (Fig. 7, left), the peak temperature (T_c) slightly shifted to higher temperatures with the increase of the molecular weight of KGM.

In the heating process, 2 peaks at T_{1h} and T_{2h} were observed in the 5/5 systems, and these peak

temperatures slightly shifted to higher temperatures with the increase of the molecular weight of KGM (Fig. 7, right). As clearly shown in Fig. 8 (right), both T_{1h} and T_{2h} shifted to lower temperatures with the increase of the ratio of KGM to CAR. Since KGM alone did not show any peak in the heating process, the total peak area increased with the decrease of the KGM content. However, the ratio of the peak area of the lower endothermic peak (ΔH_{1h}) to that of the higher one (ΔH_{2h}) increased with the increase of the KGM content in the mixture, suggesting that KGM contributes to the formation of the network structure of the mixed gels.

The peak temperatures T_c for the mixed systems were higher than that for 0.75w/w% CAR alone (Fig. 7, left), but lower than that for 1.5w/w% CAR (Fig. 7, left), which agrees well with the observation of the dynamic viscoelasticity (Fig. 5). ΔH_{1h} observed in the 5/5 mixture became larger and ΔH_{2h} became smaller with the increase of the molecular weight of KGM. This fact suggests that KGM molecules with a high molecular weight have a stronger

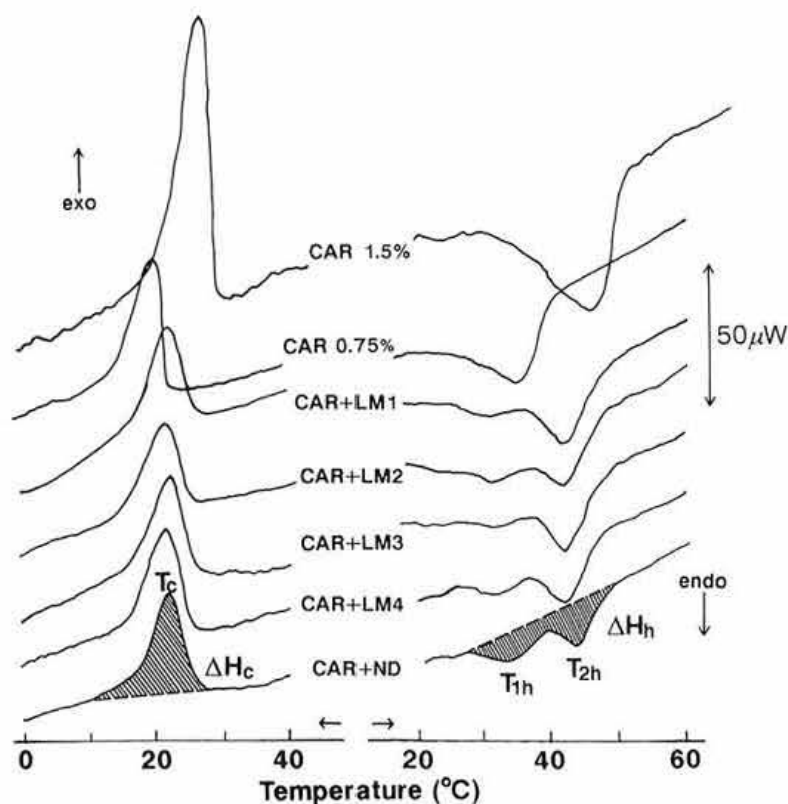


Fig. 7. DSC curves of cooling (left) and heating (right) processes for CAR and KGM mixtures

Total gum content for 5/5 mixtures of CAR and KGM: 1.5w/w%. Scanning rate: 1.0°C/min. The upward direction corresponds to the exotherm. Examples of the peak temperatures are depicted for T_c , T_{h1} and T_{h2} . Examples of the heat required for the transition are shown by the shaded area. The enthalpy for the sol-gel or gel-sol transition (ΔH_c or ΔH_h) was calculated by dividing the area by the amount of CAR (g).

tendency to interact with CAR molecules than KGM molecules with a lower molecular weight. Some of the CAR molecules, which occurred in small numbers in the systems containing higher molecular weight KGM and which did not interact with KGM, formed junction zones by themselves.

When the mixed gel was heated, the weaker junction zones of CAR and KGM broke down at a lower temperature (T_{h1}), while the stronger junction zones formed by the CAR molecules alone melted at a higher temperature (T_{h2}). The number of weak junction zones increased while the number of junction zones made by CAR-CAR decreased with the increase of the KGM molecular weight in the 5/5 mixture, because the formation of weaker junction zones by CAR-KGM interaction was promoted by the increase of the molecular weight of KGM. As a result, the number of CAR molecules that were able to form

junction zones by CAR-CAR interaction decreased.

Since CAR in the mixed systems was common, the fact that the values of the viscoelastic parameters of 1.5w/w% CAR gels were much larger than those of any mixed gels of CAR and KGM indicates that the number of junction zones, hence the number of elastically active chains, was larger in the gels of CAR alone than in the gels of CAR-KGM mixtures with the same total polysaccharide content. The DSC observation shows that the junction zones formed by CAR alone were also more heat-resistant. However, the number of stronger junction zones formed by CAR alone is likely to decrease in mixed gels containing KGM with a higher molecular weight.

Conclusion

The following 2 characteristics are useful for new

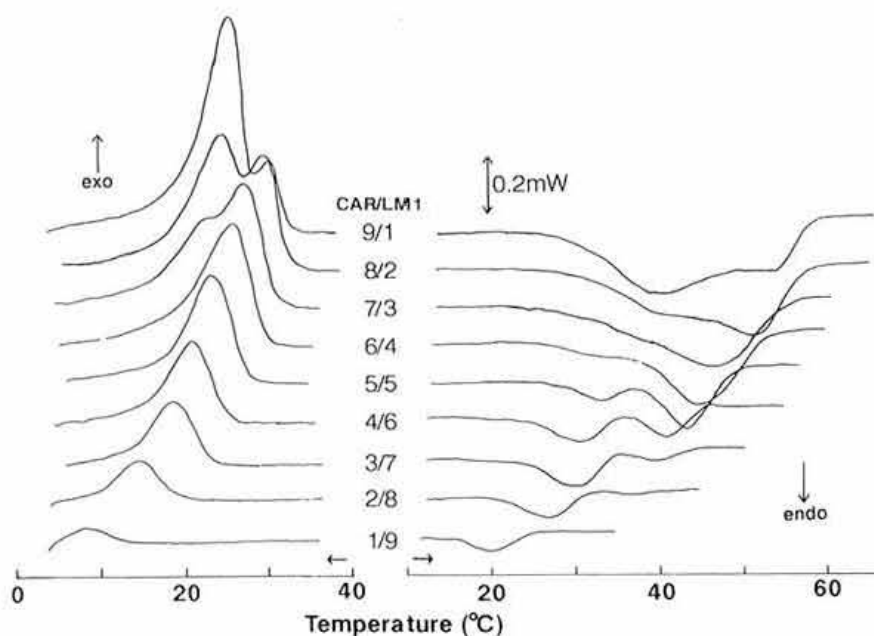


Fig. 8. DSC curves of cooling (left) and heating (right) processes for 1.5w/w% mixtures of CAR and KGM in various ratios
Scanning rate: 1.0°C/min. KGM sample is denoted as LM1. Figures beside DSC curves indicate the ratio of CAR/KGM.

applications of KGM as a texture modifier.

1) KGM in water or 4M urea exhibited coil overlap and entanglement even at a low concentration of about 0.01%.

2) The mixed gel of KGM and CAR involved 2 crystalline regions: one formed by CAR molecules alone and the other by the interaction between CAR and KGM. The latter showed a lower thermal stability than the former. The junction zone consisting of CAR and KGM can be easily formed in a mixed system with a higher KGM ratio, or containing KGM with a higher molecular weight.

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