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Annealing induced gelation of xanthan/water systems

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The effect of annealing at a temperature higher than the gel–sol transition temperature on the junction formation in the gelation process of xanthan/water solutions was investigated by the falling ball method (FBM) and differential scanning calorimetry (d.s.c.). Aqueous solutions of xanthan dissolved at room temperature were inhomogeneous. Although gel-like solutions were formed after subsequent cooling, the solutions could not be categorised as a gel. In contrast, when the solutions were annealed at 40°C, firm gels were formed by subsequent cooling. The gel–sol transition temperature (T_{g-s}) was clearly observed by FBM. It was found that T_{g-s} gradually increased from 27°C with increasing annealing time and approached a constant value, i.e. 33°C for 1 wt% sample and 40°C for 2 wt% sample. The annealing time, where T_{g-s} levelled off, depended on sample concentration and annealing temperature. During annealing from 0 to 12 h, it was observed that the amount of non-freezing water estimated by d.s.c. fluctuated, although a steady increase of T_{g-s} was observed by FBM. This phenomenon is interpreted as a homogenisation of the solution, i.e. xanthan molecules become free from their molecular assembly through desorption of non-freezing water by annealing. The above results indicate that xanthan/water solutions form the gel state when they are fully annealed in the sol state. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: xanthan; gelation; annealing)

INTRODUCTION

Xanthan gum is a polysaccharide produced by bacterium *Xanomonaus campestris*, which is considered to take a rod-like 51 double helix in aqueous solution[1,2]. Xanthan gum has been considered as a non-gelling polysaccharide in aqueous solution[3–10]. However, we recently found that xanthan/water systems form gels above a threshold concentration (0.5 wt%) by cooling, when they are annealed at a temperature higher than the gel–sol transition temperature[11]. It was suggested that polysaccharide solutions were in a thermodynamically non-equilibrium state. The nature of the sol state necessarily related with the thermal behaviour of water molecules tightly bound with polysaccharide molecules. It is thought that the structure of water varied in the course of junction zone formation of xanthan hydrogels[11].

In this study, structure change of xanthan/water solutions during annealing is investigated by the falling ball method (FBM) and differential scanning colorimetry (d.s.c.).

EXPERIMENTAL

Sample and sample preparation

Xanthan gum powder was provided by Mitsubishi Chemical Co. Ltd. The commercial name is Soaxian. The weight average molecular weight was ca. 1.0 × 10^5. It was used as supplied without further purification. Aqueous solutions of xanthan were prepared using pure water and all glassware were sterilised before use.

Falling ball method (FBM)

A desired amount of xanthan gum powder and 5 ml of pure water were sealed into a glass tube, which was ca. 35 cm in length and 10 mm in diameter, with a stirrer chip. After maintaining at room temperature with occasional stirring, the sample tube was annealed at 40 ± 0.5°C for a predetermined annealing time. Then, it was immersed in a water bath controlled at 10°C and kept for 12 h to make a gel. The glass tube was opened and a steel ball of ca. 0.5 mg with 0.8 mm diameter was inserted into the gel. The gel in the glass tube was heated from 10°C at a rate of ca. 0.5°C $\min^{-1}$ in a water bath. The position of the steel ball was measured by a cathetometer and recorded as a function of temperature. The gel–sol transition temperature was determined as the intersection of a horizontal straight line in the low temperature region and an oblique straight line in the high temperature region from the interpolation method.

Differential scanning calorimetry (d.s.c.)

A Seiko dynamic work station SDM 5500 equipped with a Seiko DSC-200 was used through all the thermal analysis measurements. The scanning rate was 10°C $\min^{-1}$. The

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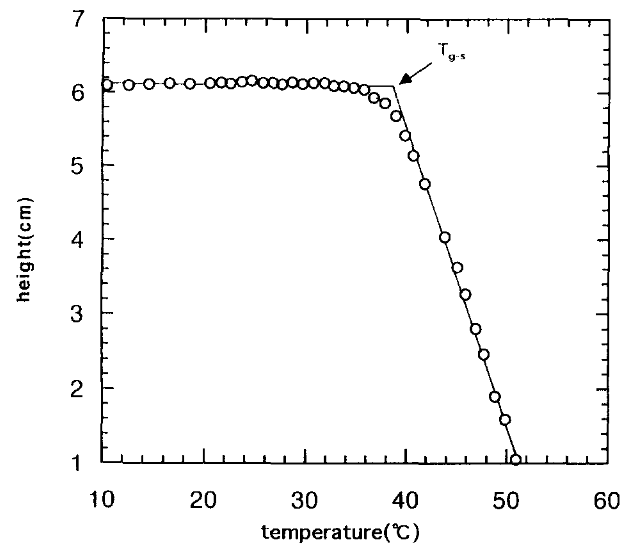

Figure 1 Relationship between the height of the steel ball and the temperature of the water bath for 2 wt% gel obtained by annealing for 12 h

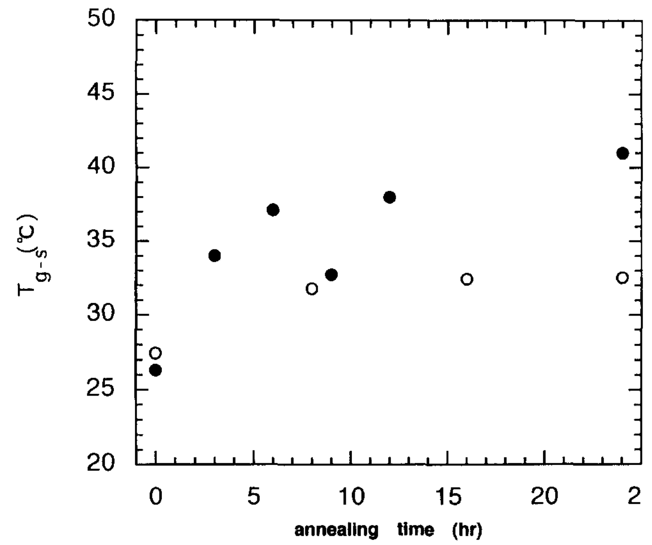

Figure 2 Relationship between gel–sol transition temperature $T_{g\text{-}s}$ and annealing time at 40°C for 1 wt% (○) and 2 wt% (●) xanthan/water systems

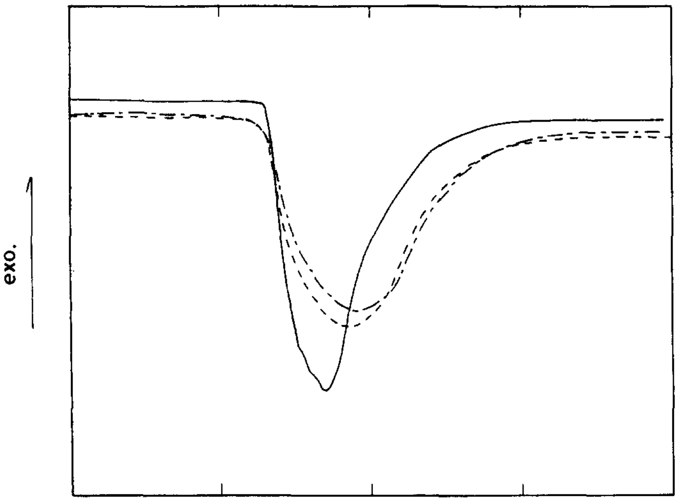

Figure 3 Representative endotherms for pure water (———) and pre-annealed samples with concentrations of 1 wt% (· · ·) and 3 wt% (– • –)

sample weight was ca. 6 mg. Enthalpy of melting of water in the sol state of xanthan/water systems was determined as reported previously[12]. Amount of non-freezing water was calculated by subtracting the amount of freezing water from the total amount of water in the system[13].

RESULTS AND DISCUSSION

Xanthan aqueous solutions were visually inhomogeneous when dissolved at room temperature. They became gel-like solutions by maintaining them at room temperature for a few days. Although they show visual gel-like features, they are not as tough as which ordinary gels. However, firm gels were formed, if the solutions were annealed at 40°C for an appropriate time interval and subsequently cooled to 5°C. The solution became homogeneous after annealing.

Figure 1 shows a representative FBM curve of the sample (2 wt%) prepared by annealing at 40°C. As shown in *Figure 1*, falling time of the steel ball markedly decreased at around 38°C. Similar curves are obtained in FBM for various types of ordinary gels, such as polyethylene/decalin, polypropylene/toluene and ethylene–propylene random copolymer/toluene[14]. The gel–sol transition temperature ($T_{g\text{-}s}$) was defined as indicated by the arrow. A similar pattern shown in *Figure 1* was observed for all of the samples which were formed after annealing, although $T_{g\text{-}s}$ varied as a function of annealing time at 40°C.

Figure 2 shows the gel–sol transition temperatures ($T_{g\text{-}s}$) of 1 and 2 wt% aqueous solutions obtained by FBM as a function of annealing time. As shown in *Figure 2*, $T_{g\text{-}s}$ increased gradually and approached a constant value with increasing annealing time. $T_{g\text{-}s}$ values of 2 wt% were higher than those of 1 wt% sample in the whole range of annealing time. $T_{g\text{-}s}$ values of 2 wt% samples levelled off at ca. 40°C and those of 1 wt% at ca. 33°C. The results obtained by FBM strongly indicate that xanthan/water systems form gels, in contrast to many reports which suggest that xanthan gum is a non-gelling polysaccharide[3–10].

Figure 3 shows d.s.c. melting curves of water in pre-annealed samples measured by heating at 10°C min^{-1} after cooling from room temperature to −70°C at 10°C min^{-1} as a function of concentration. d.s.c. curves had a single peak and the existence of freezing bound water was not verified. Peak temperature increased as the concentration increased. Melting temperature was defined as the temperature at which the d.s.c. curve suddenly changed toward the endothermic direction. Melting temperature, as defined above, was observed at a temperature lower than that of pure water, although the values ranged in experimental error and showed no systematic dependence on the concentration.

The peak area of melting curve decreased with increasing concentration. It is expected that the peak area was reduced by the addition of xanthan gum due to hydrogen bond formation between the hydroxyl group of xanthan and water molecules. However, the extent of the reduction was much larger than expected, even when the presence of xanthan gum was taken into account. The d.s.c. melting curves shown in *Figure 3* have been corrected with respect to the coexisting mass of xanthan gum and the enthalpy of melting (ΔH_m) per milligram of water in the sol state of xanthan/water systems calculated.

Figure 4 shows ΔH_m for pre-annealed samples with various concentrations. It can be clearly seen that ΔH_m decreases with increasing concentration, suggesting that a small amount of non-freezing water exists and the amount increases with increasing concentration[13]. It is

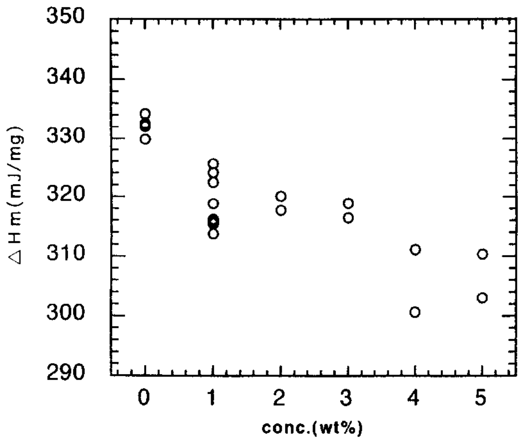

Figure 4 Relationship between the amount of enthalpy of melting (ΔH_m) and concentration of pre-annealed samples

well known that a certain number of water molecules are restrained in the junction zone when polysaccharides form hydrogels[15–18]. Water molecules restrained tightly by the hydroxyl groups of polysaccharide or trapped in well-organized gel network structures behave as non-freezing water and/or freezing bound water. It is thought that the structure change in xanthan/water systems can be revealed through the change in the non-freezing water content of xanthan/water systems.

Figure 5 shows d.s.c. melting curves of water in the sol-state of 2 wt% xanthan/water systems at various annealing times. Peak temperature decreased with the progression of the annealing. However, melting temperature was not changed by annealing. This is appropriate, if it is considered that the major portion of the gel is free water and the maximum amount of non-freezing water is a limited amount[19].

Figure 6 shows ΔH_m of xanthan aqueous solutions obtained by annealing at 40°C as a function of annealing time. The value of ΔH_m changed in the initial state of annealing (12 h), and then approached a constant. The time interval where ΔH_m markedly changed, agreed well with the time interval in which $T_{g\text{-}s}$ increased sufficiently (see *Figure 2*). The facts suggest that the amount of non-freezing water affects the gelation process.

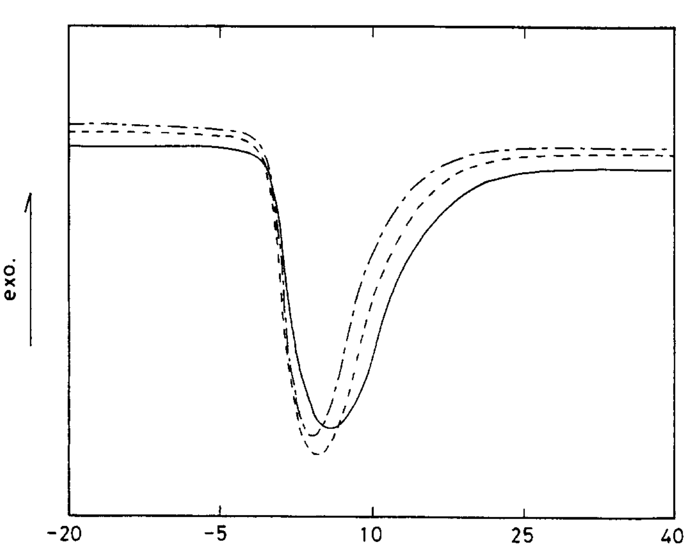

Figure 5 Representative endotherms of 2 wt% xanthan/water systems annealed for 0 (———), 6 (· · ·) or 24 (– · –) h

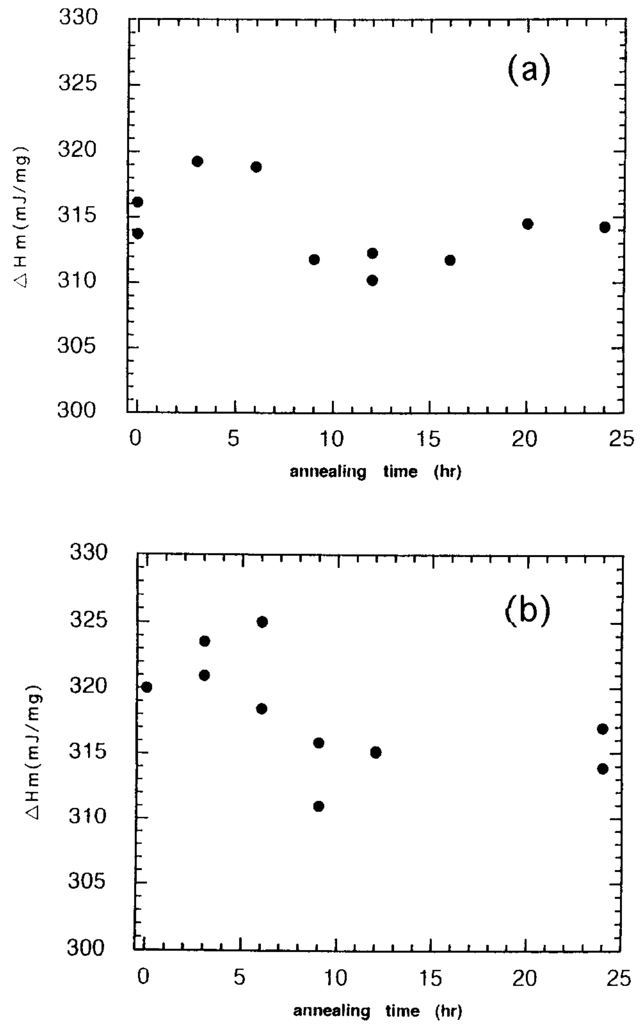

Figure 6 Relationship between the amount of the enthalpy of melting (ΔH_m) and annealing time at 40°C for (a) 1 wt% and (b) 2 wt% systems

From the above results, it is thought that gelation of xanthan/water systems takes place as follows: when xanthan is dissolved in water at room temperature, large scale molecular assemblies are formed. The molecular assemblies consisting of xanthan molecules are suspended in a large amount of free water. Once these molecular assemblies are established, visual gel-like solutions are established, even after being maintained at room temperature for 2 days. Xanthan molecules do not fully expand, even in an excess amount of free water and molecular chains cannot be rearranged in order to form a junction zone in which molecular chains are interpenetrating. Thus, the inhomogeneous solutions do not form real gels. This is why many researchers reported that gelling properties were not observed in xanthan/water systems[3–10].

However, when the above inhomogeneous solutions were annealed at 40°C, firm gels were obtained. As shown in *Figure 2*, $T_{g\text{-}s}$ ranges from ca. 27 to 40°C depending on concentration and annealing time. The annealing temperature (40°C) used in this experiment was an appropriate temperature from the results of FBM. When we assume that the sample is annealed for a long time and attains a sufficiently stable junction zone, $T_{g\text{-}s}$ shows the levelling off value which is close to annealing temperature. As shown in *Figure 6*, the amount of freezing water increased during transient time of gel formation. This suggests that the desorption and adsorption of non-freezing water may easily occur at the sol state. If xanthan molecules are free from molecular assembly by molecular enhancement at a high temperature and the mobility of water molecules increases, the molecular chains move freely and the systems attain homogeneity. Owing to the complex chemical structure of xanthan molecular chain, it takes a long time for rearrangement of molecular chains in the sol state, compared with the gelling behaviour of other polysaccharide hydrogels, such as agarose or gellan gum[20,21]. In the homogeneous state thus obtained, the firm gels were formed by subsequent cooling. It is thought that the above process is universally acceptable for any kind of polyelectrolyte polysaccharides, although conditions for molecular arrangements depend on each characteristic feature of the polysaccharide. In order to define the general scheme of non-equilibrium nature of hydrogels, further investigation is necessary.

To conclude, gelling ability in xanthan gum/water systems, when xanthan aqueous solutions are well annealed at the sol state, was confirmed. At the same time, a small quantity of non-freezing water molecules plays an important role in the above gelation process.

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