

Review of Konjac Glucomannan¹

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The paper reviews the solution and gelling properties of konjac glucomannan (KGM) and its interactions with other hydrocolloids such as xanthan and carrageenan for food applications. Research activities in the area of KGM processing in environmentally friendly aqueous environments have been discussed for coatings and packaging applications.

KEY WORDS: Konjac glucomannan; polysaccharides; hydrocolloids; gelation; aqueous processing; liquid crystalline phases.

INTRODUCTION

Polysaccharides of the mannan family are abundant in nature [1, 2]. Mannan is a homopolymer of (1→4) linked β-D-mannose residues which has been found in cell walls of some types of algae and as storage carbohydrates in bulbs. Glucomannans in which some of the mannose residues are replaced by D-glucose are found in softwoods, tubers, and bulbs. Konjac mannan is a high molecular weight, water-soluble, nonionic glucomannan found in tubers of the *Amorphophallus konjac* plant. Konjac glucomannan (KGM) is a linear random copolymer of (1→4) linked β-D-mannose and β-D-glucose. It has mannose and glucose units at molar ratio of 1.6:1 with a low degree of acetyl groups (approximately 1 acetyl group per 17 residues) at the C-6 position [3, 4]. The degree of water solubility is controlled by the presence of the acetyl units. There are also certain short-chain branches at the C-3 position of the mannoses [5]. Takahashi *et al.* [6] isolated and studied the structures of four glucomannooligosaccharides from the hydrolytic products of KGM produced by β-mannanase from *Streptomyces* sp. They also investigated the mode of enzyme action of mannanase on the hydrolysis of

KGM. Figure 1 shows the chemical structure of KGM as proposed by Maeda *et al.* [7].

SOLUTION PROPERTIES

Torigata *et al.* studied the molecular weight and the conformation of nitro-KGM in aqueous solution by light scattering and viscometry [8]. The root mean square end-to-end distance ($\langle R^2 \rangle^{1/2}$) and the weight-average molecular weight (M_w) were determined to be 1380 Å and 2.7×10^5 , respectively. Based on the Mark-Houwink-Sakurada (M-H-S) constants ($K = 1.16 \times 10^{-3}$ and $a = 0.95$), it was concluded that nitro-KGM was a rigid molecule in aqueous solution. Solution properties of water-soluble KGM samples were determined by light scattering [9]. The molecular weight (M_w) and the root mean square radius of gyration ($\langle S^2 \rangle^{1/2}$) were determined to be 6.8×10^5 to 1.9×10^6 and 9.1×10^2 to 2.3×10^3 Å, respectively. These values were dependent on the strain and the production site of KGM. Water-soluble methylated KGM samples were prepared with a degree of substitution of about 0.45 [10]. The molecular properties of these samples were not dependent on the strain and the place of production as determined by Sugiyama [9]. The molecular weight, radius of gyration, and intrinsic viscosity were determined to be approximately 1×10^6 , 1.2×10^3 Å, and 19 dl/g, respectively [10, 11]. Based on the M-H-S constants ($K = 6.37 \times 10^{-4}$ and $a = 0.74$), it seemed that the meth-

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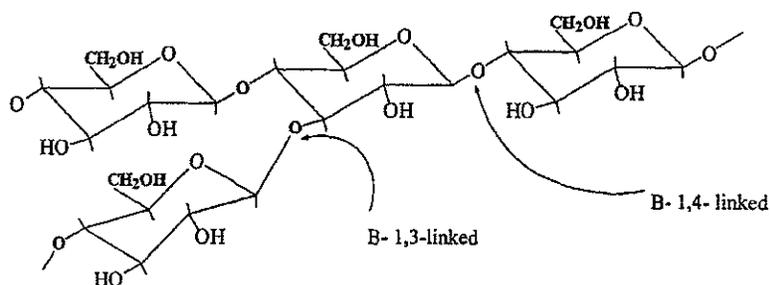


Fig. 1. Structure of konjac glucomannan.

ylated KGM samples were semirigid in aqueous solutions. The expansion coefficient (α_s) was found to be 1.3 and it can be considered that methyl-KGM molecules were stretched random coils in water [12]. Viscometric measurements were also conducted on fractionated KGM samples [13], and the molecular parameters were similar to those obtained for several other polysaccharides [14]. KGM formed very high-viscosity solutions with values higher than those of guar and locust bean gum, which indicated that the molecular mass of KGM was possibly higher assuming similar chain stiffness [15]. Solution properties of KGM were examined by measurement of specific volume at different temperatures, concentrations, and pH's [16]. The partial specific volume of KGM increased abruptly at about pH 11, and the results suggested that the change of molecular structure was necessary for gelation of KGM to occur at high pH values.

The crystallization behavior of five glucomannans was studied by Chanzy *et al.* [17]. The recrystallization of KGM was performed from dilute aqueous solutions in the temperature range of 50 to 140°C. The addition of ammonia to the solutions was required in order to remove the acetyl groups (deacetylated KGM) and induced the formation of a hydrated gel-forming pseudo-fibrillar precipitate. The electron-diffraction diagram illustrated strong- and medium-intensity rings at 4.5 and 4.0 Å, respectively, indicative of mannan II-type crystallization. The formation of mannan II polymorph with long ribbonlike elements was persistently obtained at all temperatures, and in no case could mannan I be detected. However, when the molecular weight of KGM was reduced by mild acid hydrolysis, it formed a mannan I polymorph and indicated the effect of molecular weight on the polymorphism of glucomannan. Similar examples of polymorphism have been observed with other polysaccharides such as amylose [18], dextran [19], and cellulose [20]. The crystalline polymorphs of glucomannans were studied by X-ray diffraction, and the

structures were determined to be orthorhombic, with the possibility of an extended twofold helical structure [21].

GELATION MECHANISM

The gelling mechanism of KGM has been investigated by Maekaji [22, 23]. The turbidity and viscosity of sol, consumption of the alkali (sodium carbonate), and infrared spectra were measured during the gelation of KGM. The acidic moieties with carbonyl groups (C=O) were eliminated by the alkalies and were identified as acetic acid. The gelation of the KGM molecules possibly occurred through the formation of a network structure supported by hydrogen bonding. Therefore, the acetyl groups associated with KGM inhibited gel formation. The presence of mild alkali in a KGM solution cleaved the acetyl groups and resulted in heat-stable and thermally reversible elastic gels, which retained their structure under various conditions. Gelation was enhanced by heating, in contrast to many other thermoreversible gels. The gels could be solubilized under mild conditions with reagents (e.g., urea) which would disrupt the hydrogen bonds, serving as evidence that the KGM gels did not consist of chemical cross-links [12]. The gelation of KGM was studied by rheological measurements with low-amplitude oscillation experiments in the presence of different salts, and compared with those of gelatin, methylcellulose, pectin, and acrylamide [24]. The rate order of gelation of KGM was determined to be 1.5, which indicated a complex mechanism. Surprisingly, it exhibited a rubber-like elastic response similar to that of covalently cross-linked structures (vulcanized rubber, acrylamide), even though the KGM structure was not covalently linked as it melted above 95°C.

The crystal structure of KGM served as a model for the junction zones in gels and for interactions with other polysaccharides. The diffraction pattern of KGM

exhibited reflections of an orthorhombic unit cell with $a = 9.14 \text{ \AA}$, $b = 16.46 \text{ \AA}$, and $c = 10.3 \text{ \AA}$ [25]. Native KGM packed isomorphously with the mannan II structure in the solid state and indicated that the replacement of mannose by glucose did not disrupt the molecular associations adopted by hydrated mannan [25]. The diffraction pattern was due to the crystalline regions in the specimen that consisted of unsubstituted segments of the backbone. This showed that the gel formation possibly involved associations of acetate-free stretches of KGM in the junction zones. Therefore, gel formation occurred on deacetylation since the acetate-free stretches were long enough for associations in junction zones to be energetically favorable [26].

KGM-Xanthan Interactions

In order to elucidate the molecular basis for gelation, X-ray diffraction studies were conducted on the fibers obtained from the gels of xanthan-KGM mixtures by Brownsey *et al.* [27]. The X-ray diffraction pattern of native acetylated KGM exhibited highly crystalline material with a mannan II lattice and demonstrated that acetyl substituents did not prevent molecular association and crystallization. Upon deacetylation, it is expected that there will be an increase in tendency to crystallize and gel which can result in a decrease in solubility, as there will be an increase in the number of potential intermolecular hydrogen bonds. In order to eliminate the complications caused by the gelation of the KGM component alone, studies were conducted on xanthan-native (acetylated) KGM blends [27]. Gelling in the KGM and xanthan blends occurred only when the xanthan structure was denatured (i.e., helix to coil transition) [28, 29]. The mixed gel melted at about 63°C , and deacetylation of xanthan lowered the gel melting and setting temperatures by 20°C [30]. Recognizable gels were formed at total polysaccharide levels of 0.02%, and it was the lowest gelling concentration observed for the carbohydrate system [31]. It seemed that the formation of the gel structure was a result of specific interaction with xanthan rather than a property of KGM. Shatwell *et al.* [32] determined that the gel strengths between xanthan and KGM were also dependent on the degree of acetylation of xanthan. Degree of acetylation of 7.7 and 1.5% formed no gels to thermoreversible gels, respectively, with KGM. Further evidence of an intermolecular binding and gelation mechanism between xanthan and KGM were studied by rheological, electron spin resonance spectroscopy, and differential scanning calorimetry measurements [33–36]. Recently, synergistic interactions and the influence of deacetylation of ace-

tan polysaccharide (a structure similar to xanthan with longer pentasaccharide side chains) [37] and xanthan polytetramer [38] with locust bean gum and KGM were studied using different techniques.

KGM-Carrageenan Interactions

Interactions between KGM and κ -carrageenan were studied by using X-ray fiber diffraction [39], and the results indicated that there was no interaction between the polymers, as new diffraction patterns were not observed. Strong thermoreversible gels were obtained between the two polymers in the presence of potassium salts [40], and the influence of storage temperature on the gel strength and thermoreversibility was investigated [41]. Interactions between KGM and κ -carrageenan were determined to be stronger than those between locust bean gum and κ -carrageenan which resulted in corresponding strong and weak gels, respectively [42]. These findings contradict those obtained by Cairns [39]. A study on the gelation mechanism in κ -carrageenan and KGM mixtures was studied using differential scanning calorimetry and electron spin resonance spectroscopy [43]. The results indicated the formation of mixed aggregates of κ -carrageenan helices and KGM and possibly involved bundles of self-aggregated κ -carrageenan helices covered with surface-adsorbed KGM chains. Recent investigations on gels of xanthan and κ -carrageenan with locust bean gum and KGM, respectively, have been reported with detailed discussions on the binding and exclusion synergistic interactions between the polymers [44]. Effects of sugars on the gelation of agarose and the mixtures of KGM and κ -carrageenan were studied in relation to their applications in the food industry [45]. The number of junction zones increased but their size became smaller by the addition of sucrose in the agarose gels. The gels of the mixtures of KGM and κ -carrageenan seemed to consist of a carrageenan network strengthened by weak interactions between KGM and carrageenan. A small amount of sucrose (5–10%) in the mixed gels resulted in more rigid gels than those with no sucrose or 20% sucrose due to the formation of junction zones with small amounts of sugar.

The physicochemical properties of KGM were discussed in an earlier review article, some of which are not covered in this paper [46].

AQUEOUS PROCESSING

A major problem concerning the thermal processing of polysaccharides is the strong interchain interac-

tions which exist due to extensive hydrogen bonding. These interactions result in a polymer system which typically undergoes thermal decomposition before reaching its melting point. Thus, native polysaccharides are, in general, not processable by conventional thermoplastic methods without the use of water or an equivalent plasticizer. The main objective of our research is to utilize traditional polymer processing techniques to fabricate films, fibers, and molded materials from biopolymers from renewable resources. The formation of these materials will allow proper characterization of the physical properties to identify suitable applications. The most important factors that are considered include the utilization of liquid crystalline phases during processing and minimizing the use of organic solvents by selecting materials which can be processed in environmentally friendly aqueous environments. The formation of liquid crystalline phases is an important solution property of many polysaccharides such as cellulose [47-50], cellulose derivatives [51-54], chitosan [55, 56], chitosan derivatives [55, 57, 58], xanthan [59, 60], schizophyllan [61], and levan [62]. This property, adopted with the rheological behavior, may provide aqueous processing opportunities for certain polysaccharides to optimize material functions.

The research on KGM so far has been limited to the isolation, characterization of the solution and bulk properties, and gelling behavior, mainly for food applications. In addition, KGM can be extruded into films for coatings and packaging applications. Dielectric, viscoelastic, and NMR study of KGM films indicated a mechanical and dielectric loss peaks at 100°C due to the rotational motion of hydroxymethyl group attached to the C-5 atom in the glucose and mannose residues [63]. The second moments of KGM decreased rapidly at 0 and -60°C and indicated that the motions of hydroxymethyl groups of KGM were hindered in comparison to those of amylose, pullulan and dextran. Mechanical properties [64] and water sorption [65] of KGM and pullulan blends were studied in the presence of glycerol. It was determined that the tensile strength and modulus of the blends increased with increasing amounts of KGM and glycerol was an efficient plasticizer for the blends. The water sorption isotherms of the films showed that the moisture uptake was higher for the blends than for the pure KGM and pullulan films.

Processing of the KGM solutions from the liquid crystalline (LC) state can be very useful, as the solidified product will retain the orientational molecular order, which will lead to improved stiffness and strength of the material. We have reported preliminary investigation of the LC behavior of KGM [66]. Detailed LC

rheological, and thermal properties of KGM in aqueous solutions were studied for the identification of optimal processing conditions [67]. KGM formed a biphasic LC phase in water at a 7% (w/w) concentration and became completely anisotropic above a 10% (w/w) concentration as observed by polarized optical microscopy and circular dichroism. From capillary rheometer measurements, KGM solutions were found to be pseudo-plastic and relatively independent of temperature, and optimum processing conditions were determined. KGM solutions from 30 to 35% concentrations were found to be appropriate for preparing fibers and films, as they exhibited preferential orientation as determined by wide-angle X-ray scattering.

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