

## Note

Rheological Properties of Depyruvated Xanthan in Aqueous Media<sup>†</sup>

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In preceding studies,<sup>1,2)</sup> we have demonstrated that xanthan molecules are associated in a quaternary structure through charged trisaccharide side chains. The acetate residue, which is attached to the inner mannose side chain,<sup>3,4)</sup> contributes to its intramolecular association. We have proposed that the methyl groups of acetate residues may associate with the hemiacetal oxygen atoms of the D-glucose residues at the branching backbone, while the methyl groups of the pyruvate residues, which are attached on two-thirds of the outer mannose side chains, may associate with the acetal and ketal oxygen atoms on different molecules with the hydrogen force.<sup>5)</sup> Depyruvation can be done without further modification of the polymer structure by mild oxalic acid treatment.<sup>6)</sup> In this investigation, we studied the viscosity and dynamic viscoelasticity of depyruvated xanthan, and its rheological properties were analysed in more detail with respect to its association characteristics.

The xanthan (Taiyo Kagaku Co., Ltd.) was identical with those used in our preceding studies,<sup>2,5,7~9)</sup> and purified as previously described.<sup>5)</sup> By a spectrophotometrical estimate as the 2,4-dinitrophenyl derivative,<sup>10)</sup> this sample had a pyruvate content of 5.7%, which meant that 67% of the terminal mannosyl groups bore a pyruvate moiety. The pyruvate groups were removed by heating a solution of xanthan (1 g/l in 1 mM oxalic acid, 0.1 M KCl, pH 3.0) for 2 hr, at 95°C.<sup>6)</sup> Under these conditions, about 84% of the pyruvate groups were removed, so that 1/10 of the terminal mannosyl groups bore a pyruvate moiety, but the acetate content was 4.5%, and unaltered.<sup>11)</sup> Viscosity and dynamic viscoelasticity were measured with a rheogoniometer (IR 103, Iwamoto Seisakusho Co., Ltd.), and apparent viscosity ( $\eta$ ), shear rate ( $D$ ), shear stress ( $S$ ), dynamic viscosity ( $\eta'$ ), and dynamic modulus ( $G'$ ) were calculated as described in a previous paper.<sup>5)</sup>

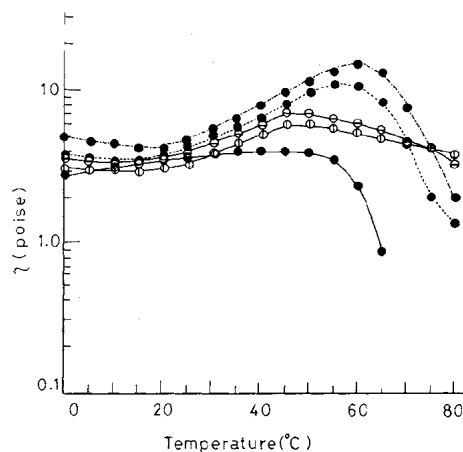


FIG. 1. Effects of Temperature on Viscosity of Depyruvated and Native Xanthan at Various Concentrations at a Shear of  $9.50 \text{ sec}^{-1}$

●, Depyruvated xanthan; ○, native K salt of xanthan; ⊙, native Na salt of xanthan. Concentration: —, 0.5%; - - - -, 0.8%; - - - -, 1.0%.

The flow curves of depyruvated xanthan at 25°C approximated plastic behavior and yield values were estimated from the flow curves by extrapolation of the  $D$  vs.  $S$  plot to the intercept to be 12, 20, 30, and 42  $\text{dyn/cm}^2$  at 0.3, 0.5, 0.8, and 1.0%, respectively.

As shown in Fig. 1, the apparent viscosity of the depyruvated xanthan at 0.5% at  $9.50 \text{ sec}^{-1}$  was low at a low temperature (0°C) and increased gradually with increasing temperature up to 35°C, then it was constant until 55°C, which was estimated to be a transition temperature, and decreased rapidly with further increases in temperature. On the other hand, the apparent viscosity of the K and Na salts of native xanthan showed clear sigmoid curve during increases in temperature, as reported previously,<sup>1,5)</sup> and remained high even at higher temperature (80°C), 3.8 and 3.3 poise, respectively. Despite showing sigmoid curves at high concentrations (0.8 and 1.0%), the apparent viscosity of depyruvated xanthan decreased rapidly over 60°C and showed a value of 1.2 and 1.8 poise at 75°C. The rapid decrease of the apparent viscosity of the depyruvated xanthan may be due to a 1/10 substitution of pyruvate residues on xanthan molecules.

Although the dynamic viscosity,  $\eta'(\omega)$ , and elasticity,  $G'(\omega)$ , of depyruvated xanthan at 3.77 rad/sec decreased gradually with increasing temperature below 0.5% solution, it showed a little increase up to 30°C, then decreased gradually, and after reached 60 and 65°C, which was thought to be a transition temperature, it decreased

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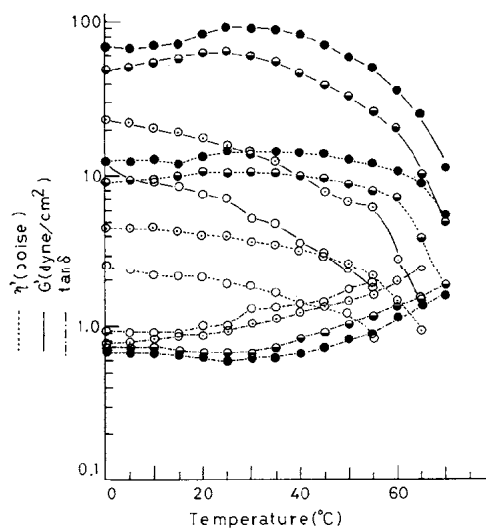


FIG. 2. Effects of Temperature on Dynamic Viscoelasticity of Depyruvated Xanthan at Various Concentrations at a Frequency of 3.77 rad/sec.

○, 0.3%; ⊙, 0.5%; ⊖, 0.8%; ●, 1.0%.

rapidly for 0.8 and 1.0% solution as shown in Fig. 2. The  $\tan \delta$  of the depyruvated xanthan decreased from 0.9 to 0.6 with increasing concentrations from 0.3 to 1.0% at 25°C. The value of the latter was higher than that of native (K salt),<sup>1)</sup> 0.4; deacetylated, 0.3<sup>2)</sup>; and Ca salt, 0.3<sup>3)</sup> of xanthan. The tendency, showing high value at 1.0% solution of depyruvated xanthan may be due to less formation of intermolecular association than in the others.

The dynamic viscoelasticity of depyruvated xanthan at 0.5% and 0°C increased at an alkaline and acid range, and showed the maximum value at pH 8.6 or 5.6 upon the addition of KOH (100 mM) or HCl (100 mM), respectively.

It has been found that the depyruvated xanthan has a smaller number of intermolecular association than those of native (K<sup>1)</sup> and Ca<sup>3)</sup> salt and deacetylated<sup>2)</sup> xanthans. This indicates that the pyruvate residues of xanthan

molecules contribute to its intermolecular association at higher temperatures as in methylcellulose.<sup>12)</sup> Thus, an intermolecular hydrogen bonding<sup>5)</sup> between methyl groups of pyruvate residues and adjacent acetal ring oxygen atoms of the side chains on different molecules may occur. As the pyruvate residues are attached on two-thirds of the outer D-mannose side chains, they may also associate with the adjacent hemiacetal oxygen atom of the outer D-mannose side chains that are free from pyruvate substitution on different molecules, in the same manner as the intramolecular hydrogen bonding to which acetate methyl groups contribute.<sup>5)</sup>

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