ELSEVIER

Carbohydrate Polymers 41 (2000) 421–424

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Short Communication

Effect of sugar and sorbitol on the formation of low methoxyl pectin gels

C.R.F. Grosso[a,*], P.A. Bobbio[a], C. Airoldi[b]

[a]Faculdade de Engenharia de Alimentos, UNICAMP-Campinas, CP 6121, Campinas, S.P. Brazil
[b]Instituto de Quimica, UNICAMP-Campinas, CP 6121, Campinas, S.P. Brazil

Received 20 September 1993; received in revised form 15 October 1994; accepted 1 January 1995

Abstract

Pectin gels were made with amidated low methoxyl pectin using sucrose, glucose, fructose and sorbitol as sweetening agents. The adsorption of water at controlled activity was measured by determining sorption isotherms and by differential scanning calorimetry. These results were correlated with the gel formation mechanism. ^{1}H NMR spectra were measured for sugar with and without Ca^{2+} or La^{3+} cations. Results demonstrated no correlation between water adsorption on sugars and gel rigidity. The effects of the different sugars appear to be associated with the competition between each sugar and the pectin for calcium cations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pectin gels; Sugars; Water adsorption

1. Introduction

Amidated low methoxyl pectins (LMP) are extensively used in the preparation of gels, specially where low calorie products are required. In these preparations the presence of calcium ions are essential for gel formation.

According to Smidsrod, Haug and Whittington (1972) the gel formation process involves the simultaneous bonding of calcium ions to carbonyl groups of two adjacent pectin molecules and to two hydroxyl groups from one of the molecules. This arrangement cannot take place intramolecularly. For the association to be stable a number of calcium ions have to be involved in a single “junction zone”.

An egg-box like model was proposed by Grant, Morris, Rees, Smith and Thom (1973) to explain the structure of pectin molecules bound by the calcium ions. The rigidity of the gel is increased by adding sugars as suggested by Gerdes, Burns and Harrow (1987).

The possibility of bonding between sugar molecules and some metallic ions, including Ca^{2+}, was established by Angyal (1972). From configurational arguments based on the presence of an axial–equatorial–axial structure for sugars or threo–threo configuration for polyalcohols, it was concluded that this is the appropriate arrangement for Ca^{2+} complex formation. The complexation of sugars with ions has been reviewed by Dhew-Andries and Perez (1983).

In this paper we report the effect of glucose, fructose, sucrose and sorbitol on the formation of LMP gels and on their effect on the rigidity of the gels. This effect was correlated with: (i) sugar interaction with Ca^{2+}; (ii) water adsorption capacity; and (iii) water associated with the gel constituents.

2. Materials and methods

Amidated LMP was obtained from Braspectina (Limeira, Brazil) and was purified by dissolving the pectin several times in distilled water followed by precipitation with ethanol. Finally, the solid was dialyzed until free of soluble sugars. The purified product was dried under reduced pressure before storage.

Lanthanum chloride was prepared from lanthanum oxide following the procedure described by Taylor and Carter (1962). All other reagents were analytical grade or food grade products.

2.1. Gel preparation and drying

The gels were prepared according to the National Academy of Sciences (1972) directions and the following sugars were used: sucrose, glucose, fructose and sorbitol. The LMP gels were prepared by dissolving 6.0 g of the pectin and 180 g of sugar in 425 ml of water. To this solution were added 5.0 ml of a 54.3% solution of citric acid, 10.0 ml of a 6% solution of sodium citrate and 25.0 ml of a 2.2% solution of calcium chloride. The mixture was carefully

---

* Corresponding author.

PII: S0144-8617(99)00099-5

Table 1
Calorimetric data and SAG values for LMP gels

Gels with	Glucose	Sucrose	Sorbitol	Fructose
SAG[a]	18.0 ± 0.4	15 ± 0.3	$\geqslant$ 26.0	$\geqslant$ 26.0
Free water (g/100 g gel)[b]	23.0	19.0	21.0	22.0
Enthalpy (J/100 g gel)[b]	7615	6025	7029	7489

[a] Gel without sugar: 20.0 ± 0.3.

[b] SD $< 3\%$, dry gel.

heated to evaporate water until a final weight of 600 g was attained. Each gel was prepared in triplicate. The solution was distributed in special glasses suitable for SAG evaluation. Rigidity of each gel was estimated through the SAG values determinated with an Hagel-Atlas 85 Ridgelimeter Cox-Higby type. The gels were freeze-dried and stored over P_2O_5 under vacuum for at least 48 h before use.

2.2. Sorption isotherms

Sorption isotherms were obtained as described by Labuza (1984) by equilibrating each dried gel in dessicators under vacuum at 20.0 ± 0.5°C over the following saturated solutions prepared as described by Multon (1984): (water activity, a_w) $MgCl_2 \cdot 6H_2O$ (0.33), $K_2CO_3 \cdot 2H_2O$ (0.44), $Mg(NO_3)_2 \cdot 6H_2O$ (0.54), $NaNO_3$ (0.74), NaCl (0.75), $BaCl_2 \cdot 2H_2O$ (0.91) and Na_2PO_4 (0.95). The results in the isotherm sorption curves were the average of three measurements for each a_w. After reaching equilibrium at each a_w samples were dried at 55°C under vacuum (28 mmHg). The water activity of the solutions were measured with a Novasina Thermoconstanter Humidat-Aw Box.

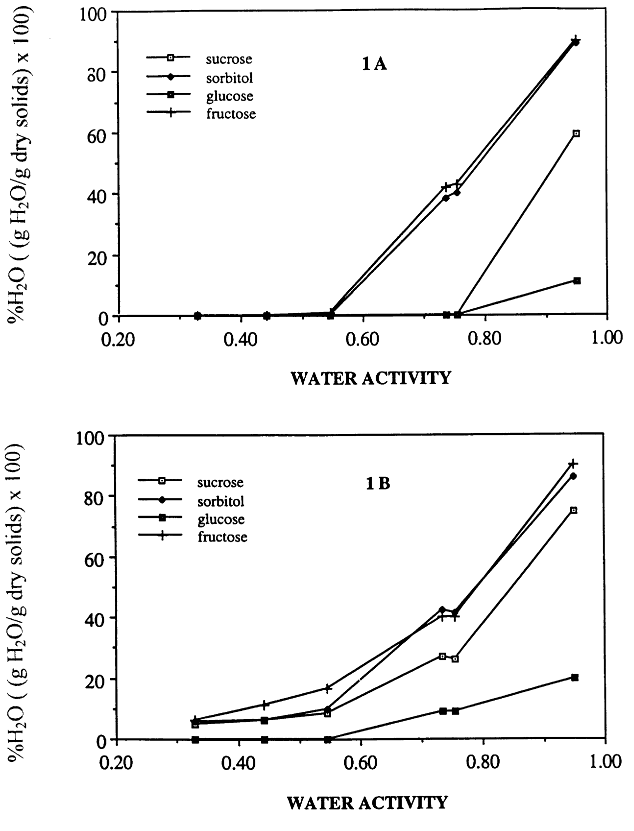

Fig. 1. Adsorption isotherms for (A) sugars and (B) low methoxyl pectin gels.

2.3. Differential scanning calorimetry

Bound and free water were determined by this technique. For each run duplicate samples were assayed with a deviation of the mean less than 3%. The dried gel (5–10 mg) were weighed in aluminum pans and then stored over saturated barium chloride solution ($a_w = 0.91$) at 20.0 ± 0.5°C until constant weight was reached.

Each sealed pan was cooled to −80°C in liquid nitrogen. The DSC curves were obtained by heating each sample to 40°C at a rate of 10°C/min using a DuPont model 910 differential scanning calorimeter, coupled to a thermoanalyzer. The bound and free water were calculated according to Ross (1978).

2.4. NMR spectra

^1H NMR spectra for fructose and fructose plus lanthanum chloride spectra were obtained with a Varian Gemini spectrometer operating at 300 MHz with 36k data points, a sampling rate of 0.18 Hz/point and without using solvent supression and line broadening. The spectra for sorbitol and sorbitol plus $CaCl_2$ or $LaCl_3$ were taken with a Bruker AC 300/P spectrometer, 36k data points, line broadening of 0.3, sampling rate of 0.368 Hz/point, without solvent suppression. Solutions of 0.3–0.7 M of each sugar with 0.57 M of $CaCl_2$ or $LaCl_3$ in D_2O (Angyal, 1972) were used for the spectra.

3. Results and discussion

The decreasing order of rigidity (SAG values, Table 1) of the gels prepared with amidated low methoxyl pectin with different sugars or without sugar was sucrose, glucose, no sugar added, fructose and sorbitol, i.e. the higher the SAG value the less rigid the gel. Considering that the sugar was the most abundant water binding component of the gel, the type of the sugar added should have played an important role in determining the rigidity of the gels. Another factor was the total water content and how it was associated in the gel. In high methoxyl pectin gels (Grosso & Bobbio, 1993) gel rigidity (SAG value) was directly proportional to the capacity for water sorption of the sugars used. The capacity of complex formation between sugar and pectin with Ca^{2+} as well as the water holding capacity of the sugars must be important in promoting gel rigidity in LMP gels.

Fig. 1(A) and (B) shows that there are similarities between the sorption isotherms for the sugars and the corresponding gels. This would be expected since sugar is the

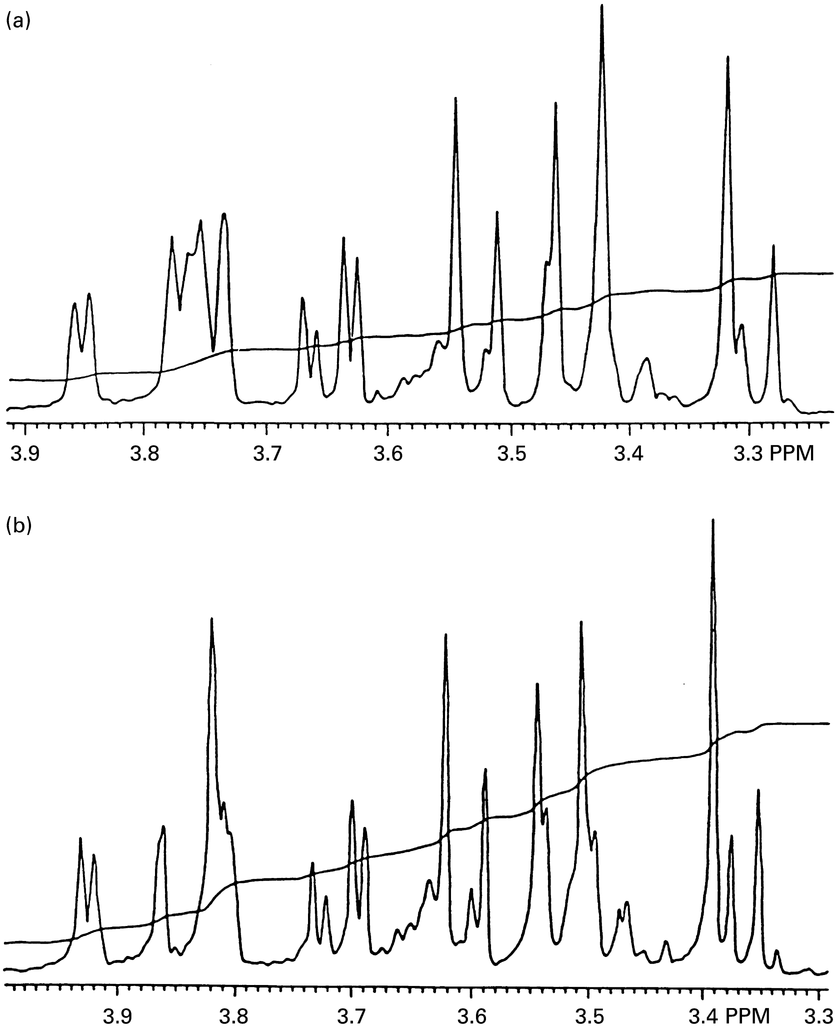

Fig. 2. ^1H NMR spectra of (a) fructose (0.5 M) in lanthanum chloride solution (D_2O) and (b) fructose (0.5 M) solution (D_2O).

main component of the gel although the degree of sugar crystallinity may be different between the two systems.

The gel rigidity as evidenced by the SAG values does not correlate with the sorption isotherms or increase with amount of bound water calculated from DSC thermograms as described by Duckworth (1971) (Table 1). Indeed the weakest gels with fructose and sorbitol have the highest content of bound water.

The experimental data indicate no direct correlation between gel rigidity and total water contents or type of water bonding. However, the nature of the sugar used and its capacity to complex ions in competition with pectin during the gel formation could be important factors in promoting gel rigidity.

To confirm the possibility of complex formation between Ca^{2+} or La^{3+} ions with glucose, fructose and sorbitol, ^1H NMR spectra were analyzed for sugars solutions with and without cations. According to Angyal (1974) surcose does not complex Ca^{2+} and this is supported by the low SAG value for the gel with this sugar (Table 1) suggesting no apparent competition between pectin and sugar for Ca^{2+}. The same behavior was observed for glucose. The position of hydroxyl groups on these two sugars does not appear to favor the formation of a complex with these cations as proposed by Angyal (1974). Due to the lack of complex formation, the SAG values were lower than that found for fructose and sorbitol gels. The absence of complex formation between Ca^{2+} or La^{3+} and glucose and sucrose is supported by their NMR spectra which showed no alteration, indicating the absence of cation complex formation.

Craig, Stephenson and Stevens (1974) pointed out the existence of a fructose complex with Ca^{2+}, which is unexpected according to the Angyal model (Angyal, 1972). The high SAG value for the fructose gel may be attributable, therefore to this complex formation, as confirmed by the NMR data (Fig. 2(a) and (b)). By the same token, the gel with sorbitol shows a very high SAG values and also a considerable variation in the NMR spectra (Fig. 3(A)–(C)) which can be considered as unequivocal evidence of complex formation. For both sugars, changes in the splitting pattern and in the chemical shifts of the ^1H MNR spectra of the corresponding Ca^{2+} or La^{3+} solutions were assigned to complex formation.

In conclusion, NMR data suggest that when sugars are added, pectin and sugar molecules could compete for cations. Depending on the sugar structure a stable complex can be formed between the sugar and Ca^{2+}. This interaction can be unfavorable to the formation of the gel, due to the decrease of Ca^{2+} available to associate with pectin molecules and therefore, decreasing the gel rigidity. This behavior might have considerable importance in dietary gels.

In low methoxyl pectin gels the rigidity is essentially dependent on the capacity of the sugar to compete with the pectin for the calcium ions. The interaction between sugar and water is a secondary effect.

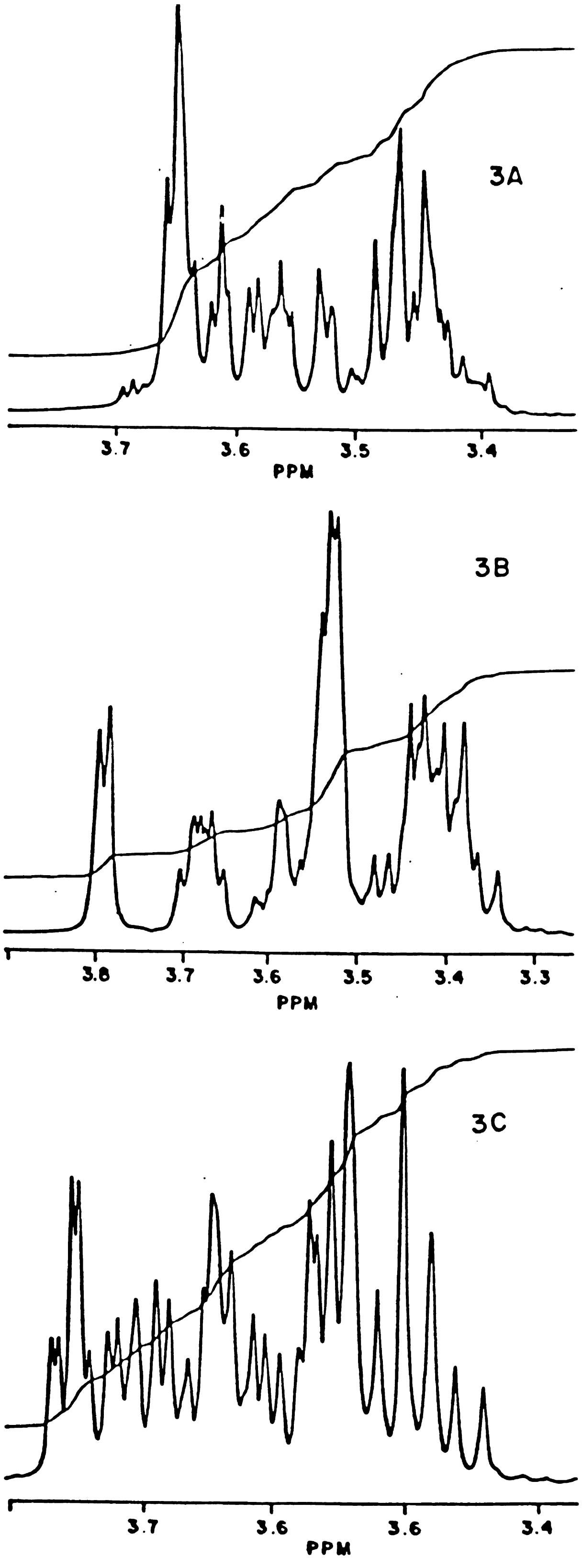

Fig. 3. ^{1}H NMR spectra of: (A) sorbitol (0.5 M) solution (D_2O); (B) sorbitol (0.5 M) in lanthanum chloride solution (D_2O); and (C) sorbitol (0.5 M) in calcium chloride solution (D_2O).

Acknowledgements

We are indebted to Instituto de Química-UNICAMP for the ^{1}H NMR spectra (Ms Paula M.H. Pilli).

References

Angyal, S. J. (1972). Complexes of carbohydrates with metal cation. I. Determination of the extent of complexing by NMR spectroscopy. *Australian Journal of Chemistry*, *25*, 1957–1966.

Angyal, S. J. (1974). Complexing of polyol with cations. *Tetrahedron*, *30*, 1695–1702.

Craig, D. C., Stephenson, N. C., & Stevens, J. D. (1974). β-D-Fructopyranose–calcium chloride dehydrate. *Crystal Structure Communications*, *3*, 277–281.

Dhew-Andries, M. L., & Perez, S. (1983). Geometrical features of calcium-carbohydrates interactions. *Carbohydrate Research*, *124*, 333–337.

Duckworth, R. B. (1971). Differential thermal analysis of frozen food systems. I. The determination of unfreezable water. *Journal of Food Technology*, *6*, 317–327.

Gerdes, D. L., Burns, E. E., & Harrow, L. S. (1987). Some effects of gelling agents and sweeteners on high and low sugar content carbohydrate gels. *Lebensmittel Wissenschaft und Technologie*, *20*, 282–286.

Grant, G. T., Morris, E. R., Rees, D. A., Smith, P. J. C., & Thom, D. (1973). Biological interactions: the egg box model. *FEBS Letter*, *32*, 195–198.

Grosso, C. R. F., & Bobbio, P. A. (1993). Effect of sucrose, sorbitol and fructose on the rigidity of high methoxyl pectin gels. Unpublished data.

Labuza, T. P. (1984). Determination of moisture sorption isotherm measurement and use. In T. P. Labuza (Ed.), *Moisture sorption: practical aspects of isotherm measurement and use*, (pp. 64–83). St. Paul, MN: American Association of Cereal Chemists, chap. 4.

Multon, J. L. (1984). Conclusion provisoires des travaux de la comission aliments a humidite intermediare du CERNA. *Industries Alimentaires et Agricoles*, *101*, 1125–1140.

National Academy of Sciences. (1972). Monograph on pectin. *Food Chemical Codex II* (p. 557). Washington, DC: National Academy of Sciences.

Ross, K. D. (1978). Differential scanning calorimetry of non-freezable water in solute–macromolecule–water systems. *Journal of Food Science*, *43*, 1812–1815.

Smidsrod, O., Haug, A., & Whittington, S. G. (1972). The molecular basis for some physical properties of polyuronides. *Acta Chemica Scandinavia*, *26*, 2563–2566.

Taylor, M. D., & Carter, C. P. (1962). Preparation of anhydrous lanthanide halides, especially iodides. *Journal of Inorganic and Nuclear Chemistry*, *24*, 387–391.