Structural change of xanthan gum association in aqueous solutions

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Abstract

Changes of viscoelasticity and structure of water were studied for xanthan (XA)/water systems in annealing and subsequent cooling induced gelation process. Viscoelasticity of XA/water systems was investigated by parallel plate type rheometer. The storage modulus G' of 2 wt.% XA aqueous solution slightly increased with the progression of the annealing time when the solution was annealed at 40°C. Immediately after annealing at 40°C for 18 h, G' of the solution was measured at the gelation temperature $T=5$°C. G' of the annealed solution was remarkably larger than that of the non-annealed solution. The time evolution of the G' of the system annealed at 40°C for 48 h was measured at $T=5$°C. G' of non-annealed solution was maintained at constant values at 5°C, in contrast with the G' of the annealed solution increased with increasing gelation time. Structural change of water in the system was measured by differential scanning calorimetry (DSC). The amount of non-freezing water in the system annealed at 40°C for 24 h changed oscillationally, whereas that of the system annealed at 40°C for 1 h remained almost constant. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Xanthan gum (XA) has been considered as a non-gelling polysaccharide [1–8]. However, we found that XA forms hydrogels by cooling when the solution was annealed in the sol state (annealing and subsequent cooling induced gelation) [9–11]. The gel–sol transi-

tion was investigated by falling ball method (FBM) and dynamic viscoelastic measurements. The FBM and dynamic viscoelastic measurements are typical and well-established methods of investigating the gel–sol transition of gels [12–14]. The transition temperature is around 35°C and depends on the annealing time at the sol state [10,11]. At the same time, the amount of non-freezing water in XA/water systems was measured by differential scanning calorimetry (DSC) [10,11]. It was revealed that the amount varies during annealing and subsequent cooling. Especially in the

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annealing process, the amount of non-freezing water measured by DSC varied oscillationally as a function of annealing time [10]. These experimental results suggest that the structural change which enables the system to form gels takes place in the annealing and subsequent cooling induced gelation process [9–11]. The anomalous behavior of non-freezing water in the annealing process was interpreted as the result of the competition between the interaction of polysaccharide molecules which leads to form molecular assemblies and the diffusion of polysaccharide electrolyte molecules. The anomalous behavior of non-freezing water was phenomenologically considered based on the above physical picture and the equation describing the annealing time dependence of the amount of non-freezing water was derived [15]. The agreement between the experimental results and the theory was good. In order to investigate the structural change of XA/water systems in annealing and subsequent cooling induced gelation further, the change of viscoelasticity of XA/water systems during annealing and gelation was investigated.

2. Experimental

2.1. Sample and sample preparation

XA powder provided by Mitsubishi Chemical was used as supplied without further purification. XA solutions were prepared using pure water provided by Wako Pure Chemical Industries at room temperature with stirring. The concentration of the XA aqueous solution measured in this study was 2 wt.%. All glassware used was sterilized before use. Solutions thus prepared (non-annealed solution) were kept in a refrigerator controlled at ca. 5°C before measurements.

2.2. Viscoelastic measurements

An advanced rheometric expansion system (ARES) (Rheometric Scientific, USA), equipped with either a 25 or 40 mm parallel plate measuring system, was used for all rheological measurements in this study. Frequency sweeps were carried out over the range 0.1–200 rad/s. The torque of each measurement was maintained at 0.2–200 μ Nm. The temperature was controlled within ±0.5°C.

2.3. Differential scanning calorimetry (DSC)

In DSC measurements, the enthalpy of melting ΔH_m per 1 mg of water in the system was measured. A Seiko DSC 200 was used throughout all the measurements. The non-annealed aqueous solution, weighing ca. 5 mg, was sealed in an Al sealed pan. The sample thus prepared was annealed at 40°C for a desired annealing time and then cooled to 5°C for a desired gelation time to obtain hydrogels. The annealing and gelation times were determined as the time period passed after the system reached the annealing temperature (40°C) and the gelation temperature (5°C), respectively. After that, the sample was cooled to −70°C at 10°C/min, and ΔH_m of water in the system was measured in the heating process up to 55°C at 10°C/min by DSC. ΔH_m thus determined is smaller than that of pure water. Since the value of ΔH_m is proportional to the number of water molecules which constitute crystal ice formed in the system in the cooling process to −70°C at 10°C /min, the difference between ΔH_m of the system and that of pure water is proportional to the number of non-freezing water molecules. In our previous papers, annealing time dependence of ΔH_m was measured for a sample by repeating the annealing and measurements at desired annealing times [10]. However, in DSC measurements of gelation time dependence of ΔH_m, the sample is heated to a temperature higher than the gel–sol transition temperature, T_{g-s}, and returns to the sol state. Further, the structure of sol state thus reached seems to be no longer the same as that of the solution immediately after the annealing. Therefore, there is no criterion to determine the gelation time of this sample even if we try to determine the gelation time dependence of ΔH_m by the subsequent gelation of this sample. Hence, we cannot determine the gelation time dependence of ΔH_m by the subsequent gelation of this sample. Here, we previously prepared many samples and annealed for the same annealing time. In measurements of gelation time dependence of ΔH_m, the annealed samples thus prepared gelled for each 2–4 samples for the same gelation time. Then, the average value of ΔH_m for 2–4 samples was finally adopted as the value of ΔH_m at the gelation time in order to avoid the scatter of ΔH_m of each sample. The amount of water evaporated during all
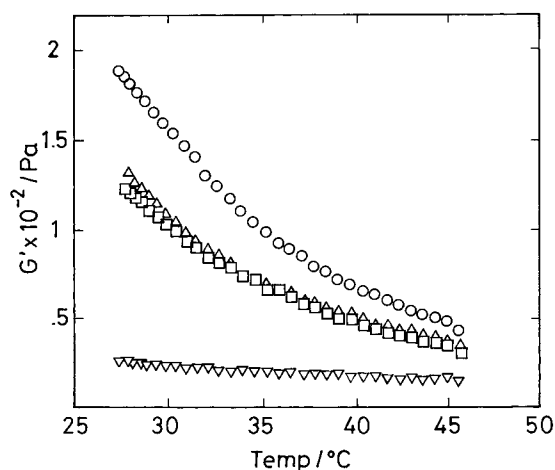
Fig. 1. Temperature dependence of G' at π rad/s for the non-annealed aqueous solution ($\triangledown$) and the gels obtained by gelation at 5°C for 24 h after annealing at 40°C for 6 ($\square$), 9 ($\triangle$) and 24 ($\bigcirc$) h measured at heating process from room temperature to 46°C.

the experimental procedure was around 1% and hence the change of the concentration of the system was around 0.01 wt.%.

3. Results and discussion

Fig. 1 shows temperature dependence of storage modulus G' of non-annealed solution and gels with various annealing times measured in the heating process from room temperature to 46°C. In our previous study, it was shown that the gel–sol transition temperature measured by FBM increased with increasing annealing time [10]. In Fig. 1, it is revealed that G' increased with increasing annealing time and largely decreased at around gel–sol transition temperature measured by FBM. The increase of G' with the annealing time strongly supports the idea reported in our previous studies. That is, the structural change which enables the system to form gels takes place in the annealing and subsequent cooling induced gelation process [9–11,15].

Fig. 2 shows the temperature dependence of G' and G'' of the gel obtained by annealing the aqueous solution at 40°C for 24 h and subsequent cooling to 5°C and keeping at the temperature for 24 h. They were measured in the process of heating from 5 to 50°C and subsequent cooling to 5°C. In low tempera-
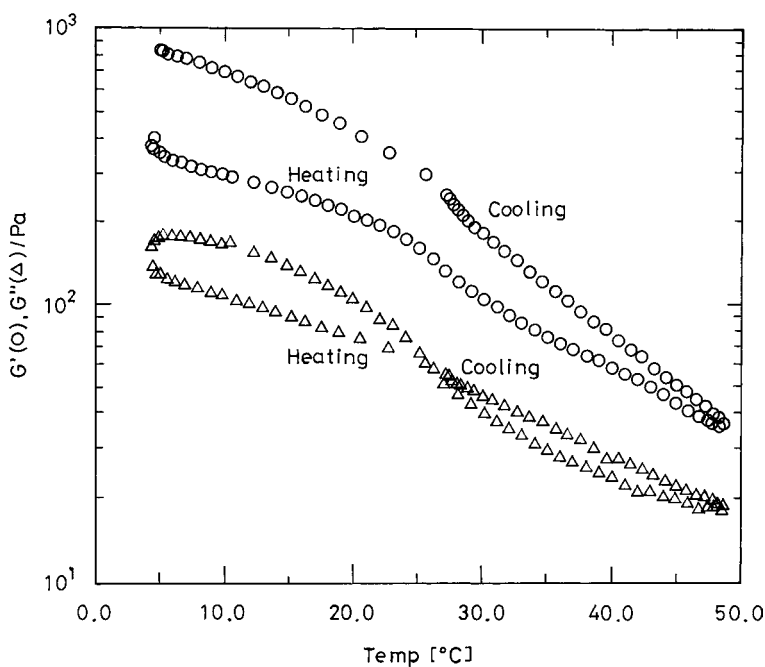

Fig. 2. Temperature dependence of G' ($\bigcirc$) and G'' ($\triangle$) at π rad/s for the gel obtained by gelation at 5°C for 24 h after annealing at 40°C for 24 h measured in heating and cooling processes.

ture region, weak dependency on temperature is observed for both G' and G''. This fact seems to show that G' and G'' approach the rubbery plateau region with the temperature decrease. G' and G'' in the cooling process are larger than those obtained in the heating process except for the region from $T=25$ to $50°C$. This fact seems to show that further structural change occur when the temperature reaches the temperature ($\sim 50°C$) higher than the annealing temperature ($=40°C$). In the following section, the change of viscoelasticity in the annealing and cooling processes will be discussed.

Fig. 3 shows frequency dependence of storage modulus G', loss modulus G'' and complex viscosity η^* of non-annealed aqueous solution at $T=5°C$. Both G' and G'' were maintained at constant values, even when the solution was kept in a refrigerator. The frequency sweep of the non-annealed solution was also carried out at $40°C$, as shown in Fig. 4. Sweep patterns of Figs. 3 and 4 are similar, although G' and G'' values measured at $40°C$ are lower than those measured at $5°C$.

When the solution was maintained at $40°C$ for a longer period, the increase of G' values was observed as a function of storing time. Fig. 5 shows time evolution of G' at 0.1, 1, π and 100 rad/s measured at $40°C$. The change of viscoelasticity described above seems to prove that the anomalous behavior of water observed by DSC reported in our previous work [10] is caused by the structural change of the system, i.e., the oscillational change of non-freezing water during
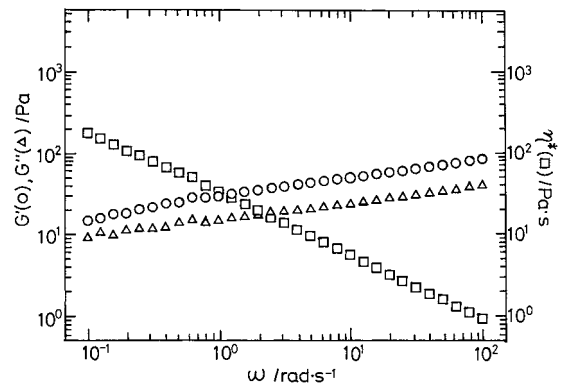

Fig. 4. Frequency dependence of G' ($\bigcirc$), G'' ($\triangle$) and complex viscosity η^* ($\square$) of non-annealed xanthan aqueous solution at $40°C$.

annealing process is closely related to the structural change observed through variations of G', G'' and η^*. In our previous papers, the anomalous behavior of non-freezing water in annealing process was interpreted as the adsorption and desorption of water molecules in polysaccharide chains which took place in the processes of dissociation of polysaccharide molecular assemblies by the annealing at the relatively high temperature and subsequent homogenization of the systems by the diffusion of polysaccharide molecules removed from molecular assemblies [10–11,15]. When the system become homogeneous, the formation of entanglements of polysaccharide chains and the reformation of molecular assemblies occur. These
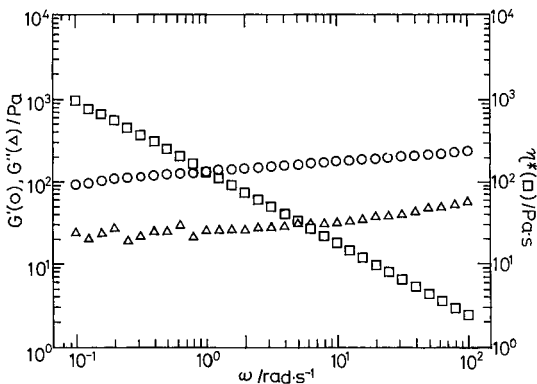

Fig. 3. Frequency dependence of G' ($\bigcirc$), G'' ($\triangle$) and complex viscosity η^* ($\square$) of non-annealed xanthan aqueous solution at $5°C$.
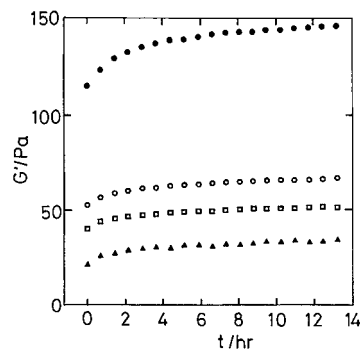

Fig. 5. Time evolution of G' at 0.1 ($\blacktriangle$), 1 ($\square$), π ($\bigcirc$) and 100 ($\bullet$) rad/s of non-annealed xanthan aqueous solution during annealing at $40°C$.
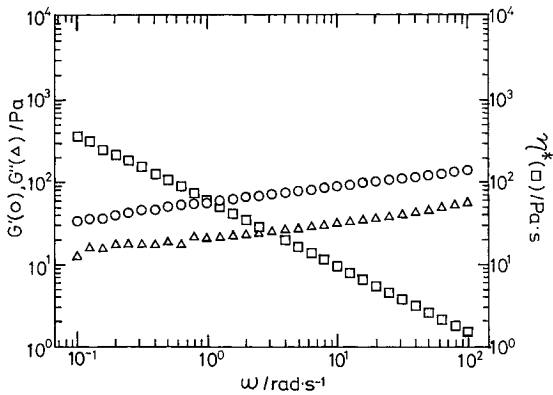
Fig. 6. Frequency dependence of G' (○), G'' (△) and complex viscosity η^* (□) at 40°C of xanthan aqueous solution annealed for 18 h at 40°C.
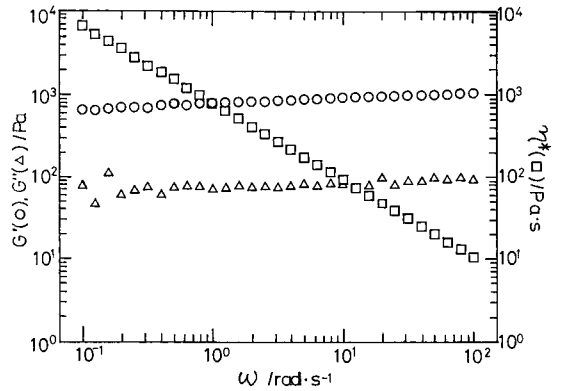

Fig. 7. Frequency dependence of G' (○), G'' (△) and complex viscosity η^* (□) at 5°C of xanthan aqueous solution annealed for 18 h at 40°C.

entanglements and molecular assemblies cannot behave as junction points because of the relatively high annealing temperature (=40°C), but can be expected to behave as pseudo-junction points. The increase of G' may be interpreted as the result of the formation of the entanglements of the polysaccharide chains and the molecular assemblies.

Fig. 6 shows frequency dependence of viscoelasticity of the aqueous solution annealed at 40°C for 18 h.

The increase of G' is clearly observed when the values shown in Fig. 6 are compared with those of Fig. 4.

Fig. 7 shows the frequency dependence of viscoelasticity of the solution measured at 5°C after annealing at 40°C for 18 h. A remarkable increase of G' is seen if the values of Fig. 7 are compared with those of Fig. 3. From Fig. 7, it is concluded that the structure formation which enables the system to form hydrogels occur by the annealing.
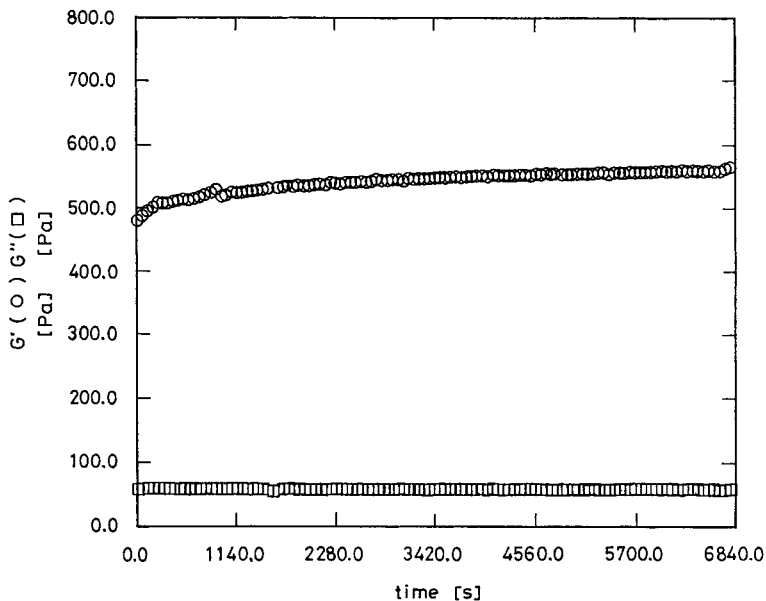

Fig. 8. Time evolution of G' (○), G'' (□) of xanthan aqueous solution annealed at 40°C for 48 h during gelation process at 5°C.
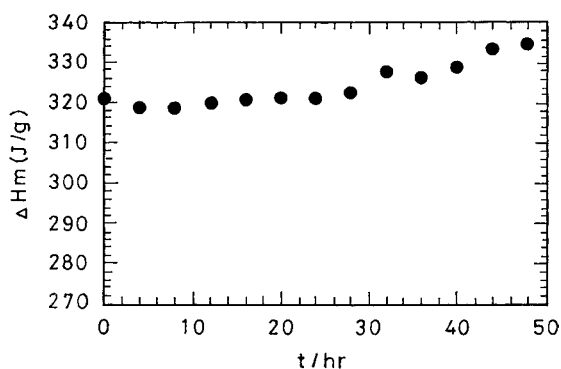
Fig. 9. Time evolution of ΔH_m of the 2 wt.% system annealed at 40°C for 1 h during gelation process at 5°C.
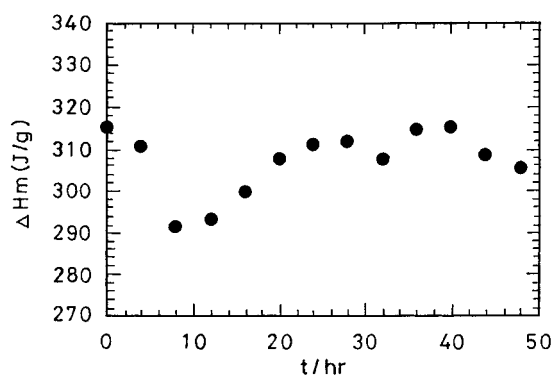

Fig. 10. Time evolution of ΔH_m of the 2 wt.% system annealed at 40°C for 24 h during gelation process at 5°C.

By maintaining the solution annealed at 40°C for about 1 day at 5°C, a firm hydrogel was obtained as reported previously [9,10]. Fig. 8 shows time evolution of G' and G'' in gelation process at 5°C of the solution annealed at 40°C for 48 h. As shown in Fig. 8, G' gradually increased with increasing gelation time. It is clear that the junction zone is formed at this temperature.

Figs. 9 and 10 show time evolutions of ΔH_m of XA/ water systems annealed at 40°C for 1 and 24 h in gelation processes at 5°C, respectively. Oscillational change of ΔH_m in Fig. 10 shows that the formation of junction points, i.e., gelation, in the system annealed at 40°C for 24 h is enhanced in the gelation process and the kinetics of junction formation may be essentially the same as that of the structure formation in the annealing process. In contrast, Fig. 9 shows that ΔH_m tends to increase slightly, but remains almost constant when the annealing time ($=1$ h) is short. This indicates that the formation of gels is difficult in this system because of the incompleteness of the homogenization of the system by too short annealing.

Acknowledgements

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