

SYNERGISTIC INTERACTION BETWEEN XANTHAN AND GUAR GUM*

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ABSTRACT

The non-Newtonian behavior and dynamic viscoelasticity of a series of aqueous mixtures of xanthan and guar gum were measured with a rheogoniometer. At a concentration of 0.2% of total gums, gelation did not occur at room temperature but occurred at a low temperature (0°). A much stronger interaction was observed with a mixture of deacetylated xanthan than that with native xanthan. The maximum dynamic modulus was obtained when the ratio of xanthan to guar gum was 2:1. The transition temperatures of dynamic viscoelasticity for mixtures with native and deacetylated xanthan were observed at 25 and 30°, respectively. It was concluded that the side chains of the guar gum molecule prevent an intermolecular interaction with the side chains of the xanthan molecule. An intermolecular interaction between xanthan and guar gum at low temperature might be promoted between the periphery of the side chains of the xanthan molecule and the backbone of the guar gum molecule and dissociation takes place at the transition temperature.

INTRODUCTION

Xanthan produced by *Xanthomonas campestris* is an extensively investigated polysaccharide because of its unique rheological properties and commercial importance¹⁻⁴. The structure of xanthan consists of a (1→4)-β-D-glucan chain, as in cellulose, to which is linked, at O-3 of alternate D-glucosyl residues, a trisaccharide side-chain bearing a charge^{5,6}. The internal D-mannose residue of the side-chain is substituted at O-6 by an acetyl group. About one-half or one-third of the terminal D-mannosyl groups bears a pyruvic acid group depending on the culture conditions⁷.

We have proposed that xanthan molecules are associated in a quaternary structure through charged trisaccharide side-chains⁴. Morris and assoc.^{8,9} have attributed the unusual rheological properties of xanthan to its intramolecular association. Smith *et al.*¹⁰ have suggested that the intermolecular association of

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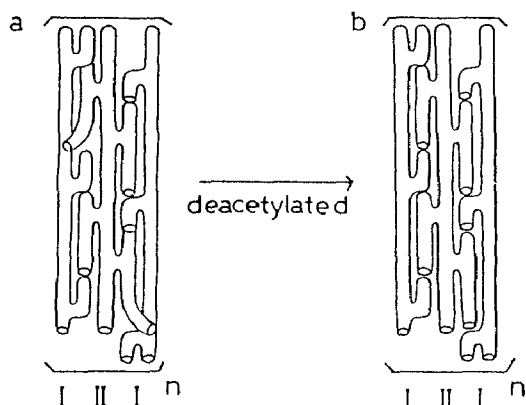


Fig. 1. Possible mode of intermolecular interaction between xanthan and locust-bean gum molecule in aqueous solution. The models are viewed perpendicular to the axis. A molecule of xanthan may combine with two or more molecules of locust-bean gum: (a) Incomplete interaction may exist as the side chains of the xanthan molecules are somewhat rigid owing to the intramolecular association between acetyl residues and backbone. (b) Interaction takes place after deacetylation of xanthan (I) Locust-bean gum molecule; (II) xanthan molecule.

xanthan molecules may be enhanced by the interaction of the pyruvate methyl group, which essentially agrees with the quaternary association that we have proposed⁴. Morris *et al.*¹¹ have also suggested that the microgels of xanthan appear to consist of a side-by-side association of molecules in aqueous media.

On the other hand, the synergistic interaction between xanthan and locust-bean gum is well known^{12,13}. Dea and Morris¹⁴ have proposed a mode of interaction between the single-stranded helix of the xanthan molecule and the smooth segments of the backbone of the locust-bean gum molecule without taking into consideration the role of the side chains of the xanthan molecule. We confirmed that the characteristics of the association between the gums depend on the charged trisaccharide side-chains of the xanthan molecule^{4,15}. After analysis of the rheological behavior of a mixture with locust-bean gum, a lock-and-key mode of interaction was proposed (Fig. 1). As the tertiary structure of the xanthan molecule may keep a five-fold, single-stranded helix¹⁷, its side chains are inserted into the adjacent, unsubstituted segments of the backbone of locust-bean gum molecule, which is extended into a two-fold, ribbon-like structure^{14,18}. On the basis of this mode of interaction, a molecular chain of xanthan may be associated with two or more molecular backbones of locust-bean gum, the ratio depending on the favored conformation in aqueous solution. The experimental results suggested that 5/2 or 5/3-fold structure was favored in an aqueous solution, because the maximum interaction achieved was at the xanthan-to-locust bean-gum ratio of 1:2.

In the mixture with deacetylated xanthan, a very strong interaction was also obtained at the ratio of 1:3, and the degree of dynamic modulus was about two times over a wide range of ratios. As the side chains of the native molecules of xanthan are somewhat rigid because of the intramolecular association contributed

by acetyl residues, an incomplete interaction may exist and greater interaction may result from deacetylation.

Although it has been reported that the side-chains of the locust-bean gum molecule are distributed in uniform blocks along the backbone of the mannan molecule^{19,20}, the mode of interaction is independent of the structure, because each junction may take place within three sugar residues of the xanthan molecule, including the pyruvate and acetate residues. The stronger interaction in the mixture with deacetylated xanthan suggests some regular branching units in the locust-bean gum molecule as illustrated in Fig. 1. We describe herein the rheological behavior, with respect to their synergistic interaction, of a mixture of xanthan and guar gum, the structure of which is the same as that of locust-bean gum, except that the side chains are linked to every other unit¹⁹, or two to four units²⁰.

EXPERIMENTAL

Materials. — The xanthan and guar gum were identical with those used in previous studies^{16,21} and were obtained from Taiyo Kagaku Co., Ltd. A solution of 0.1% xanthan in distilled water was heated at 90° for 30 min, and then cooled to room temperature, centrifuged at 12 000g for 1 h, and filtered through Celite 545 (which had been treated with boiling 3M HCl for 30 min, and washed with distilled water until the pH was 6.5). In the presence of 0.5% KCl, ethanol (2 vol.) was added to the filtrate, and the precipitate was dried *in vacuo*. A solution of 0.5% guar gum in distilled water was filtered through Celite 545, ethanol (2 vol.) added, and the precipitate dried *in vacuo*. For deacetylation, an aqueous 0.2% solution of purified xanthan was treated under N₂ with 10mM KOH in the presence of 1.0% KCl at room temperature¹. Aliquots were removed periodically and titrated with 10mM H₂SO₄. The original acetyl content was 4.6% and the hydrolysis was completed within 10 h. The solution was made neutral with 50mM HCl, and the product isolated as described earlier. Various solutions of xanthan and guar gum having a total concentration of 0.2% were prepared by dissolving guar gum in distilled water and adding xanthan.

Liquid chromatography. — A solution of guar gum (50 mg) in 2M HCl (25 mL) was heated at 100° for 3 h. After being cooled in an ice bath, the hydrolyzate was made neutral with Ag₂CO₃ and filtered through Celite 545. The excess of Ag ions were precipitated with H₂S, and the solution was concentrated and filtered through Celite 545 into a 10-mL volumetric flask. Liquid chromatography was performed with a Shimadzu LC-4A chromatograph, equipped with a column of ISA-07/S2504, and a mobile phase of 2.0M boric acid, adjusted to pH 8.5 with 0.1M KOH; temperature, 150°, and flow rate, 0.5 cm/min.

Specific rotation. — Specific rotation was measured at 589 nm with an automatic digital polarimeter DIP-180 (Japan Spectroscopic Co., Ltd.) for solutions of 0.5% (w/v) in water.

Molecular weight. — The molecular weight of guar gum was determined by

the viscometric method according to the relationship²² $[\eta] = 3.8 \times 10^{-4} \cdot \text{mol. wt.}^{0.723}$. Intrinsic viscosity $[\eta]$ was determined for each solution having a concentration from 0.05 to $\sim 0.3\%$ by measuring the specific viscosity with an Ostwald-type viscometer at 25° . The flow rate for water was 44 s.

Viscosity and dynamic viscoelasticity measurements. — Viscosity at different shear rates ($1.667\text{--}66.685 \text{ s}^{-1}$) and dynamic viscoelasticity at steady angular velocity (3.768 rad/s) were determined with a rheogoniometer consisting of a coaxial cylinder (1.6 cm diam.) with a rotating outer cylinder (2.2 cm diam.), 6.0 cm long (IR-103, Iwamoto Seisakusho Co., Ltd.). The temperature of the sample was controlled by circulating oil from a Thermo-cool (LCH-130F, Toyo, Co., Ltd.) over the temperature range of $0\text{--}60^\circ$ and raised at a rate of $1^\circ/\text{min}$ by steps. Shear rate (D), shear stress (S), and apparent viscosity (η), were calculated with the equation of Margules²³. Dynamic viscosity (η') and elasticity (G') were calculated by a modification of Markovitz's equation²⁴.

RESULTS

As the intermolecular interaction between xanthan and D-galacto-D-mannan molecules is closely correlated with the degree of substitution of the mannan chain, the degree of substitution of guar gum was determined by l.c. and calculated to be D-mannose to D-galactose 2.0:1.0; mol. wt. 235 000; and $[\alpha]_{589}^{20} +52^\circ$ (c 0.5, water).

In order to compare the rheological behavior of a mixed solution of xanthan and guar gum with that of a mixed solution with locust-bean gum, the viscosity and dynamic viscoelasticity measurements were performed under the same conditions as those of the previous study¹⁶. Gelation did not occur, for the mixture with xanthan (native and deacetylated) and guar gum, at a total concentration of gum of 0.2% at room temperature. Flow curves, at 25° , of a mixture of native (Fig. 2A) and

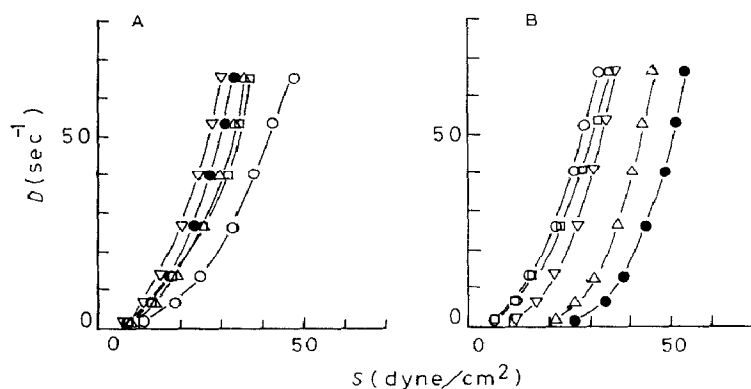


Fig. 2. Flow curves, at 25° , of xanthan solution mixed with guar gum solution at a total concentration of gum of 0.2%. Ratio of xanthan to guar gum: ▽, 1:3; ○, 1:2; □, 1:1; ●, 2:1; and △, 3:1. (A) Native xanthan, and (B) deacetylated xanthan.

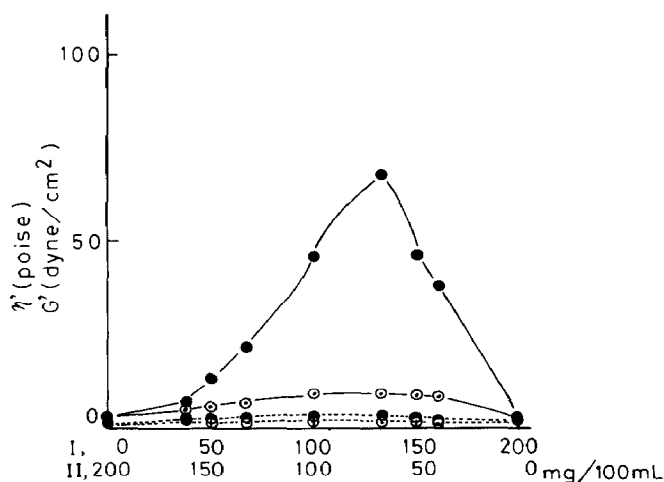


Fig. 3. Dynamic viscoelasticity, at 3.768 rad/sec and 25°, of a 0.2% xanthan–guar gum solution as a function of the ratio of components: (○) native xanthan; (●) deacetylated xanthan. The broken lines refer to the dynamic viscosity and the full lines to the dynamic modulus. (I) Xanthan, and (II) guar gum.

deacetylated (Fig. 2B) xanthan with guar gum solutions at varying ratios of the gums, but keeping the total concentration constant at 0.2%, are shown in Fig. 2. The solutions showed plastic behavior, in which the values for S of the mixtures with deacetylated xanthan were higher than the value of the mixtures with native xanthan.

Figure 3 shows the effect, at 25°, of the ratio of xanthan (native and deacetylated) to guar gum in solution on the dynamic viscoelasticity at a total gum concentration of 0.2%. In the case of the mixture with native xanthan, little synergistic increase in dynamic viscoelasticity was observed. However, the synergistic interaction was enhanced in the mixture with deacetylated xanthan, indicating that the intermolecular interaction resulted from deacetylation of xanthan. The maximum dynamic modulus was achieved when the mixing ratio of xanthan to guar gum was 2:1.

The effect of temperature on the dynamic viscoelasticity of a mixed solution of native or deacetylated xanthan and guar gum were measured with a rheogoniometer. The dynamic modulus increased at a low temperature, and showed the highest value at the xanthan-to-guar gum ratio of 2:1, which agrees with the result illustrated in Fig. 3. However, the dynamic modulus of the mixture showed a value lower than that of the mixture with locust-bean gum, which was too high to be determined at a low temperature¹⁶. The dynamic modulus of the mixture with guar gum was insensitive to the increase in temperature from 0 to 15°, but it decreased rapidly with a further increase of the temperature. The transition point at which the dynamic modulus decreased gradually was observed at 25 and 30°, respectively, for the mixtures with native and deacetylated xanthan. The dynamic viscosity of the mixture with native and deacetylated xanthan also showed a similar

transition point at the same temperatures. The transition temperature implies that the intermolecular interaction dissociates up to this temperature. The intermolecular interaction of the mixture with deacetylated xanthan is more stable than that of the mixture with native xanthan with an increase in temperature.

The dynamic viscoelasticity of a mixed solution of xanthan (native and deacetylated) and guar gum decreased in the presence of urea (4.0M) or NaCl (0.1%), which agrees with the results for locust-bean gum previously reported¹⁶.

DISCUSSION

A new mode of interaction between xanthan and locust-bean gum involving the side chains of the former and the backbone of the latter molecule (Fig. 1) has been proposed¹⁶. This model provides an explanation not only for the rheological characteristics of the cooperative interaction with locust-bean gum but also of those of xanthan alone in aqueous media^{4,15,16}. In the present study, the rheological behavior of a mixture of solutions of xanthan and guar gum was analyzed. Synergistic interaction was not observed at room temperature. Thus, it was concluded that weak interaction may be due to the presence of side chains at every other unit or at every two to four units of the guar-gum molecule. These side chains may prevent the insertion of the charged trisaccharide side-chains of the xanthan molecule into the backbone of the guar-gum molecule. However, synergistic interaction occurred with deacetylated xanthan at room temperature, indicating that the xanthan molecules had become more flexible and could associate with the guar-gum molecules more easily, probably because they were free from the intramolecular association to which the acetyl residues contribute¹⁵. The branched chain of the guar-gum molecule is still under discussion. According to the key-and-lock interaction proposed, the two-to-four alternating structure seems acceptable, because, in an alternating structure, a slight interaction may be enhanced by deacetylation.

On the other hand, gelation of a mixture of xanthan and guar-gum solutions occurred at a low temperature. The maximum gelation was achieved when the ratio of xanthan and guar gum was 2:1, this ratio was reversed for the mixture with locust-bean gum¹⁶. The transition temperatures of the dynamic viscoelasticity were observed at 25 and 30° for the mixture with native and deacetylated xanthan, respectively. Such transition temperature was not observed for the mixture with locust-bean gum¹⁶. The dissociation that occurs up to these temperatures may be due to the Brownian motion of the gums. Thus, the interaction that takes place at low temperature between the periphery of the side chains of the xanthan molecule and the backbone of the guar-gum molecule may be due to a decrease of the Brownian motion. As the maximum interaction was achieved when the ratio of xanthan to guar gum was 2:1, the backbone that was on the opposite side of the branches of the guar-gum molecule also would contribute to the interaction. Such an interaction is likely to dissociate readily up to the transition temperature.

The experimental results thus obtained support the mode of interaction between xanthan and locust-bean gum previously suggested¹⁶.

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