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Exothermic events on heating of semi-dilute konjac glucomannan-water systems

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Abstract

Differential scanning calorimetric experiments were designed and conducted to investigate the occurrence of two intriguing exothermic events, hitherto never reported before, on programmed heating of semi-dilute ($\leq 1.0\%$, w/w) aqueous konjac glucomannan (KGM) solutions to temperatures above 70 °C. These exothermic transitions, with peak temperatures of 74–80 °C and 115–132 °C, respectively, were attributed to disorder-order transitions of different kinds. The results of storage and annealing experiments suggest that these transitions were time-dependent. The ordered structures formed on heating were heat-stable, at least up to 180 °C.

Keywords: Konjac glucomannan; Thermal analysis; Exothermic transitions

1. Introduction

Konjac glucomannan (KGM), a neutral polysaccharide, is the main component of the tuber of *Amorphophallus konjac* C. Koch. It consists of β-1, 4-linked D-mannose and D-glucose in the ratio 1.6:1, with about 1 in 19 units being acetylated (Kato & Matsuda, 1969). It forms a thermally stable gel (*konnyaku*) upon addition of an alkaline coagulant. *Konnyaku* is a popular traditional Japanese food. In recent years, studies on the gelation behaviour of semi-dilute KGM systems (Huang, Kobayashi, & Nishinari, 2001; Williams et al., 2000; Zhang et al., 2001) have proliferated due to the emergence and application of KGM as a food additive in the West. KGM is known to interact synergistically with other hydrocolloids such as carrageenan (Cairns, Atkins, Miles, & Morris, 1991; Kohyama, Sano, & Nishinari, 1993; Nishinari, Williams, & Phillips, 1992; Williams, Clegg, Langdon, Nishinari, & Piculell, 1993) and xanthan gum (Nishinari et al., 1992; Williams, Day, Langdon, Philips, & Nishinari, 1991). However, aqueous KGM systems, in the absence of alkali, do not appear to form gels but viscous solutions (Takigami, 2000; Yoshimura, Takaya, & Nishinari, 1996). A heat-stable gel may, however, be formed through the application of heat (Case & Hamann, 1994). Nishinari et al. (1992) have given an extensive review on the physico-chemical characteristics and properties of KGM.

When polysaccharides are heated in the solid state and/or in aqueous environments, they undergo a series of interrelated physical transitions and chemical transformations that are manifested by changes in their physical properties including heat capacity, enthalpy, weight, volume and crystallinity. Dynamic thermal analysis methods (such as DSC, DTA, TGA and DMTA), because of their ability to monitor these properties, have proven powerful tools to probe the extent, rate and sequence of thermal events in both natural and synthetic polymer systems. A survey of recent literature shows that thermal methods, primarily differential scanning calorimetry (DSC), have been applied to study aqueous KGM + κ-carrageenan systems (Kohyama & Nishinari, 1997; Williams et al., 1993), KGM + gellan systems (Nishinari, Miyoshi, Takaya, & Williams, 1995), KGM + xanthan gum systems (Annable, Williams & Nishinari, 1994; Goycoolea, Richardson, Morris & Gidley, 1995); and KGM + corn starch systems (Yoshimura et al., 1996). In the majority of those studies, it has always been

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pointed out that aqueous systems containing KGM alone (usually at relatively high concentrations of ~10%) did not exhibit any thermal transitions on heating (Yoshimura et al., 1996). Our own experience lead us to believe that the lack of such thermal events may be due to the high KGM concentration used and/or the way the KGM samples were prepared in those experiments. KGM samples were usually conditioned at high temperatures (above 80 °C) over a significant period of time prior to DSC analysis. Thus, any temperature- and/or time-dependent thermal events may have already taken place before thermal analysis.

The present study was conducted to investigate the thermal properties of semi-dilute KGM solutions on programmed heating to sufficiently high temperatures reflective of the normal conditions encountered in the application of KGM as a food ingredient. The possibility of any transition showing time-dependency was studied by annealing, i.e., holding the KGM samples isothermally at different temperatures.

2. Materials and methods

2.1. Preparation of KGM-water samples

A sample of refined KGM powder, Propol® A, was obtained from Shimizu Chemical Co. (Japan) and was used without further purification. The initial moisture content of the powder, determined from the loss in weight on drying duplicate samples at 105 °C to constant weight) was 3.04% (wwb). Samples of KGM powder were then accurately weighed (on dry basis) and dispersed in distilled water at room temperature with stirring (at 360 rpm) for 1 h, using a magnetic stirrer, to ensure complete hydration, swelling, and dissolution of the Propol® particles before DSC measurement. The initial pH of the1% KGM solution was ~ 6.5.

2.2. DSC measurement

A DuPont 2910 differential scanning calorimeter (E.I. duPont de Nemours & Co., Inc., Wilmington, Del., USA), equipped with a standard DSC cell and a Thermal Analyst 2000 Controller, was used. About 10 mg of KGM solution, weighed to 0.01 mg, was sealed in a hermetic aluminium DSC pan. The pan was then placed in the DSC cell, quench-cooled to 20 °C using ice-water, and then heated to 140–200 °C at 1 °C min^{-1} or 10 °C min^{-1} with a constant purge of nitrogen gas. An empty aluminium pan was used as the reference pan to balance the heat capacity of the sample pan. All measurements were performed in duplicate. Heat flow and temperature were calibrated using pure indium. Data analysis was carried out using the DuPont DSC Standard Data Analysis Program Software (Version 4.0).

2.3. Storage of KGM solutions

KGM solution (1.0%, w/w) was prepared as mentioned in Section 2.1. Samples were sealed in hermetic aluminium DSC pans which were then stored in an incubator at 30 °C. A sample pan was withdrawn at appropriate intervals of time (0, 3, 8 and 24 h) for DSC measurement. The experiment was repeated using another freshly prepared KGM solution.

2.4. Annealing at different temperatures

KGM solution (1.0%, w/w) was prepared as described in Section 2.1 and samples were hermetically sealed in the DSC pans. Each pan was then placed in the DSC cell, quench-cooled to 20 °C using ice-water, and then heated to 60, 70 or 90 °C at 1 °C min^{-1} with a constant purge of nitrogen gas. On reaching the targeted temperature, the sample was then held isothermally and the isothermal profile was recorded. The experiment was conducted in duplicate.

2.5. Statistical analysis

The test data were statistically analyzed by one-way ANOVA (for comparing more than two means) when necessary, using *SPSS Version 10.0.1 For Windows* (SPSS Inc., Chicago, Illinois). Duncan test was also carried out to perform comparison of means at 95% probability level.

3. Results

3.1. Effects of heating rate

Fig. 1 gives a comparison of the DSC thermograms obtained using heating rates of 1° min^{-1} and 10 °C min^{-1}. The thermogram obtained using the slower scanning rate was definitely much smoother with better resolution. In both

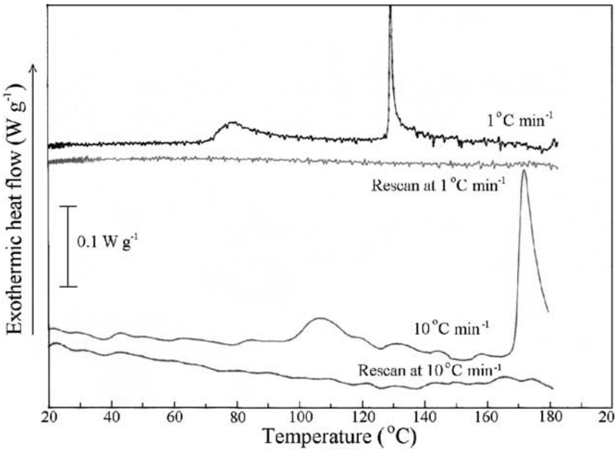

Fig. 1. Effect of scanning rate on 1% KGM solutions.

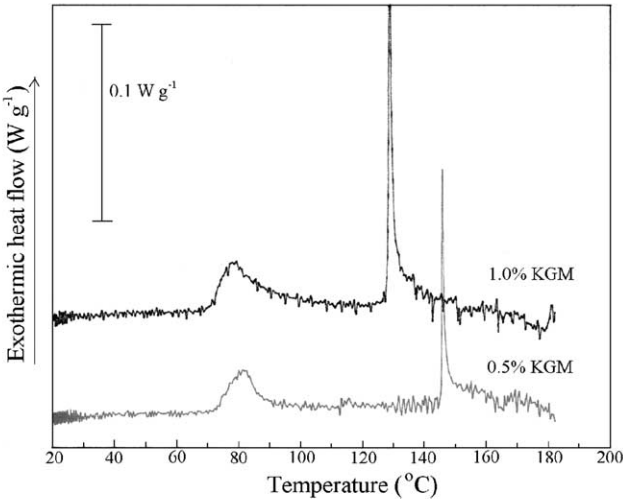

Fig. 2. DSC thermograms of 0.5% and 1.0% KGM solutions.

cases, two major exothermic events were noted, the transition occurring at the higher temperature being very much sharper than the lower temperature exotherm. Both transitions also occurred at correspondingly higher temperatures and were larger when a faster heating rate was employed. Immediate rescanning of the heated samples after quench-cooling revealed a relatively flat curve without significant transitions within the temperature range studied. Subsequent experiments were carried out using a heating rate of 1 °C min^{-1}.

3.2. *Effects of KGM concentration*

Fig. 2 shows the DSC thermograms of KGM-water systems at two KGM concentrations, i.e., 0.5% and 1.0% (w/w). KGM concentrations ≥2.0% (w/w) could not be studied using the present sample preparation technique because the systems became too viscous to be stirred after the first 15 min. Both samples yielded the same two exothermic transitions on heating at 1 °C min^{-1}. Table 1 gives the peak temperature (T_p) and enthalpy (ΔH) data obtained. Subsequent experiments were conducted using a KGM concentration of 1.0% (w/w).

3.3. *Effects of storage*

Fig. 3 shows the DSC thermograms of 1.0% (w/w) KGM solutions stored for different lengths of time at 30 °C after sample preparation. The measured parameters (T_p and ΔH) are given in Table 2. The following interesting features were noted:

(i) The lower temperature transition (X_1) with its temperature location (T_{p1}) being slightly shifted to progressively lower temperatures while its enthalpy (ΔH_1) does not change significantly with storage time at 30 °C.
(ii) The higher temperature transition (X_2) with both its temperature location (T_{p2}) and enthalpy (ΔH_2) not affected significantly by storage time.

Interestingly, the exothermic peaks were still clearly in evidence after storage of a 0.5% KGM solution for 2 days at 30 °C (DSC thermogram not shown).

3.4. *Effects of annealing at different temperatures*

Fig. 4 shows the isothermal thermograms obtained during annealing of 1.0% (w/w) KGM solutions at different temperatures. In the first case, heating to 60 °C (i.e., below the predicted onset temperature of X_1), as expected, did not yield any thermal transitions. However, holding the

Table 1
Peak temperature (T_p) and enthalpy (ΔH) of the phase transitions obtained on heating 0.5% and 1.0% KGM solutions

KGM concentration	X_1[a]		X_2[a]	
	T_{p1} (°C)	ΔH_1 (J/g)	T_{p2} (°C)	ΔH_2 (J/g)
0.5%	88.9±11.5	11.3±1.1	144.2±1.6	8.9±0.3
1.0%	80.8±3.6	14.7±6.9	129.8±1.3	15.2±1.4

[a] Mean±standard deviation (n=2).

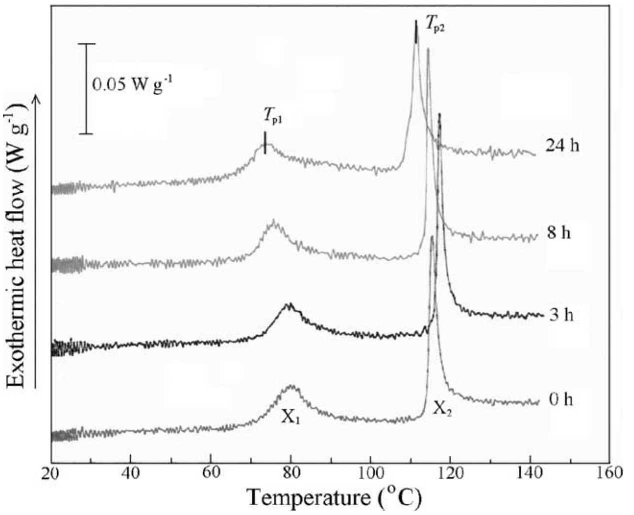

Fig. 3. DSC thermograms of 1.0% KGM solutions stored at 30 °C for different lengths of time.

Table 2
Peak temperature (T_p) and enthalpy (ΔH) of the phase transitions obtained on heating 1%KGM solutions as a function of storage time at 30 °C

Storage time (h)	X_1[a]		X_2[a]	
	T_{p1} (°C)	ΔH_1(J/g)	T_{p2} (°C)	ΔH_2 (J/g)
0	81.1±1.2^{a}	10.4±1.9^{a}	111.2±5.6^{a}	14.2±0.7^{a}
3	78.6±2.0^{ab}	9.99±1.6^{a}	113.2±5.8^{a}	12.9±3.5^{a}
8	76.2±0.8^{bc}	11.5±2.4^{a}	114.5± 0.02^{a}	16.1±2.5^{a}
24	73.9±0.6^{c}	12.6±0.3^{a}	115.7±6.3^{a}	16.5±0.3^{a}

[a] Mean±standard deviation (n=2). Means within a column with the same superscript letter are not significantly different at 95% probability level.

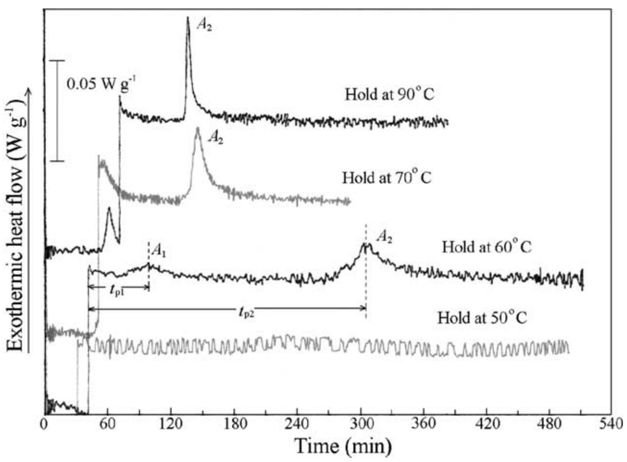

Fig. 4. Effect of isothermal annealing at different temperatures on the exothermic events of a 1.0% KGM solution.

temperature constant at 60 °C gave rise to two exothermic transitions (A_1 and A_2). In the second case, annealing at 70 °C (i.e., within the predicted temperature range of X_1) yielded a partial exothermic transition (A_1) followed by a second (and larger) exotherm (A_2). In the third case, heating to 90 °C (i.e., after the expected completion of X_1) caused the expected appearance of an exotherm (X_1). Subsequent annealing at that temperature gave rise to only one sharp exotherm (A_2). Holding the temperature constant at 50 °C did not yield any thermal transitions even after 8 h.

The time period (t_p) between the occurrence of any exothermic event (measured from the peak) and the start of annealing as well as the enthalpy (ΔH) of the transitions were determined and are presented in Table 3. It is worth noting that the A_2 transition became increasingly narrower and sharper (i.e. the transition range decreased) while ΔH and t_p also decreased progressively as annealing temperature was raised from 60–90 °C.

4. Discussion

When we first noticed the intriguing exothermic transitions on programmed heating of dilute aqueous KGM solutions prepared from Shimizu's Propol® A, we decided to repeat the DSC runs using KGM that we extracted and purified (using ethanol) from konjac flour obtained from a different source. Qualitatively, the two exothermic transitions were again observed (DSC thermograms not shown), thereby authenticating the thermal events. Zhang, Huang, Nishinari, Watase, and Konno (2000) have reported the possibility of an interaction between non-preheated silver pans and water above 120 °C that could give rise to a large exothermic peak observed at 140–190 °C when a 2% aqueous suspension of curdlan was heated. No such exothermic event was evident when preheated silver pans were used. To investigate the possibility, although remote, of a similar artifact arising from the use of aluminium pans, we repeated the DSC runs on Propol® A using aluminum pans preheated to 200 °C. The reference pan used was either a preheated aluminum pan filled with distilled water or a preheated empty aluminum pan. Qualitatively, similar thermal events were again observed (DSC themograms not shown).

Table 3
Effects of annealing temperature on the phase transition time (t_p) and enthalpy (ΔH) of a 1.0% KGM solution

Annealing temperature (°C)	A_1[a]		A_2[a]	
	t_{p1} (min)	ΔH_1 (J/g)	t_{p2} (min)	ΔH_2 (J/g)
60	58.3±0.1	5.4±2.4	253.4±13.7^a	30.7±5.8^a
70	–	–	84.0±15.2^{bc}	21.3±0.5^{ab}
90	–	–	72.4±9.2^c	14.9±2.2^b

t_p Refers to time period between the peak of A_1 or A_2 and the time when the isothermal holding began.

[a] Mean±standard deviation (n=2). Means within a column with the same superscript letter are not significantly different at 95% probability level.

Failure on the part of previous researchers (Kohyama & Nishinari, 1997; Miyoshi, Takaya, Williams, & Nishinari, 1996; Williams et al., 1993; Yoshimura et al., 1996) to detect such exothermic events in their DSC studies on KGM and KGM-biopolymer blends may be due to the following reasons:

1. Method of sample preparation—the KGM samples were subjected to heat treatment at 80–110 °C for a significant period of time before being cooled down prior to DSC analysis (Kohyama & Nishinari, 1997; Miyoshi et al., 1996). This heat pretreatment most probably eliminated at least the lower temperature exothermic event (X_1).
2. The high KGM concentration (10%) of samples used by Yoshimura et al. (1996)—it is likely that whatever disorder-order transitions that occur could be accelerated by an increase in macromolecular concentration and be completed even before DSC analysis so that no exothermic events were evident. Yoshimura and Nishinari (1999) have reported that gelation time of KGM solutions became shorter and gelation rate became faster with increasing concentration. In the present study, a DSC scan of a 10% KGM sample did not reveal any exothermic transitions (thermogram not shown).

The most important question arising from the present findings is: what are the origins of the two exothermic events obtained on thermal ramping of semi-dilute KGM solutions? It is suggested that KGM undergoes unique disorder-order transitions on heating, leading to the formation of at least two kinds of ordered structures with different degrees of ordering and thermal stabilities. The exact nature of these ordered structures await elucidation. It is also not possible at this stage to say whether the existence or occurrence of the X_2 event is dependent on the X_1 event. Conformational changes, intermolecular associations (including junction zone formation), and/or hydrophobic interactions, to varying degrees of cooperativity, may be involved in enhancing structural order.

Case and Hamann (1994) have reported that KGM is able to form heat-stable gels upon addition of mild alkali and/or application of heat. Heat-set KGM gels are not normally thermo-reversible when heated to 100 °C. Based on rheological measurements, Yoshimura and Nishinari (1999) observed that the gelation kinetics of fractionated KGM showed an unusual phenomenon in that a pronounced initial peak in storage shear modulus was evident for samples heated at temperatures higher than 70 °C. This coincides remarkably well with the temperature location of the X_1 exothermic transition even though the present study involved the use of semi-dilute KGM solutions, the concentration of which is below the reported critical limit for gel formation. The unusual gelation phenomenon noted earlier may not after all be an experimental artefact due to slippage between sample and measuring geometry as suggested by Yoshimura and Nishinari (1999).

The two exothermic transitions obtained in the present study may proceed, albeit slowly, during storage at 30 °C, as evidenced by the fact that T_{p1} decreased slightly with time (Fig. 3). This is also supported by the fact that annealing of KGM solutions at temperatures below the onset temperature of the X_1 exotherm gave rise to two similar exothermic transitions, A_1 and A_2, which appear to correspond, respectively, to the X_1 and X_2 exotherms obtained on programmed heating. It is clear that the higher the annealing temperature, the faster the appearance of the exothermic transitions (Fig. 4). In particular, the A_2 exotherm became progressively sharper, indicating the formation of an increasingly ordered structure.

Shimizu Chemical Co. (2000) has reported that the viscosity of a 1% solution of Propol® increased progressively with time until a maximum viscosity was reached 5–6 h after initial dissolution. This maximum viscosity was maintained for over 120 h. However, the enthalpy of both the X_1 and X_2 exotherm in this study did not show significant difference with storage hour (Table 2), which may be due to different time-scale between their viscosity measurement and our thermal event measurement or other factors which await to be unravelled. In the present study, the enthalpy of the A_2 exotherm was found to decrease with an increase in annealing temperature. This is consistent with the fact that the viscosity of a 1% Propol® solution is greatly decreased at high temperatures, but is not significantly influenced at room temperature (Shimizu Chemical Co., 2000).

5. Conclusions

KGM possesses unique thermal properties. The present DSC experiments indicate that at least two different kinds of disorder-order transitions, which are temperature-, time- and concentration-dependent, proceed on dissolution of KGM. Because of that, particular attention to experimental details (including method of preparation of KGM solutions) is vital to achieve reproducibility of results in any study concerning KGM.

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