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Carbohydrate Research 316 (1999) 6–13

CARBOHYDRATE RESEARCH

Characterization of crosslinked guar by thermal analysis

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Received 7 April 1998; accepted 19 January 1999

Abstract

Guar gum (GG) was crosslinked with increasing amounts of glutaraldehyde (GA). The resulting crosslinked products were analyzed by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and wide-angle X-ray diffraction (WAXD) to determine the influence of crosslinking on the polysaccharide structure. Each crosslinked product thermogram was characterized by two or three sharp endothermic peaks and a wide exothermic peak, with the latter indicating that a decomposition chain reaction occurred. It was observed that: (a) crosslinking altered the structure of GG; (b) the thermal stability of crosslinked GG depended on the amount of GA used with excess amount of the crosslinker reducing the stability of crosslinked GG; (c) the reaction of GG with GA occurred either by inter- or intra-crosslinking, depending on the amount of GA used; (d) crosslinking of GG with GA resulted in the formation of new regions in the polysaccharide, characterized by modified structures, whose abundance and density were crosslinker concentration dependent.

Keywords: Guar gum; Cross-linking; Glutaraldehyde; Thermal analysis; Differential scanning calorimetry; Thermogravimetric analysis; Wide-angle X-ray diffraction

1. Introduction

Natural polysaccharides are widely used as thickening agents in food and drug products. They are also used for the extended release of drugs after oral administration. It has recently been suggested that biodegradable plant polysaccharides, such as pectin, dextrans and galactomannans, could be used for the specific delivery of drugs into the human colon if properly modified (e.g., by crosslinking to form hydrogels) to reduce their water solubility [1–4]. Guar gum (GG) is a natural polysaccharide made of long linear β-(1→4)-mannose backbone to which α-(1→6)-linked galactose residues are attached as single unit side chains [5]. Its major use is in the food industry either in its native or modified form [6]. In a previously reported study GG was crosslinked with glutaraldehyde (GA) to reduce its swelling properties. The reduction in the swelling properties was required to prevent entrapped drug leakage right after its oral ingestion. The resulting hydrogel was characterized, and its biodegradation was verified in vitro in the presence of typical enzymes as well as in vivo in the cecum of conscious rats [4].

The study of the thermal behavior of polysaccharides, especially in the range of 100 °C and above, can contribute to their

Abbreviations: DTG, differential thermal gravimetric analysis; DSC, differential scanning calorimetry; GA, glutaraldehyde; GG, guar gum; TGA, thermal gravimetric analysis; WAXD, wide-angle X-ray diffraction.

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0008-6215/99/$ - see front matter

PII: S0008-6215(99)00025-7

physical characterization. For example, by measuring the thermal stability of crosslinked polysaccharides, the effect of crosslinker on the modified polymer could be elucidated. Thermal analysis of polysaccharides at sub-zero temperature ranges has been reported [7–11]. Yet, little has been done to determine the effect of crosslinking on the thermal behavior and microstructure of polysaccharides at temperatures higher than 100 °C [12–15].

The goals of the present study were to check how crosslinking affects the microstructure of GG by the use of thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD).

2. Materials and methods

Synthesis of the crosslinked GG hydrogels.—In separate experiments, GG was crosslinked with increasing amounts of GA as follows. Acidified (H_2SO_4) aqueous dispersions (800 mL) of GG (0.5% w/v, pH 2) were mixed with 1.2, 12, 36, or 60 mL (0.1, 1, 3 and 5 equivalents, denoted as GG-0.1, GG-1, GG-3 and GG-5, respectively, and respective to the equivalents of GA used) of 25% w/v aqueous solution of GA (E. Merck, Darmstadt, Germany) for 48 h. The hydrogels obtained were rinsed with 0.5% w/v of aq $NaHSO_3$ solution for 2 h, followed by distilled water until no traces of GA could be detected at 235 nm (polymeric GA) and 280 nm (monomeric GA) [16,17]. The hydrogels were lyophilized and kept desiccated until thermal analysis measurements were taken.

Thermal analysis.—DSC measurements were carried out in air using a Mettler-TA4000 instrument with a Mettler TC II TA processor (Mettler Instruments, Switzerland). All measurements were carried out at a heating rate of 10 °C/min using an aluminum pan. An empty aluminum pan was used as a reference. The weight of the samples (in a powder form) was 5–10 mg.

The change in the heat capacity (expressed in mV) of GG and the three crosslinked products, GG-1, GG-3 and GG-5, was measured at a heating rate of 10 °C/min over a temperature range of 50–500 °C. TGA and DTG (the rate of the weight loss) were determined at a heating rate of 10 °C/min over a temperature range of 70–600 °C, in an air atmosphere. The activation energy was calculated using Mettler processor TA4000 according to the equation provided with the Mettler instrument manual.

The state of the water in specimens GG-0.1, GG-1 and GG-3 was measured using multiple DSC experiments. Each of the specimens was placed (accurately weighed) in a sealed aluminum pan, in which three holes were then drilled. The specimens were dried at 110 °C for 10 min, then cooled to 25 °C and weighed. Water was then added to each aluminum pan to achieve a ratio (w:w) of 1:1, 4:1 and 10:1 between water and polymer. Each of the pans containing the dry polymer was then covered with an outer pan, which was hermetically sealed and left overnight in order to allow maximum, homogenous penetration of the moisture to the polymer. Each sample was cooled to −100 °C at a rate of 10 °C/min. After 10 min the specimens were heated to 50 °C at a rate of 10 °C/min, and the melting temperature of the frozen water was recorded. The fraction of the non-frozen bound water (f_0) was calculated using two methods:

(a) Back calculation (by subtracting the known fraction of the free water and bound water from 1) as follows [27–29]:

$$f_0 = \frac{334 - [\Delta H(f_1) + \Delta H(f_2)]}{334} \quad (1)$$

where $\Delta H(f_2)$ and $\Delta H(f_1)$ are the fusion enthalpies of the free water fraction (f_2), and the frozen bound water fraction (f_1), respectively, and 334 is the enthalpy of the fusion of pure water (in J/g).

(b) Plotting of the water fraction versus ΔH of the freezeable water, which results in a linear graph. The intercept of this graph at $\Delta H = 0$ is an estimation of the fraction of unfreezeable water from the total specimen weight (water and polymer), which can then be translated into the fraction of the total water content.

Wide-angle X-ray diffraction (WAXD).—Measurements were carried out using a Philips model PW1710 refractometer (anode: Cu Kα, nickel filter, wavelength: 1.5418 Å, 40 kW, 35

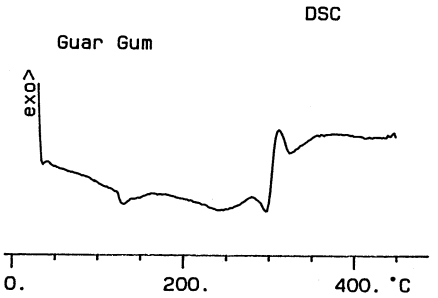

Fig. 1. DSC curve of GG at a temperature range of 50–500 °C and a heating rate of 10 °C/min.

mA), with a diffraction angle range of 5–60° and resolution of 0.04°, at a rate of 2°/min at room temperature (rt). The measurements were taken on powdered polymer specimens randomly poured on metallic discs.

3. Results

Fig. 1 shows the thermal behavior of GG. Endothermic peaks were detected at 246 and 296 °C, and an exothermic peak was detected at 310 °C. The temperature values of all peaks (whether endothermic or exotherrnic) of GG and the three crosslinked GG products are summarized in Table 1.

Fig. 2 shows the TGA and the DTG of GG. Its weight loss begins at a temperature of 180 °C (T_0). Maximum weight loss (T_{max}) was reached at 300 °C, an observation that supports the DSC thermogram shown in Fig. 1. Table 1 also summarizes the DTG measurements of GG and the various crosslinked products, showing a T_{max} at 300, 290, 280 and 270 °C for GG, GG-1, GG-3 and GG-5, respectively. An additional fraction loss at 440 °C ($T_{max} = 440$ °C) for GG-3, and 400 °C ($T_{max} = 400$ °C) for the higher crosslinked product, GG-5, was detected (T_{max}II in Table 1). The activation energy (E_a) that was calculated from the DSC data (shown in Table 1) indicates that as the crosslinking increased, the activation energies required for the polymer decomposition (as calculated by the Mettler processor) also increased. The dependency between the temperature and the percent weight loss of GG, GG-1, GG-3 and GG-5 is shown in Fig. 3.

The change in the crystallinity of GG due to its crosslinking with GA, as assessed by WAXD, is shown in Fig. 4. The crystalline regions of GG at the angles (2θ) 20.2 and 38.4 disappeared, and new crystalline regions appeared at the angles (2θ) of 32.6, 37.8, 38.6 and 44.1.

Fig. 5 shows the DSC curves of three different hydrated crosslinked products, GG-0.1, GG-1 and GG-3, at temperatures ranging from -50 to 30 °C. Each curve is composed of two peaks corresponding to the fusion of the frozen bound water (f_1) and the fusion of the free water (f_2). The thermal analysis values of the curves are summarized in Table 2. The data indicate that an increase in the amount of crosslinker caused a reduction in the f_1 melting temperature but did not cause a change in the melting temperature of f_2. The f_0 fraction decreased and the f_2 fraction increased with the increase in the amount of the GA.

Fig. 6 is a gravimetric profile that connects identical weight-loss values of different prod-

Table 1
Summary of the thermal behavior of GG and the three crosslinked products GG-1, GG-3, and GG-5 as analyzed by DSC and DTG[a,b]

Aldose	DSC			DTG	
	Endothermic peak temperature (°C)	Exothermic onset peak temperature (°C)	E_a (kJ/mol)	T_{max}I (°C)	T_{max}II (°C)
GG	246 ± 2, 296 ± 3	310 ± 3	22.5	$300 + 2$	
GG-1	152 ± 5, 205 ± 2, 250 ± 2	290 ± 1	20.1	290 ± 1	
GG-3	145 ± 3, 220 ± 2, 258 ± 5	300 ± 5	34.6	280 ± 2	440 ± 5
GG-5	139 ± 4, 275 ± 5	320 ± 2	90.6	270 ± 2	400 ± 5

[a] T_{max}II are the decomposition peaks of the products GG-3 and GG-5.
[b] See also Fig. 2.

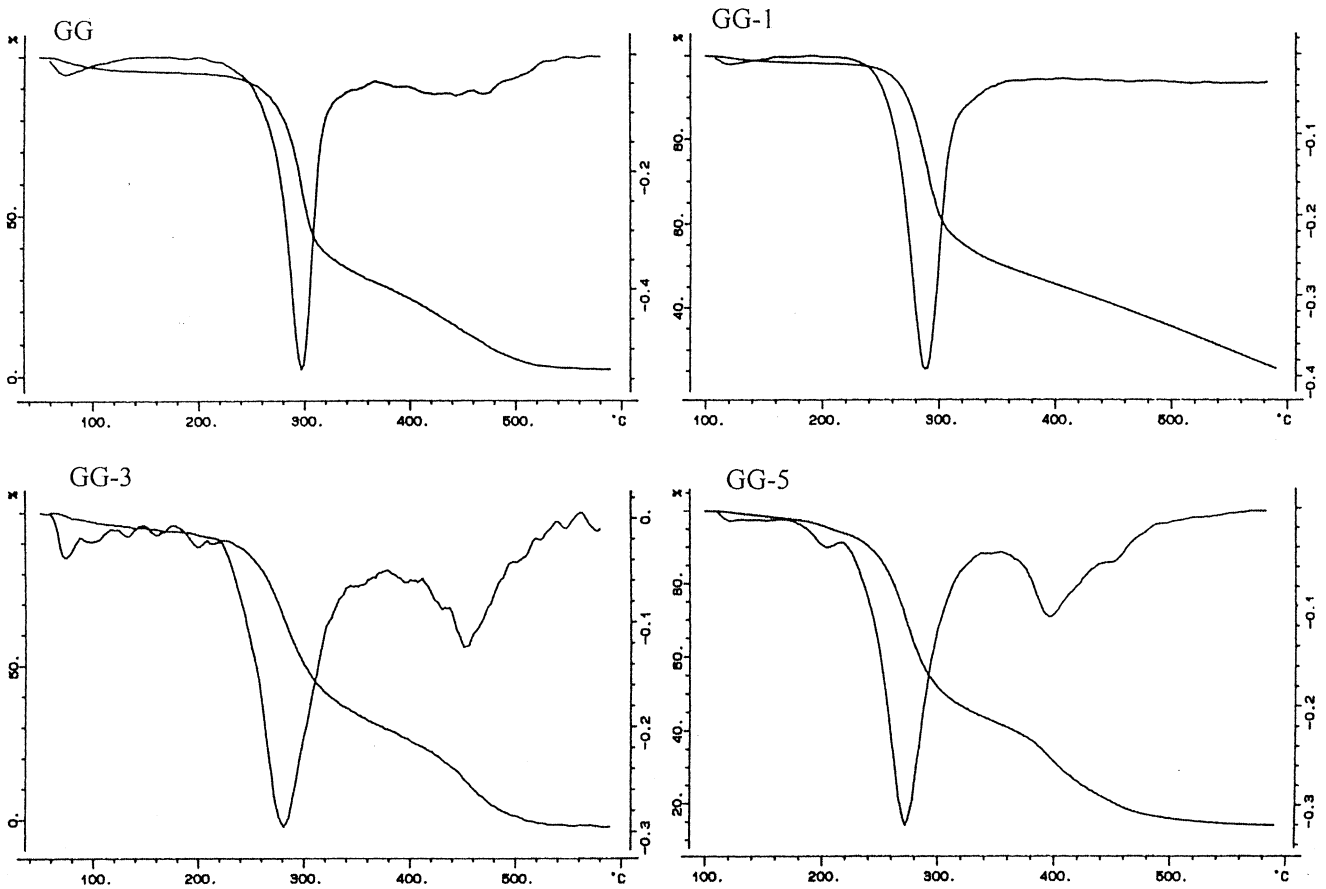

Fig. 2. TGA and derived DTG curves of GG and crosslinked GG at a temperature range of 50–400 °C and a heating rate of 10 °C/min.

ucts (see Section 4). The relation between the different water fraction and the melting ΔH of the total freezeable water, which resulted in linear graphs, is shown in Fig. 7. The intercept of the lines gives an estimation of the fraction of non-frozen water from the total specimen weight. The fraction of the non-frozen water was then calculated and summarized in Table 2. Figs. 5 and 7 and Table 2 demonstrate a reverse dependency between the degree of crosslinking and the amount of non-frozen bound water.

4. Discussion

By crosslinking GG with GA, new covalent bonds are introduced to the polysaccharide. GA substitutes part of the hydroxyl groups, and the crosslinking causes a change in the polymer structure. These physico-chemical changes are reflected in the thermal behavior of the crosslinked GG.

The calorimetric profile of GG was composed of endothermic and exothermic peaks. The first two endothermic peaks correspond to early decomposition and initiation of combustion, respectively (Fig. 1). The exothermic peak corresponds to the ongoing decomposition (thermal and oxidative) of the polymer,

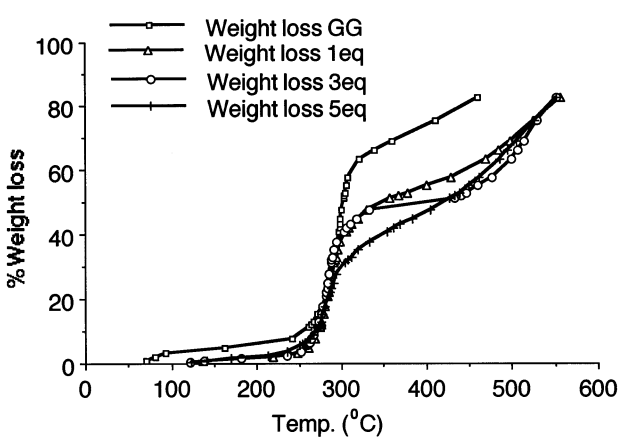

Fig. 3. Dependency between % weight loss and temperature of GG, GG-1, GG-3 and GG-5.

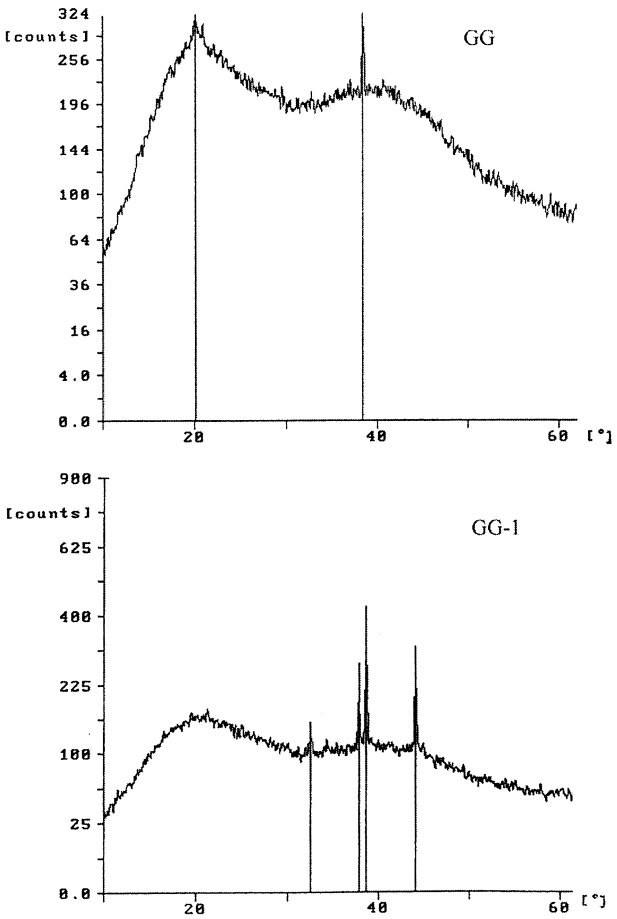

Fig. 4. WAXD curves of GG and GG-1.

vaporization and elimination of volatile products [18,19]. Pyrolysis of polysaccharides starts by a random scission of the glycosidic bonds, followed by a further decomposition [20–22]. Therefore, it is reasonable to assume that the wide decomposition peak of GG shown at 246 °C (Fig. 1) is caused by a sequence of processes in which galactose and mannose cleave from the GG backbone and then decomposition occurs. The temperature values of the wide decomposition peak of GG were verified by the TGA and the DTG thermograms of the polysaccharide (Fig. 2), showing a weight loss that started at 180 °C (T_0) and a T_{max} at 290 °C. Similar T_{max} values for GG have been reported by Shailesh and coworkers [13].

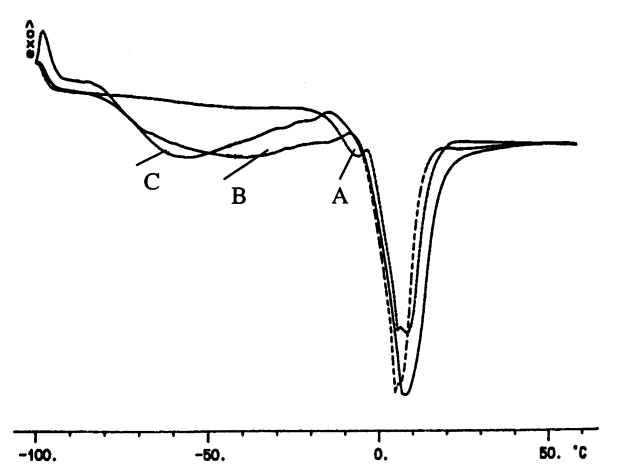

Fig. 5. DSC melting curves of the crosslinked products GG-0.1 (A), GG-1 (B) and GG-3 (C) after drying.

Wide exothermic peaks were observed for all three crosslinked products (Table 1). In general, an increase in the amount of GA led to an increase in the decomposition temperature (the exothermic peak) of the crosslinked products, with the exception of GG-1 in which the decomposition temperature was lower than that of GG. This may be explained by the acid catalysis which caused an initial reduction in the degree of polymerization and a destruction of previously existing hydrogen bonds in those regions where crosslinking occurred. A similar phenomenon was reported by Rodrig and co-workers who investigated the pyrolytic behavior of cellulose and crosslinked cellulose under similar conditions [12]. Increasing the amounts of GA, beyond one equivalent, increased the thermal stability of the crosslinked GG (Table 1). This increase in the thermal stability is confirmed by the resulted values of energy of activation required for the decomposition of each product as shown in Table 1. This table summarizes the decomposition temperatures of GG and the three crosslinked products GG-1, GG-3 and GG-5, as analyzed by DTG and derived from the weight-loss thermogravimetric profiles (e.g., Fig. 2). A second T_{max} peak was observed in the case of GG-3 and GG-5, demonstrating that GG 'completed' 60% of its weight loss at temperature values lower than those of the three crosslinked products, with the latter possessing an additional fraction which was lost at higher temperatures. The higher energy (heat) required to decompose GG-1, GG-3 and GG-5, compared with native GG, is an indication of their increased stability. The increased stability of the crosslinked products is demonstrated in the TGA profiles of weight loss as shown in Fig. 3. GG is less

Table 2
DSC analysis of the water melting profiles of the crosslinked products GG-0.1, GG-1 and GG-3, shown in Fig. 5, and the mathematical evaluation of the graphs in Fig. 7[a]

Product	Melting temperature (°C)		ΔH (J/g)		Calculated water fractions			
	f_1	f_2	f_1	f_2	f_1	f_2	af_0	bf_0
GG-0.1	2 ± 1	4.4 ± 1	2.9	97.7	0.0087	0.29	0.7	0.56
GG-1	-51.3 ± 2	2.1 ± 3	75.7	116.6	0.23	0.35	0.42	0.15
GG-3	-57.5 ± 2	5.2 ± 2	81.4	125.8	0.24	0.38	0.38	0.043

[a] f_1, Bound freezing water; f_2, free water; af_0, bound non-freezing water calculated using method (a); bf_0, bound non-freezing water calculated from method (b).

stable than the crosslinked products since a lower temperature is required to cause it an 80% weight loss.

To emphasize the differences among the three crosslinked products whose TGA plots are shown in Fig. 3, a manipulation was carried out to delineate gravimetric profiles that connect identical weight-loss values of different products. The profiles obtained are shown in Fig. 6 and demonstrate a clear elevation pattern in the 50% weight-loss profiles of the products. In the 70 and 80% gravimetric profiles, a plateau was observed, suggesting that GA addition (above three equivalents) does not contribute to thermal stability of the crosslinked product. A possible explanation could be the formation of intra-crosslinking reactions among the polysaccharide chains, which in turn interfere with hydrogen bonds, weakens the crosslinked polymers' structure and reduces its thermal stability, as was previously suggested by Rodrig and co-workers [12]. The magnitude of such a process depends primarily on the crystallinity of the crosslinked network (as analyzed by WAXD, see below).

Figs. 2 and 6 can serve as qualitative tools to assess the relative amount of those regions in the crosslinked products that are less crosslinked. These regions are the less stable ones in the polymeric network, and their amount is inversely proportional to the amount of crosslinker used.

The change in the crystalline regions of GG as a result of its reaction with GA was assessed by WAXD. Fig. 4 shows a shift in the typical angle of native GG [23,24]. Korsmeyer and Peppas crosslinked PVA with GA and found an increase in the crystallinity of the polymer in a concentration dependent manner, although the overall degree of crystallinity was not high [25]. In our work, increasing the crosslinking of GG resulted in a minor change in the WAXD curve, which was observed in all three crosslinked products (data not shown).

The glass transition of GG-0.1 was found to be between 60 and 70 °C (data not shown); however, the transition was shifted to a lower temperature (-5 °C) in the wet GG-0.1 (Fig. 5). The decrease in the glass transition temperature can be attributed to the plasticizing effect of water. This plasticizing effect demolished the increase in the crosslinking and resulted in stiffer polymers.

The most dominant change in the microstructure of GG as a result of its reaction with GA was in the melting water behavior. In a hydrogel network absorbed water can be classified into three categories: (a) non-frozen bound water (denoted as f_0), which does not undergo melting transition, (b) frozen bound water (denoted as f_1), which exhibits melting transition, and (c) free frozen water (denoted

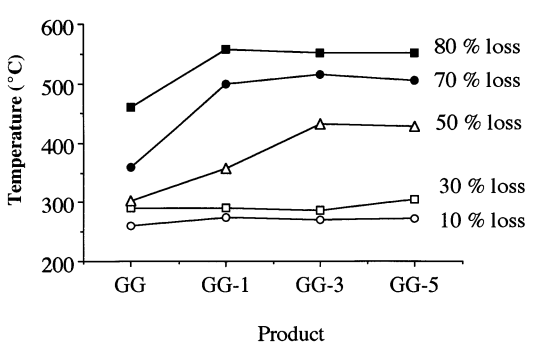

Fig. 6. Gravimetric profiles (connecting identical weight-loss values of different products) of GG, GG-1, GG-3 and GG-5.

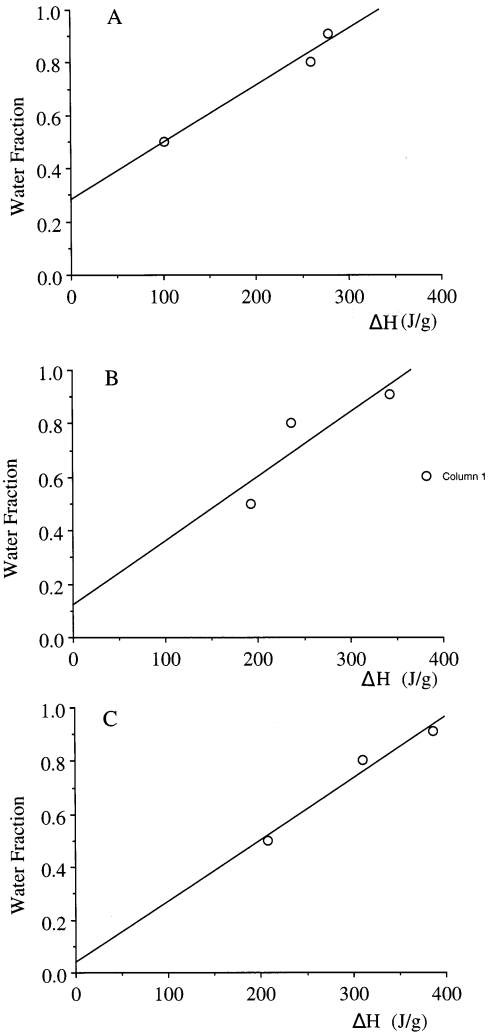

Fig. 7. Dependency between ΔH of the frozen water and moisture content of (A) GG-0.1, (B) GG-1 and (C) GG-3.

as f_2) (see Eq. (1)) [26–31]. The various water fractions were calculated, and from the results summarized in Table 2 it is obvious that the ability of GG to hold non-frozen bound water decreased with its crosslinking. Since water molecules diffuse more easily to a less crosslinked region of a polymer, the decrease in the amount of non-frozen water with the increase of GA used, suggests a change in the polysaccharide structure. In addition, since the interaction between polysaccharides and water is characterized as secondary intermolecular bonds, it is reasonable to assume that there is a decrease in the GG's available hydroxyl groups as a result of the crosslinking with GA. Both methods used in our work to calculate the fraction of non-frozen bound water showed the same effect of crosslinking on the binding of water.

The network of crosslinked GG contains spaces into which water molecules can penetrate and crystallize. The volume and the shape of these spaces change as a result of the crosslinking reaction, a change that may cause irregularities in the crystalline structure of the frozen bound water (f_1). This change increases with the amount of crosslinker and in turn, causes low thermal stability of f_1. As a result, a lower temperature is required to melt this type of frozen water, and a reduction in the melting point is observed.

In summary, the change in the structure of GG resulting from its crosslinking with GA was verified by the change in both thermal stability and capability to bind water of the modified polysaccharide.

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