ELSEVIER

Carbohydrate Polymers 48 (2002) 299–304

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

The effect of moisture content on the crystallinity and glass transition temperature of inulin

J.E. Zimeri, J.L. Kokini*

Center for Advanced Food Technology, Department of Food Science, Cook College, Rutgers University, 65 Dudley Road, New Brunswick, NJ 08901, USA

Received 13 October 2000; revised 2 May 2001; accepted 5 May 2001

Abstract

This paper focuses on the physicochemical characterization of inulin, an important fructooligosaccharide with dietary fiber properties, and its dependence on water sorption properties. The moisture sorption isotherm of inulin was determined at 25°C and fitted to the GAB model. Inulin's glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC) as a function of water content; the Gordon–Taylor equation was used to fit the experimental data. Relative crystallinity of inulin was determined by X-ray diffraction and DSC studies. Native inulin was found to be a semi-crystalline material, which, at 25°C and storage water activity values below 0.75, was found in a glassy state. When pre-solubilized, inulin's relative crystallinity depended on moisture content: crystallinity was low at low moisture contents, while, at water activities above 0.75 (conditions above T_g), it recrystallized and reached native inulin's crystallinity level.

Keywords: Inulin; Moisture sorption; Glass transition; Crystallinity; X-ray diffraction

1. Introduction

Inulin, a natural nondigestible fructooligosaccharide (FOS), occurs naturally in plants such as chicory root and Jerusalem artichoke, wheat, asparagus and onions (Pszczola, 1997). It is comprised of fructose molecules linked by β(2-1) glycosidic bonds, which are responsible for its nutritional characteristics. It may contain either a terminal β-D-fructose or an α-D-glucose molecule (Roberfroid, Gibson & Delzenne, 1993). Standard inulin, a polydisperse substance, has a degree of polymerization of 2–60; there exist high performance (HP) forms of inulin with an average degree of polymerization (d.p.) of 25, from which small molecular weight oligomers have been eliminated (Roberfroid, 1999; Nines, 1999). Partial enzymatic hydrolysis of inulin results in oligofructose, which has a d.p. of 10 or less units.

Inulin is used either as a macronutrient substitute to replace fat or as a supplement to foods, added mainly for its nutritional properties. It is combined with water to produce the same texture and mouthfeel as fat in water-based foods such as dairy products and table spreads, as well as baked goods, fillings, frozen desserts and dressings (Nines, 1999; Schaller-Povolny & Smith, 1999).

Due to its effect on water solutions at various solid levels, inulin is used primarily as a texturizer. At levels above 25%, the solution forms a particle gel with fat-like characteristics. Above 50% concentration, the gels retain their fat-like texture as they become firmer. The presence of other hydrocolloids and processing conditions, such as temperature and mixing shear, affect the gel formation characteristics (Pszczola, 1997). Inulin's solubility in water depends on temperature: at 10°C, the solubility is about 6% and at 90°C, it is approximately 35%. It has a water binding capacity of about 2:1 (Silva, 1996).

Several studies related to small carbohydrate–water systems have been reported in the literature. Slade and Levine (1988) reported values of T_g and T_m (temperature of melting) of various polyol sugars. Roos and Karel (1991) studied the effect of molecular weight, water plasticization and composition on glass transition temperature of maltodextrins, maltose and sucrose. All maltodextrins with different molecular weights were plasticized by water in a similar manner, and the decrease in T_g was linear with water activity over the range of 0.11–0.85.

X-ray diffraction has been used to understand the architecture and crystallinity of polysaccharides (Chandrasekaran et al., 1994; Chandrasekaran, 1998). For example, Zobel (1988) reviewed the non-crystalline and amorphous state of starch and its role in determining the physical properties of native and gelled starches. Cooke and Gidley

---

* Corresponding author. Tel.: +1-732-932-8306; fax: +1-732-932-8690.
E-mail address: kokini@aesop.rutgers.edu (J.L. Kokini).

PII: S0144-8617(01)00260-0

(1992) quantified the residual crystalline order after gelatinization of starch granules by powder X-ray diffraction. Radha and Chandrasekaran (1997) used X-ray diffraction patterns to describe the structural organization of arabinan, indicating that the polymorphism and the tendency of this substance to form microcrystals in the solid state might confer it fat mimetic properties. Jouppila and Roos (1997) and Jouppila, Kansikas and Roos (1998) studied the crystallization behavior of amorphous corn starch using X-ray diffraction techniques, and related it to physical state and glass transition.

The objective of this study was to characterize inulin's physical state by determining its moisture sorption properties and the effect of moisture on T_g and crystallinity. Understanding these phenomena will lead to obtaining reduced sugar and low fat products with improved texture and stability.

2. Materials and methods

2.1. Sample preparation

High performance inulin (Raftiline HP, >99.5% pure, d.p. ≥25), was obtained from Orafti (Malvern, PA). It was suspended in distilled de-ionized water (40% w/w) and heated to 90°C; mixing was provided. At this temperature, inulin is partially soluble in water (Silva, 1996) and no hydrolysis has been reported to occur (Shu, 1998). The hot solution was cooled immediately to −38°C, dried and milled into a fine powder using a laboratory mill (Glen Mills, Maywood, NJ).

Powdered pre-solubilized inulin and native inulin (as obtained from the manufacturers) were stored in desiccators containing different saturated salt solutions (P_2O_5, $MgCl_2$, $Mg(NO_3)_2$, NaCl, and KNO_3), which produced water activity (A_w) values of 0, 0.33, 0.52, 0.75 and 0.93, respectively, at 25°C (Nyqvist, 1983). The minimum storage time was 3 weeks, until the samples reached equilibrium.

2.2. Moisture sorption isotherm

After equilibration at different A_w values, the samples' moisture content was measured using the AACC method 44-19 (AACC, 1986) (convection oven, 135°C, 2 h). The A_w was measured with a Hygroscop DT hygrometer (Rotronic, Huntington, NY). The moisture sorption isotherms consisted of a plot of moisture content vs. A_w. Samples were analyzed in duplicate and the average value was reported.

2.3. Differential scanning calorimetry

A Perkin Elmer DSC7 Differential Scanning Calorimeter was used to determine T_g of the samples. Calibration of the instrument was performed using indium as a standard. Experiments were run at a heating rate of 10°C/min. Hermetic stainless steel pans were used to avoid moisture loss during the analysis. Solid CO_2 was used to obtain temperatures below room temperature (minimum possible: −10°C). Rescans were immediately performed to erase the thermal history of the samples and to confirm the existence of a T_g. Measurements were performed at least in duplicate. An empty stainless steel pan was utilized as reference. The data were analyzed with a Multitasking Software Version 3.1 (Perkin Elmer, Norwalk, CT) for thermal analysis. T_g a second-order transition, was recognized as a step change of heat flow in the DSC thermograms, as defined by Roos (1995). The midpoint of the change in slope was identified as the T_g.

The dependence of T_g as a function of moisture content was predicted using the Gordon and Taylor (1952) equation

$$T_g = \frac{x_1 T_{g_1} + (\Delta C_{p_1}/\Delta C_{p_2}) x_2 T_{g_2}}{x_1 + (\Delta C_{p_1}/\Delta C_{p_2}) x_2} \tag{1}$$

where x_i is the weight fraction of the ith-component; T_{gi} is the glass transition temperature of the ith-component; ΔC_{p_i} is the change in heat capacity at T_{gi}. The values of T_g and ΔC_p for water were taken from published studies by Kalichevsky and Blanshard (1993): $T_g = -139$°C; $\Delta C_p = 1.94$ J/g K; experimental T_g and ΔC_p values for inulin were determined by least squares fit, following the procedure used by several investigators (Kalichevsky and Blanshard, 1993; Jouppila and Roos, 1997).

2.4. X-ray diffraction

Samples for analysis included pre-solubilized and native inulin that were equilibrated at 25°C in desiccators containing saturated salt solutions of P_2O_5 and NaCl, that produced water activity values of 0 and 0.75, respectively.

The equipment used was an Enraf-Nonius FR57 rotating anode X-ray generator, equipped with a Bruker HiStar area detector and graphite monochromator (Crystallography Laboratory, Chemistry Department, Rutgers University). The instrument was operated at the following conditions: CuKα radiation ($\lambda = 0.1514$ nm); 40 kV and 50 mA; diffraction angle (2θ) fixed at 25°; sample to detector distance of 10 cm. The length of the scans was 1 h at room temperature. Results consisted of a refractogram in which peaks corresponded to rings shown on the diffraction image.

Relative crystallinity was defined as the ratio of the peak area to the total area of a diffractogram (which is the sum of peak areas and amorphous areas), expressed as a percent, following the procedure of Chinachoti and Steinberg (1986) and Kim, Kim and Shin (1997). To calculate the peak areas, each point of minimum intensity was joined by a straight line and the area of the upper region above the line was calculated (Mizuno, Mitsuiki & Motoki, 1998) using an automated image analysis software, SigmaScan Pro Version 3.00 (Jandel Corporation, 1995). Therefore, crystallinity

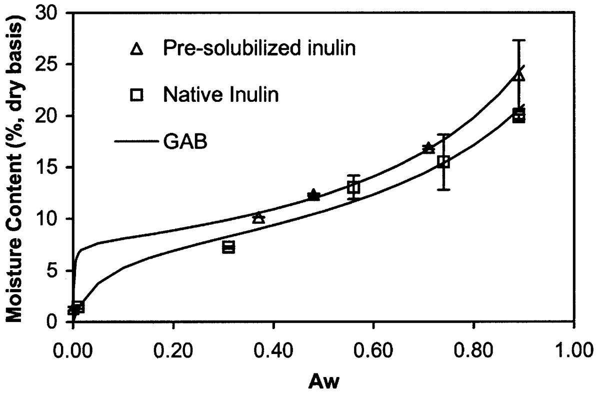

Fig. 1. Moisture sorption isotherms of native and pre-solubilized inulin (25°C) fitted to the GAB model.

represents the percent crystalline material on a total solids basis.

3. Results and discussion

3.1. Prevention of inulin's hydrolysis through sample preparation

Sample preparation (heating inulin–water suspensions at 90°C) ensured that inulin did not hydrolyze into fructose, since hydrolysis occurs when inulin is held at very low pH (below 3.0) and/or at very high temperature (higher than 100°C) for extended time. As has been reported by Shu (1998), 40% of inulin hydrolyzed into fructose when mixed with water and held at 150°C, and no hydrolysis was detected at 100°C.

3.2. Moisture sorption properties of inulin

The moisture sorption isotherm for pre-solubilized and native inulin at 25°C (Fig. 1) presented the typical sigmoid shape (type II isotherm) of biological and food materials, unlike crystalline sugars that show type III isotherms (Roos, 1995). The similarity between both the curves indicated that the samples had similar water binding capacities, although pre-solubilized inulin presented a slightly higher moisture content than native inulin at a specific value of A_w. The shape of the curve indicated that as moisture content increased, free water represented by A_w increased accordingly.

The moisture isotherms for both types of inulin were fitted to the Guggenheim, Anderson and deBoer (GAB) model. The R^2 values corresponded to 0.948 for native inulin and 0.997 for pre-solubilized inulin, indicating a good fit of the data. The values for the monolayer moisture (W_m), as well as for the Guggenheim constant (C) and the correction factor for the multilayer (K) are given in Table 1. W_m has been shown to correspond well with the moisture content at which the rates of quality loss due to chemical reactions in foods are negligible (Bell and Labuza, 2000). In the present study, the calculated values for W_m corresponded to 7.22% for native inulin and 7.56% for pre-solubilized inulin, indicating a high similarity among these values and with values reported for other food materials (Singh and Singh, 1996). The constant K is a factor correcting the properties of the multilayer with respect to the bulk liquid, while the constant C is a factor correcting the sorption properties of the first layer with respect to the bulk liquid (Singh and Heldman, 1993). The calculated values for these constants were comparable to those found in the literature (Singh and Singh, 1996; Bell and Labuza, 2000).

Table 1
GAB parameters for native and pre-solubilized inulin

GAB parameters	Native inulin	Pre-solubilized inulin
W_m	7.22%	7.56%
C	26.12	858.92
K	0.736	0.772

3.3. Glass transition temperature of inulin as a function of moisture content

Fig. 2a–c correspond to DSC thermograms for native inulin samples at the measured A_w values of 0.31, 0.45 and 0.64, respectively. Pre-solubilized inulin presented similar results, which are not shown. Both the first scan and rescan are displayed. The data were normalized by dividing the heat flow by the sample weight. On the first scan, the thermal history of the samples was erased; on the rescan, the T_g was identified as a change in the baseline corresponding to a change in the heat capacity of the samples. The presence of the T_g on the rescan confirmed its reversibility. Although the transition occurred within an interval of 20°C, T_g was identified as the midpoint of the transition. The ΔC_p values for inulin varied between 0.25 J/g K at A_w 0.31 and 0.03 J/g K at A_w 0.64, indicating that less material underwent a transition as the sample's moisture content increased. It was not possible to detect any T_g in the samples that were stored in environments with A_w equal to or above 0.75, due to limitations on the equipment's capacity to operate at temperatures below −10°C.

Fig. 3 shows the relationship between T_g of native and pre-solubilized inulin and moisture content. The data points represent the average of at least two experimental T_g values at each moisture content. The T_g of inulin decreased with increasing moisture content, confirming the plasticizing effect of water. Water acts as a plasticizer by reducing the T_g due to reduction of the inter- and intra-macromolecular forces (Matveev et al., 2000; Tolstoguzov, 2000). At room temperature, inulin's T_g occurred at 18% (d.b.) moisture content.

The experimental data were well-fitted by the Gordon–Taylor equation, as expected, since this equation has proved to be a reliable predictor of glass transition temperatures of

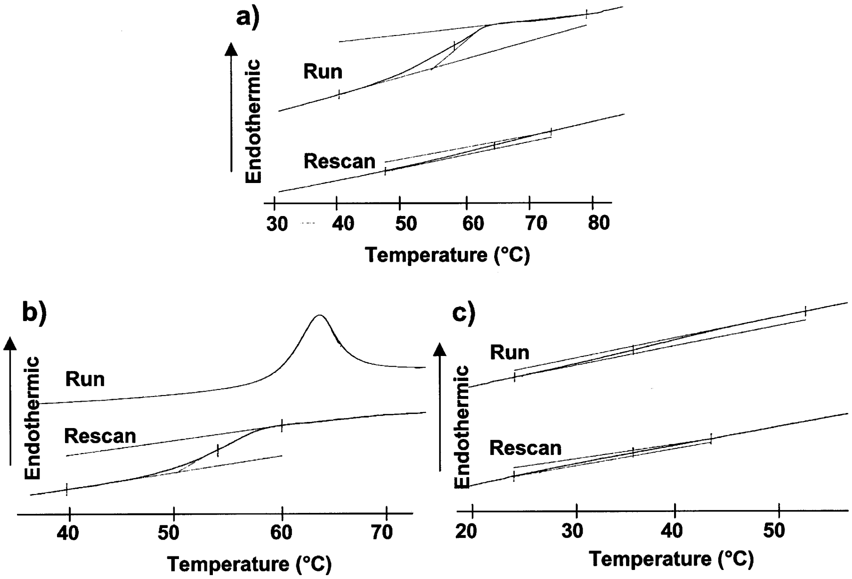

Fig. 2. DSC thermograms for native inulin at (a) 0.31; (b) 0.45; and (c) 0.64 A_w values.

various food components at different water contents (Roos et al., 1996). The calculated values of T_g and ΔC_p for anhydrous inulin corresponded to 120°C and 0.65 J/g K, respectively.

3.4. Effect of moisture on crystallinity of inulin

3.4.1. X-ray diffraction

Development of relative crystallinity during storage at 25°C at different moisture contents was studied by X-ray diffraction, as shown in Fig. 4. Fig. 4a, which corresponds to pre-solubilized inulin stored at A_w 0, shows the existence of a low relative crystallinity (13%), as calculated from the ratio of the areas of the peaks vs. the total area. Low relative crystallinity could be expected from the experimental treatment of inulin, since it became highly amorphous after solubilization and drying; moreover, at A_w 0, pre-gelatinized inulin existed in a glassy state where mobility is very limited, thus, preventing recrystallization to occur.

Fig. 4b, which corresponds to pre-solubilized inulin stored at A_w 0.75, shows the existence of peaks that occurred at similar d-spacings as those presented in Fig. 4a. Relative crystallinity, calculated as before, corresponded to 42%, indicating that recrystallization had occurred at high-moisture storage conditions. Recrystallization resulted from an increase in the system's mobility (facilitated by water), which favored reordering into a more stable crystalline structure.

Fig. 4c and 4d show the X-ray diffractograms for native inulin stored at A_w 0 and A_w 0.75, respectively. Relative crystallinity remained unchanged (40%) at these storage conditions. When comparing Fig. 4c to 4a, it can be observed that native inulin had a higher relative crystallinity than pre-solubilized inulin stored at A_w 0. These results could be linked to the moisture sorption isotherms (Fig. 1), since native inulin, with a higher relative crystallinity, had a lower equilibrium moisture content than pre-solubilized inulin at any A_w value.

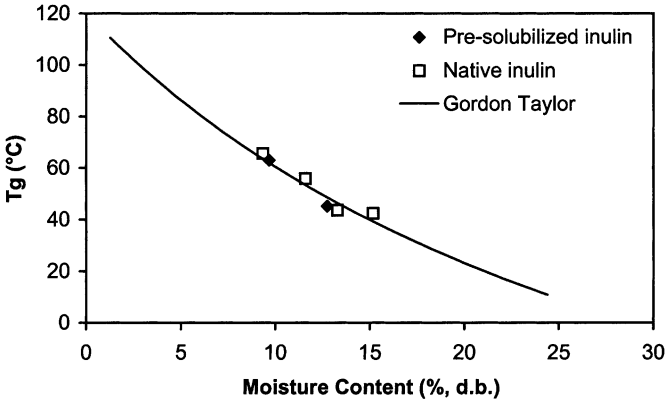

Fig. 3. T_g of pre-solubilized and native inulin compared to the Gordon and Taylor equation.

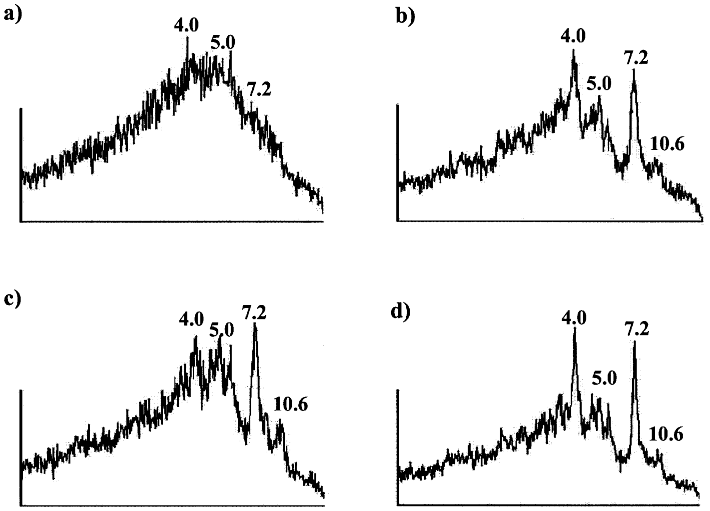

Fig. 4. X-ray diffractograms for inulin (a) pre-solubilized, stored at A_w 0; (b) pre-solubilized, stored at A_w 0.75; (c) native, stored at A_w 0 and (d) native, stored at A_w 0.75. d-Spacings given in Å.

Native inulin can then be described as a partially crystalline material. When pre-solubilized and stored at low-moisture environments, its crystallinity decreases to about 1/3 its original value. At storage conditions above T_g, pre-solubilized inulin recrystallizes and reaches the original crystallinity values of native inulin.

3.4.2. *Differential scanning calorimetry*

DSC studies confirmed the development of crystallinity in pre-solubilized inulin samples stored at different water activities, as presented in Fig. 5. The enthalpy of melting (ΔH), was calculated by integrating the area of the melting endotherm (represented by the shadowed areas in Fig. 5). The sample's degree of crystallinity was related to the magnitude of ΔH (Roos, 1995).

Fig. 5a shows the results for pre-solubilized inulin stored at A_w 0, with a melting enthalpy of 25.5 J/g. At A_w 0.33 and 0.46 (Fig. 5b and c) the enthalpy of melting remained almost constant (~28 J/g) indicating that the samples' crystallinity did not increase at these storage conditions. When pre-gelatinized inulin was stored at A_w 0.75 and 0.92 (Fig. 5d and e), the enthalpy of melting increased to 46 and 48 J/g,

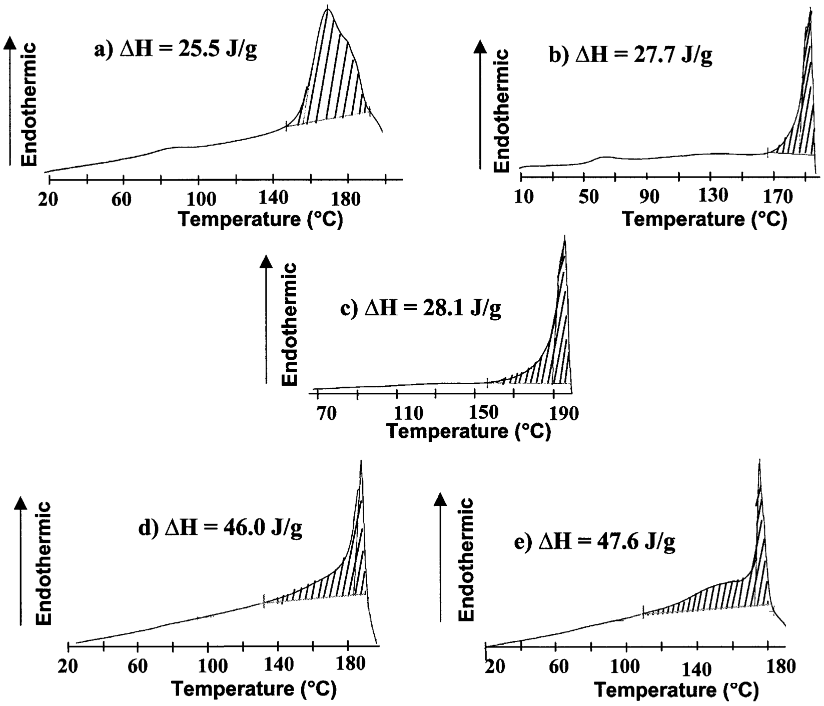

Fig. 5. Melting behavior of pre-solubilized inulin stored at (a) A_w 0; (b) A_w 0.33; (c) A_w 0.52; (d) A_w 0.75 and (e) A_w 0.93. (Note: different scales).

respectively, indicating that more material was found in the crystalline state. These results confirmed the X-ray diffraction data discussed previously.

4. Conclusion

Inulin was found to be a semi-crystalline material, which presents both the existence of a glass transition temperature and a melting transition. At room temperature, its glass transition occurred at 18% (d.b.) moisture content, corresponding to A_w values close to 0.75. When pre-solubilized and stored below its T_g, inulin remains in a low-crystalline state (~13% relative crystallinity), while at conditions above T_g, recrystallization occurs and it reaches ~40% relative crystallinity (same value as native inulin). Inulin's functionality in foods, such as fat-mimetic properties, might then be a consequence of its semi-crystalline properties and glass transition temperature, which are influenced by storage conditions such as moisture.

Acknowledgements

This is publication No. D10544-4-01 of the New Jersey Agricultural Experiment Station supported by State Funds and the Center for Advanced Food Technology (CAFT). The Center for Advanced Food Technology is a New Jersey Commission on Science and Technology Center.

References

American Association of Cereal Chemists (1986). *American association of cereal chemists approved methods*, Vol. 2. St Paul, MN: American Association of Cereal Chemists Method 44-19.

Bell, L. N., & Labuza, T. P. (2000). Moisture sorption. Practical aspects of isotherm measurement and use. (2nd ed.). (pp. 50–52). St.Paul, MN: AACC see also p. 57, 62 and 63.

Chandrasekaran, R. (1998). X-ray diffraction of food polysaccharides. *Advanced Food Nutrition Research*, *42*, 131–209.

Chandrasekaran, R., Radha, A., Lee, E. J., & Zhang, M. (1994). Molecular architecture of araban, galactoglucan and welan. *Carbohydrate Polymers*, *25*, 235–243.

Chinachoti, P., & Steinberg, M. P. (1986). Crystallinity of sucrose by X-ray diffraction as influenced by absorption versus desorption, waxy maize starch content, and water activity. *Journal of Food Science*, *51* (2), 456–459 see also p. 463.

Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinization: origin of the enthalpic transition. *Carbohydrate Research*, *227*, 103–112.

Gordon, M., & Taylor, J. S. (1952). Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. *Journal of Applied Chemistry*, *2*, 493–500.

Jouppila, K., & Roos, Y. H. (1997). The physical state of amorphous corn starch and its impact on crystallization. *Carbohydrate Polymers*, *32*, 95–104.

Jouppila, K., Kansikas, J., & Ross, Y. H. (1998). Factors affecting crystallization and crystallization kinetics in amorphous corn starch. *Carbohydrate Polymers*, *36*, 143–149.

Kalichevsky, M., & Blanshard, J. M. V. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers*, *20*, 107–113.

Kim, J. O., Kim, W. S., & Shin, M. S. (1997). A comparative study on retrogradation of rice starch gels by DSC, X-ray and α-amylase methods. *Starch/Stärke*, *49* (2S), 71–75.

Matveev, Y. I., Grinberg, V. Y., & Tolstoguzov, V. B. (2000). The plasticizing effect of water on proteins, polysaccharides and their mixtures. Glassy state of biopolymers, food and seeds. *Food Hydrocolloids*, *14*, 425–437.

Mizuno, A., Mitsuiki, M., & Motoki, M. (1998). Effect of crystallinity on the glass transition temperature of starch. *Journal of Agricultural Food Chemistry*, *46*, 98–103.

Niness, K. R. (1999). Inulin and oligofructose: what are they? *Journal of Nutrition*, *129* (7S), 1402S–1406S.

Nyqvist, H. (1983). Saturated salt solutions for maintaining specified relative humidities. *International Journal of Pharmaceutical Technology Product Manufacture*, *4* (2), 47–48.

Pszczola, D. E. (1997). Feelin' good: ingredients that add texture. *Food Technology*, *51* (11), 82–86.

Radha, A., & Chandrasekaran, R. (1997). X-ray and conformational analysis of arabinan. *Carbohydrate Research*, *298*, 105–115.

Roberfroid, M. B. (1999). Caloric value of inulin and oligofructose. *Journal of Nutrition*, *129* (7S), 1436S–1437S.

Roberfroid, M., Gibson, G. R., & Delzenne, N. (1993). The biochemistry of oligofructose, a non-digestible fiber: an approach to calculate its caloric vale. *Nutrition Review*, *51* (5), 137–146.

Roos, Y. H. (1995). *Phase transitions in foods* (pp. 49–107). San Diego, CA: Academic Press, Inc.

Roos, Y., & Karel, M. (1991). Phase transitions of mixtures of amorphous polysaccharides and sugars. *Biotechnological Progress*, *7*, 49–53.

Roos, Y. H., Karel, J., & Kokini, J. L. (1996). Glass transitions in low moisture and frozen foods: effects on shelf life and quality. *Food Technology*, *50* (11), 95–108.

Schaller-Povolny, L. A., & Smith, D. E. (1999). Sensory attributes and storage life of reduced fat ice cream as related to inulin content. *Journal of Food Science*, *64* (3), 555–559.

Shu, C. K. (1998). Flavor components generated from inulin. *Journal of Agricultural Food Chemistry*, *46*, 1964–1965.

Silva, R. F. (1996). Use of inulin as a natural texture modifier. *Cereal Foods World*, *41* (10), 792–794.

Singh, R. P., & Heldman, D. R. (1993). *Introduction to Food Engineering* (pp. 415–419). San Diego, CA: Academic Press Inc.

Singh, P. C., & Singh, R. K. (1996). Application of GAB model for water sorption isotherms of food products. *Journal of Food Processing and Preservation*, *20*, 203–220.

Slade, L., & Levine, H. (1988). Non-equilibrium behavior of small carbohydrate–water systems. *Pure Applied Chemistry*, *60*, 1841–1864.

Tolstoguzov, V. B. (2000). The importance of glassy biopolymer components in food. *Nahrung*, *44* (2S), 76–84.

Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch/Stärke*, *40* (1S), 1–7.