Synergistic Interaction of Konjac Glucomannan and Gellan Gum Investigated by Rheology and Texture Analysis

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ABSTRACT: The rheological kinetics of konjac glucomannan and gellan gum mixed sols were studied using rotational concentric cylinder viscometer. The effects of polymers weight ratio, shear rate, and temperature were systematically investigated. The curves showed a Newtonian plateau followed by strong shear thinning that can be described by a power law dependence on the shear rate. The dynamic viscoelastic character was evaluated by measurements of small-deformation oscillatory. After adding some cations, the mixed sols turned into mixed gels. The contribution of Na^+, K^+, Ca^{2+}, and Zn^{2+} at different concentration was also evaluated by texture analysis. The results reveal a strong dependence of the structural properties of different samples on their preparation conditions. A fine turning of the properties of the mixed sols is possible through the change of the temperature preparation and/or the polymer weight ratio. The texture properties of the mixed gels were also possibly influenced significantly by the cations. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1363–1370, 2012

Key words: konjac glucomannan; gellan gum; rheology; texture

INTRODUCTION

Binary mixtures of certain polysaccharides often exhibit unexpected synergistic interactions, e.g., the mixture may gel under the conditions where the individual components are nongelling. Striking example of this behavior occurs when the bacterial polysaccharide xanthan gum is mixed with some plant galactomannans.[1,2]

Konjac glucomannan is a high molecular weight water-soluble nonionic heteropolysaccharide found in tubers of the *Amorphophallus konjac* plant. Konjac glucomannan is a linear random copolymer of (1→4)-β-D-glucopyranose and β-D-mannopyranose, having glucose and mannose units in a molar ratio of 1 : 1.6 with a low degree of acetyl groups (∼ 1 acetyl group per 19 residues) at the C-6 position.[3] Because of its high viscosity property, konjac gum is generally added to other hydrocolloids to elevate the viscosity of blended colloid systems to improve food quality.[4,5] However, synergistic interactions emerge variously due to the molecular distinction in colloids. Mixing the two phases of konjac glucomannan and gelatin, they redissolved into two liquid layers,

which showed they have no synergistic interaction at all.[6] However, konjac gum and rice starch were synergistic. The addition of konjac glucomannan reduced the syneresis which moderated/reduced an increase in gel hardness in rice starch gels subjected to repeated freeze-thaw cycles.[7]

Gellan gum is an extracellular polysaccharide produced by aerobic fermentation of *Sphyngomonas elodea*.[8,9] The deacylated form is an anionic polysaccharide consisting of a linear tetrasaccharide repeating unit of [→3)-β-D-glucose-(1→4)-β-D-glucuronic acid-(1→4)-β-D-glucose-(1→4)-α-L-rhamnose-(1→].[10] It forms firm, hard, and brittle gels, with gelation being dependent on the type of cation, ionic strength, temperature, and polymer concentration.[11–13]

Synergistic interaction exists between konjac glucomannan and gellan gum. In konjac glucomannan and gellan gum mixtures, the main ordered structure may be formed by gellan molecules, and konjac glucomannan molecules inhibit gellan molecules to form the ordered structure.[14] However, the present data are obtained only from oscillatory measurements and thermal measurements, and, investigation by other method is required. At the same time, systematic study of the mixtures on rheological properties is still lacking.

In the present work a comparison among samples prepared at different weight ratios, temperatures, cations and ionic strength was reported. Apparent viscosity, dynamic rheological tests and texture analysis techniques were applied. The synergistic interaction of them was also discussed in further detail.

MATERIALS AND METHODS

Materials

Konjac glucomannan was prepared as our previous work.[15] The viscosity-average molecular weight (M_v) of the konjac glucomannan was determined by viscometry to be 1.32×10^6 according to the Mark–Houwink equation

$$[\eta] = 5.96 \times 10^{-2} M_v^{0.73} \quad \text{at } 25^\circ\text{C}$$

Deacetylated gellan polymer powder, Kelcogel, was provided by Kelco (San Diego, CA), which was used without further purification.

All other products and reagents were of analytical grade.

Konjac glucomannan and gellan gum mixed sols, gels preparation

Sols of konjac glucomannan and gellan gum at various ratios were prepared by mixing the appropriate amounts of each powder and dispersing in distilled water to a total concentration of 1 wt %. The homogenized sols left to rest for 60 min at 90°C, then cooled to room temperature. By changing the weight ratio of konjac glucomannan to gellan gum 1 : 9, 3 : 7, 5 : 5, 7 : 3, 9 : 1, a series of blend sols coded as KG1, KG3, KG5, KG7, and KG9 were prepared, respectively. The sols obtained from pure konjac glucomannan and gellan gum were coded as KGM and GG. The gels of konjac glucomannan and gellan gum were prepared as following. After the mixed solution rested for 60 min at 90°C, a specific weight of cations was added in various concentrations and stirred homogeneously. Then the hot samples were immediately transferred to a small plastic beaker, which formed the gels at room temperature.

Rheological kinetics measurement

The measurements were taken using a rotational concentric cylinder viscometer(HAAKE RV12,Germany). The prepared sols of different weight ratio were filled into the cups and shear rate was increased from 0 to 250 s^{-1}. The temperature of the sample was maintained at 30°C for controlling the stability of the sample. To determine the effect of temperature on the rheological kinetics characterization of the sols, we measured the viscosity of KG5 at 20, 30, 40, 50, and 60°C with other conditions constant.

Dynamic viscoelastic measurement

The viscoelastic behavior of the samples was assessed by dynamic oscillation test (AR500, TA,
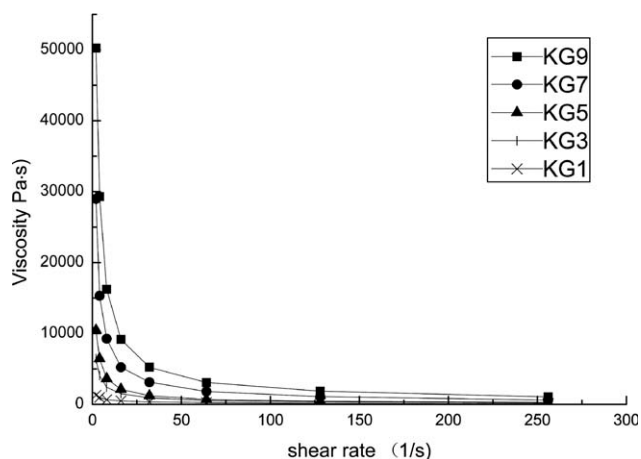
Figure 1 Effect of different proportions on apparent viscosity.

UK) through the small-deformation oscillatory which controlled the deformation of 5%. Oscillatory measurements were performed at 25°C using parallel plates, with a frequency sweep from 0.1 to 100 rad s^{-1}. All the measurements were performed within the linear viscoelastic regime. G' (storage modulus), G'' (loss modulus), and the loss tangent or tan δ (G''/G') were recorded.

Texture analysis

The textural characteristics of gels were analyzed using a TA.XT plus Texture Analyzer (Stable Micro Systems, London, UK) by texture profile analysis (TPA). The samples were prepared according to the salt ramps described above in the preparation of gels. The mixed gel samples were compressed twice by a cylinder probe (P0.5SS) with 4-mm deformation at 1 mm s^{-1}. Three replicates of each measurement were carried out. The hardness and cohesiveness were obtained from TPA curves.

RESULTS AND DISCUSSION

Rheological kinetics characterization

The hydrodynamic equations of the mixed sols

It was known that most fluid do not follow the simple Newtonian rheological model in which a linear relationship exists between shear stress (τ) and shear rate (γ), τ = η × γ. Instead of characterizing the flow behavior with a simple viscosity constant (η), at least two parameters and more complex models, non-Newtonian, are needed.

The plot of apparent viscosity against shear rate of different ratio KGM/GG sols is shown in Figure 1. There was a significant difference in the apparent viscosity of the konjac glucomannan and gellan gum mixed sols containing different ratio of konjac
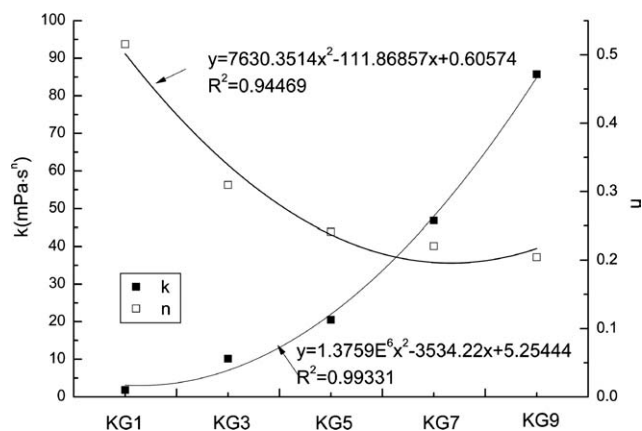
Figure 2 K and n value of KG1, KG3, KG5, KG7, and KG9.

glucomannan and gellan gum. It was observed that the viscosity of mixed sols increased quickly with the increased ratio of konjac glucomannan. The mixed sols possessed pseudoplastic or shear-thining behavior. As the shear rate increased, the particle–particle interaction was deformed and finally disrupted and resulted into a stronger molecular orientation which decreased the intermolecular force. Correspondingly, it led to a drop in viscosity.

A very widely used nontime dependent non-Newtonian model is $\tau = K \times \gamma^n$, where τ is the shear stress, γ is the shear rate, K is the consistency index (mPa s^n) which increases with increasing solids content, n is the flow behavior index as a measure of the departure from Newtonian flow. The Power law model was applied to describe the rheological kinetics characterization of the mixed sols. The value of the consistency index (K) and flow behavior index (n) were fitted to Power law model by computer. Figure 2 shows the connection among K, n and ratio of konjac glucomannan/gellan gum sols. It was observed that n value was changed from 0.5155 to 0.2043 with an increase in the ratio of konjac glucomannan. This implied that with more konjac glucomannan, the sol presented more pseudoplastic. The n value of the point near KG7 was the minimum, which showed the breaking point of the flow behavior index (n) curve. It was considered that the mixed sol showed more pseudoplastic at this point. This conclusion was consistent with our previous research.[16]

Influence of shear rate on the mixed sols

The shear rate also markedly influences the properties of the mixed sols. For the fixed ratio of a mixed sol, the viscosity of the mixture depended on the sign of the shear rate gradient in the low shear rate range but not in the high shear rate range. With increasing shear rate the sol showed unusual shear-thinning flow behavior at low shear rate range. However, the viscosity changed less when the shear rate increase in the high range (Fig. 1). This might be explained as followed: molecular chains between two polymers may form physic crosslink points by entanglements or the van der Waals interactions. These crosslink points are in a state of dynamic departures-rebuilding equilibrium. Therefore the sols constitute a transient crosslink three-dimensional structure. When the shear rate increases to a certain value, the departure speed is larger than the rebuilding speed and correspondingly causes a decrease of apparent viscosity. The sol shows the characteristic of pseudoplastic, which means the departure of entanglements leading to the decrease of viscosity during shearing.

Effect of temperature on rheological kinetics characterization

Temperature influenced apparent viscosity values significantly. As shown in Figure 3, KG5 had pseudoplastic and the shear-thinning characteristics, exhibited as Newtonian rheological behavior with the increasing of shear rate. As the temperature rose, the impact of shear rate on the apparent viscosity decreased gradually. The increasing temperature caused increase of free volume and mobility among the molecule chains, which was attributed to the decreasing interaction between molecules. The apparent viscosity decreased exponentially with the increase of temperature. Therefore, temperature is an important factor to adjust the apparent viscosity of polymers.

The value of the consistency index (K) and flow behavior index (n) at different temperature were fitted to the power function by computer. Figure 4 shows the relation among the temperature, K and n. The value of n increased from 0.1904 to 0.3565 while
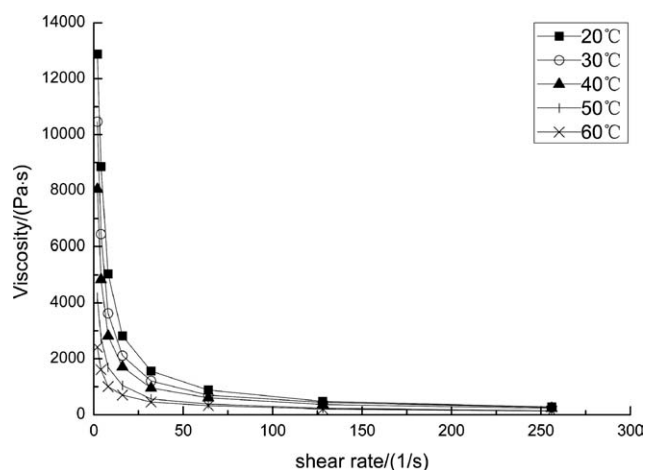

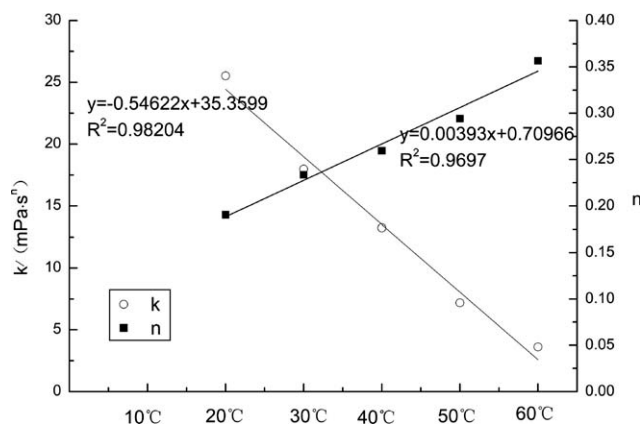**Figure 3** Effect of different temperature on apparent viscosity of KG5.

Figure 4 K and n value of different temperatures of KG5.

the value of K was in a linear decrease with the increase of temperature (Fig. 4). It means the higher the temperature, the less the pseudoplastic behavior. We may conclude that temperature control could be used to attain the needed K and n in food industry.

Dynamic viscoelastic characterization

From dynamic tests performed in the linear viscoelastic range, the storage modulus, G', the loss modulus, G'', and the loss tangent or tan δ (G''/G') can be obtained. G' value representing the elastic behavior of a sample is a measure of deformation energy stored in the sample during the shear process. On the contrary, G'' corresponding to the viscous
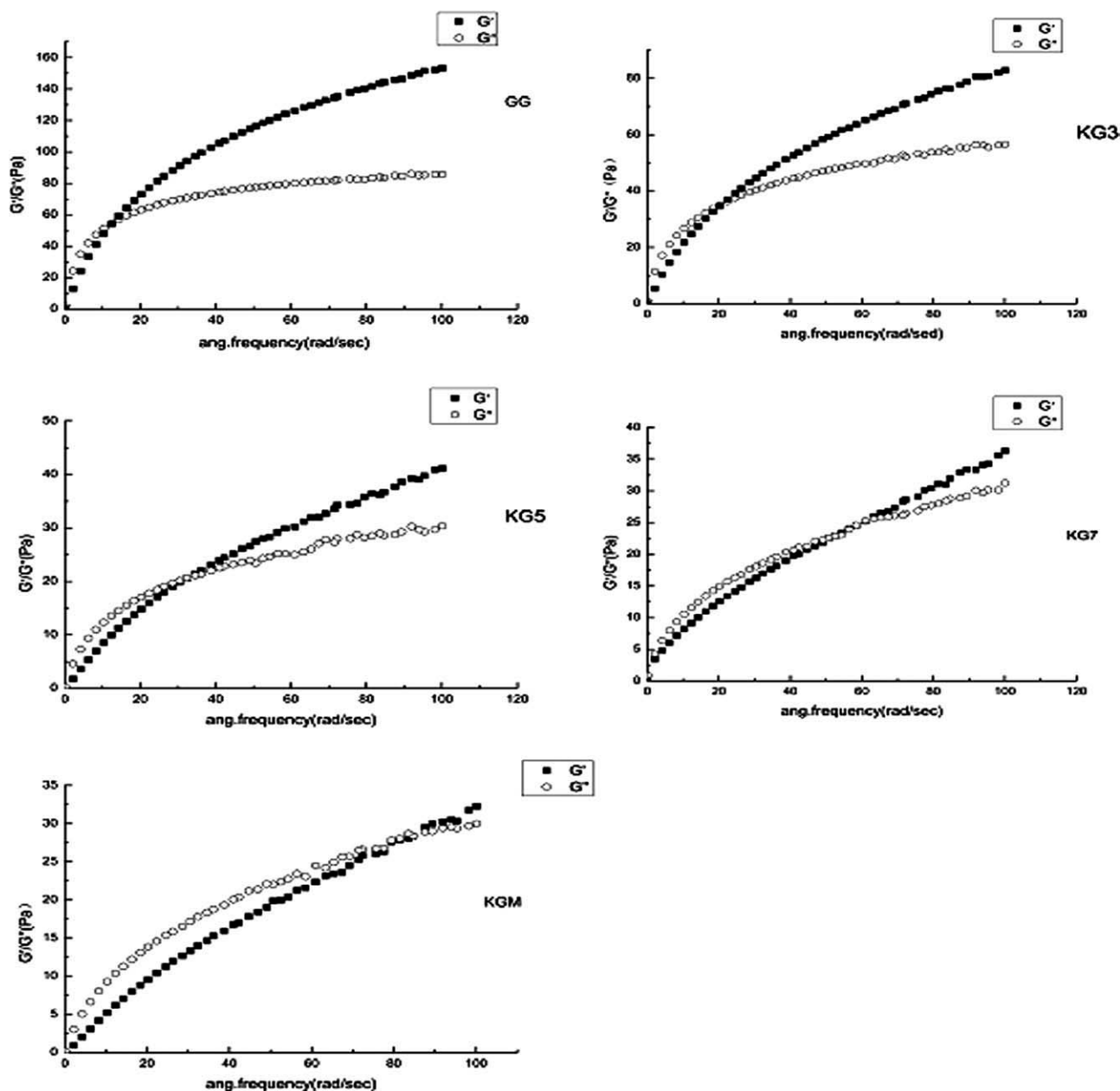

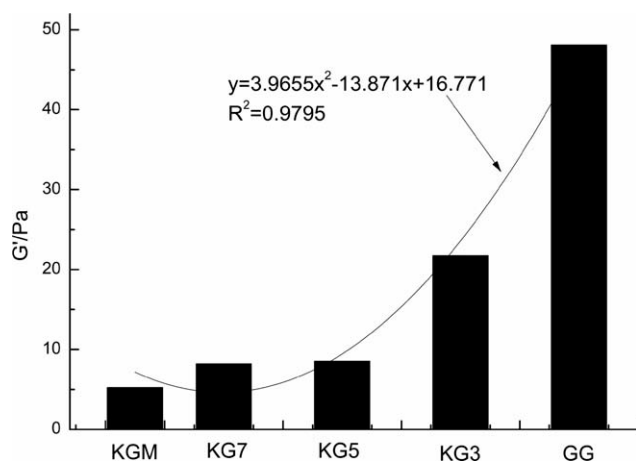**Figure 5** The viscoelastic maps of the GG, KG3, KG5, KG7, and KGM gels.

Figure 6 G' for mixtures as a function of mixing ratio ($\omega = 10$ rad s^{-1}).

component of a sample is a measure of the energy used up during the shear process and further lost from the samples.[17–19] Frequency sweep under dynamic conditions (i.e., in the linear viscoelastic region) showed that for all mixed sol systems studied, both the storage and loss moduli slightly increased with frequency which suggests a frequency dependence of both moduli. Their behavior was typical of a concentrated polymer solution: G was larger at lower frequencies but became smaller than G' at higher frequencies. But the crossover frequency shifted to higher frequencies with increasing content of konjac glucomannan (Fig. 5).

Figure 6 shows the storage modulus G' for the mixtures as a function of mixing ratio at 10 rad s^{-1} and at 25°C. In Figure 6, we observe that gellan gum make a great contribution to the mixed sols with elastic behavior. With increasing the ratio of gellan gum, there is a tendency that the mixed sol systems transform from flow-like behavior to solid-like behavior. On the contrary, the konjac glucomannan performs the viscous properties, at high frequencies, the mixed systems with more konjac glucomannan show the flow-like behavior. However, KG7 was
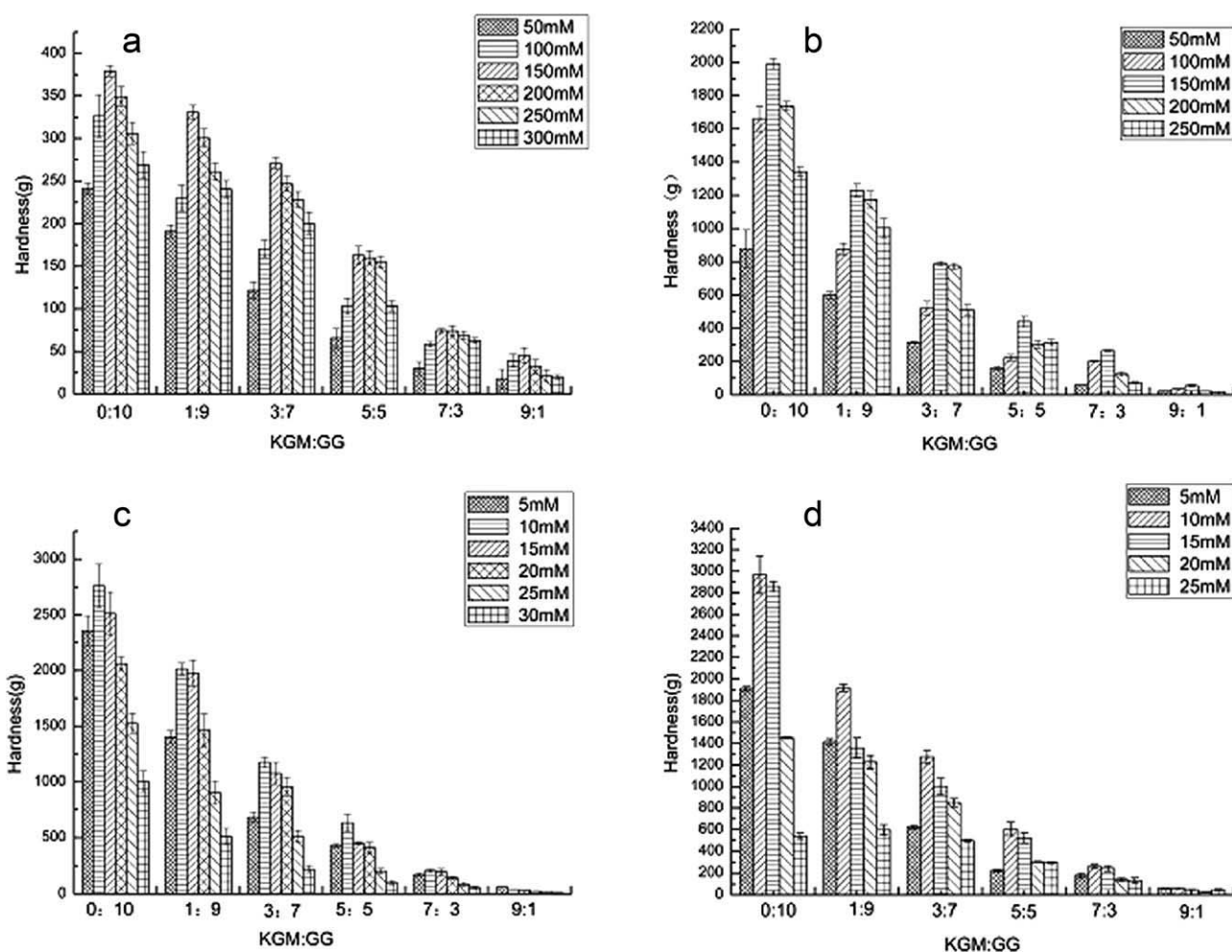

Figure 7 Hardness of KGM/gellan gum mixed gels as a function of KGM to gellan gum ratio and added cations level a: sodium ions; b: potassium ions; c: calcium ions; d: zincum ions.

Figure 8 Cohesiveness of KGM/gellan gum mixed gels as a function of KGM to gellan gum ratio and added cations level. a: sodium ions; b: potassium ions; c: calcium ions; d: zincum ions.
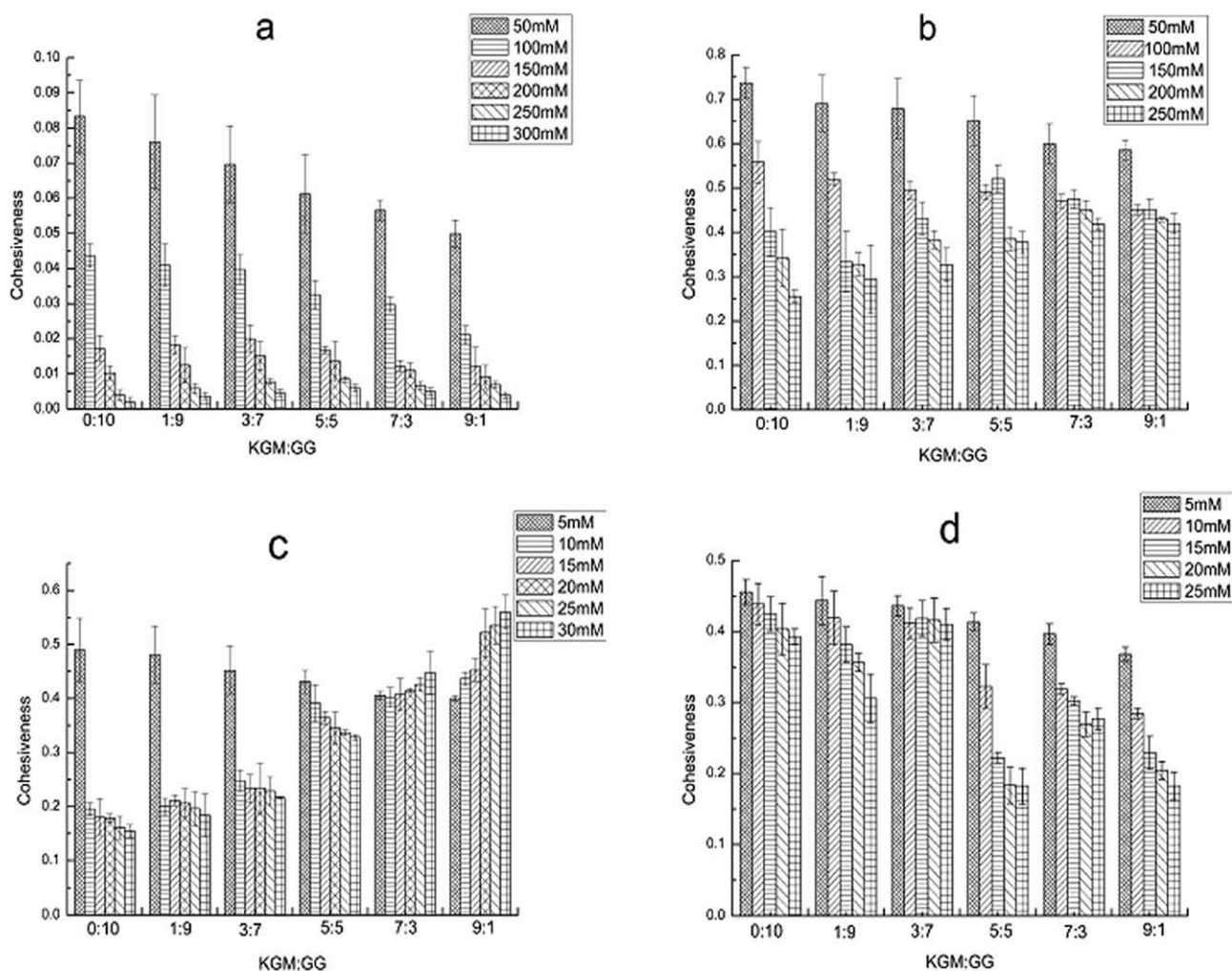
conspicuous difference from others. It's consistent with the results of rheological kinetics characterization mentioned above.

Those findings suggest that synergistic interaction occurs between gellan gum molecules in helix conformation and konjac glucomannan. At lower temperature such as 25°C, gellan gum adopts a helical conformation, however, konjac glucomannan molecules attach to the helical surface which form weak junctions. They inhibit the formation of the ordered structure of gellan gum molecules themselves. Then they form a three-dimensional network together.[14]

The effect of cations on the textural profile analysis of the mixed gels

Texture profile analysis (TPA) is a simple and rapid analytical technique that has been used extensively in the food industry. It is also used to some extent, in the pharmaceutical industry to characterize semi-solid formulations. The mechanical properties of

mixed gel systems in the presence of various concentrations of selected cations are shown below (Figs. 7 and 8).

Gelation and texture properties of the mixed gels are greatly influenced by the ratio of konjac glucomannan/gellan gum and the concentration of different cations. The hardness profiles demonstrate the addition of gellan gum had increased the mixed gels strength, in other words the hardness (Fig. 7). The increase in the mixed gels strength means that higher force was required to attain the same deformation.

In our previous discussion, the mixed sols showed the solid characteristic as the ratio of konjac glucomannan/gellan gum was less than 5 : 5, beyond this point, the mixed sols showed the flow characteristic. Howerer, there were notable increases of the elastic modulus with the addition of cations, the mixed system transformed from sols into gels. We observed that the hardness dropped sharply when the ratio of gellan gum decreased, regardless the various

concentrations of cations added. It may suggest that the elasticity of mixtures originates mainly from gellan gum. It also showed that konjac glucomannan molecules interact with gellan gum molecules weakly, thus konjac glucomannan can't form ordered structure to increase the hardness, but may lead to the occurrence of the phase separation to influence the formation of ordered structure in the whole gels.

Moreover, as shown in Figure 7, irrespective of the mixed ratio, the hardness of the mixed gels exhibited a maximum when the monovalent cations were added at the concentration of 150 mM, while the bivalent cations are at the concentration of 10 mM. The phenomenon might be explained as follows: the carboxylside groups in gellan gum molecules repelled each other by virtue of their electrostatic interactions, which inhibit the tight binding of helices and also the tight aggregation of helices,[20–22] so that the introduction of cations can shield the electrostatic repulsion and thereby permit tight binding and aggregation of helices. But beyond certain limit, excessive cations, in return may hinder the aggregation of helices and decrease the strength of the mixed gels. In addition, cation type, as well as valence had great influence on the hardness of the mixed gels. The hardness of the mixed gels was influenced much more strongly by divalent cations than by monovalent cations. The effect of Ca^{2+} was almost similar to that of Zn^{2+}, while K^+ can influence the hardness of the mixed gel more effectively than Na^+. The reason is interpreted on the basis that cations such as Na^+ are the structure ordering ions for water, and cations such as K^+ belong to the structure disordering ions.[23]

Figure 8 shows how the ratio of KGM/GG and the concentration of different cations impact on the cohesiveness of the mixed gels.

Under the effect of Na^+, K^+, and Zn^{2+}, the increase in the ratio of gellan gum resulted in the increase of the cohesiveness of the mixed gels significantly. It illustrated that the arrangement of intramolecular structure was more tight, thus the three-dimensional network structure was more stable. The cohesiveness decreased as the concentration of Na^+, K^+, or Zn^{2+} increased. The higher concentration of cations can be attributed to a reduction in the total number of junction zones in the mixed gels network, which leads to the decrease of the cohesiveness.

As for the Ca^{2+}, when the concentration was less than 10 mM, the cohesiveness increased as the ratio of gellan gum increased, but beyond this point, the cohesiveness decreased as the ratio of gellan gum increased. This remarkable difference in the ability of different cations to induce gelation of deacylated gellan may be explained as follows: Monovalent cations bind to the surface of individual helices, thus

lowering their charge-density and reducing the electrostatic barrier to aggregation. Divalent cations promote aggregation by site-binding between pairs of carboxyl groups on neighboring helices, to give structures analogous to the "egg-box" model proposed for calcium-induced gelation of alginate and pectin. In the presence of monovalent cations double helices are connected by strong carboxylate-cation$^+$ −water-cation$^+$ −carboxylate interactions, while in the presence of divalent ions stronger carboxylate-cation^{2+} −carboxylate interactions occur. The magnitude of carboxyl increased as the concentration of gellan gum increased, which inhibited the formation of the gel and weaken the interaction, as the cohesiveness decreased.[24]

With regard to Zn^{2+}, the different effect might be explained by synergy produced among the inside cations. Nevertheless, the mechanism needs further discussion.

CONCLUSIONS

Konjac glucomannan and gellan gum mixed sols showed the characteristic of non-Newtonian fluid, and rheological kinetics curves accorded with the power law $\tau = K\gamma^n$. The temperature had great influence on the viscosity of the mixed sols. The best compatibility (KG7) showed the largest pseudoplastic. With the increase of gellan gum, G' (storage modulus) increased, which meant that gellan gum played a great role in the flexibility of the sols. The ratio of konjac glucomannan/gellan gum which was more than 5 : 5 showed the fluid characteristics, and less ones demonstrated solid features. The gels texture profiles were significantly affected by the metal cations. In a certain concentration range, the increase of cations might promote the gel's hardness and cohesiveness. But when the concentration was further enhanced, the gel would be damaged homogeneity.

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