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Phase transitions of inulin–waxy maize starch systems in limited moisture environments

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Abstract

The moisture sorption isotherms of gelatinized and native waxy maize starch (WMS, constituted by 98% amylopectin) were determined, fitted to the GAB model and compared to the moisture sorption properties of inulin. Crystallinity of native and gelatinized WMS was assessed by X-ray diffraction. The glass transition temperature (T_g) of gelatinized WMS was measured by differential scanning calorimetry (DSC) as a function of moisture content. At 25 °C, T_g occurred at a moisture content of approximately 28% (d.b.). The experimental data were fitted to the Gordon–Taylor equation. Concentrated mixed samples of inulin and WMS presented two individual T_gs, which corresponded to those of the individual components, indicating that no interactions or plasticizing effects existed between them. It was concluded that phase separation had occurred; accordingly, the degree and nature of the phase separation still need to be addressed.

Keywords: Inulin; Waxy maize starch; Amylopectin; Glass transition; Phase separation

1. Introduction

The glass transition temperature (T_g) of starch (Biliaderis, 1991; Zeleznak & Hoseney, 1987) and the plasticizing effect of water on starch (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992) have been intensively studied in the last two decades using techniques such as differential scanning calorimetry (DSC) (Noel & Ring, 1992), and dynamic mechanical analysis (DMA) (Vodovotz & Chinachoti, 1996). This has proven to be a challenging task because of the small and broad transitions that starch exhibits when analyzed by the above-mentioned techniques.

Sub-T_g transitions in starch have been addressed in the literature by investigators such as Kalichevsky et al. (1992), who encountered a low temperature transition at around 50 °C on the first run in DSC experiments and thereafter only after storage. This finding was confirmed by Shogren (1992), who investigated the aging of low moisture gelatinized corn starch using DSC and found that the samples developed endothermic peaks characteristic of enthalpy changes due to structural relaxation. Other investigators who studied this enthalpic relaxation include Appelqvist, Cooke, Gidley, and Lane (1993), Bizot, Le Bail, Leroux, Davy, Roger, and Buleon (1997), Thiewes and Steeneken (1997) and Yuan and Thompson (1994).

The crystallinity of starch has also been thoroughly investigated. Zeleznak and Hoseney (1986) determined that solubilized amylopectin recrystallized after aging for 14 days at 50 and 70% water and concluded that water present during aging controlled retrogradation and that granule remnants had no influence on retrogradation. Zobel (1988b) stated that amylopectin's crystal type gave A patterns, showing three strong peaks at 5.8, 5.2 and 3.8 Å, when analyzed by X-ray diffraction. The A to B-type transition was not energetically favorable and only after the A-type was melted to an amorphous state was crystallization to B-type observed. Jouppila, Kaniskas, and Roos (1998) and Jouppila and Roos (1997) related crystallization behavior of amorphous corn starch to its physical state and glass transition using X-ray diffraction.

Several studies have addressed the interactions in mixed biopolymer systems. For example, Antonov, Pletenko, and Tolstoguzov (1987) used microscopy and ultracentrifugation to analyze phase-separated systems consisting of low concentrations of amylopectin mixed with water and hydrocolloids. Kalichevsky and Blanshard (1993) studied the effect of fructose and water on the T_g of amylopectin; at

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and below 20% fructose, the T_g was lower than predicted using the three-component Couchman–Karasz equation, indicating that phase separation had occurred in some samples. Kasapis, Morris, Norton, and Clark (1993b), studied the effect of thermodynamic incompatibility in mixed solutions of gelatin and maltodextrin systems under conditions where the individual polymers were stable as disordered coils. Concentrated mixtures of maltodextrins and gelatin showed the classic phase separation into two co-existing liquid layers (Kasapis, Morris, Norton, & Gidley, 1993c). Phase separation and inversion in mixed gels was confirmed by DSC, mechanical spectroscopy, and light microscopy (Kasapis, Morris, Norton, & Brown, 1993a). Gelation and phase separation in maltodextrin–caseinate systems was studied by Manoj, Kasapis, and Chronakis (1996). Tolstoguzov (1995, 1996, 1998, 1999, 2000) studied the phase behavior of protein–polysaccharide mixtures, whose low compatibility was influenced by a marked difference in hydrophilicity. Mousia, Farhat, Blachot, and Mitchell (2000) determined that two transitions were found in concentrated amylopectin–gelatin mixtures, indicating the existence of two distinct phases.

Inulin, a fructooligosaccharide, is used as a fat substitute in dairy, cereal and bakery products (Niness, 1999; Schaller-Povolny & Smith, 1999). It consists 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 has a degree of polymerization of 2–60; high performance (HP) forms of inulin have an average degree of polymerization of 25 (Roberfroid, 1999). Although its nutritional properties have been reviewed extensively, limited information exists on inulin's physicochemical properties and its interactions with other food components. In 2002, Zimeri and Kokini characterized the effect of moisture content on inulin's crystallinity and glass transition temperature.

The objective of this study was to characterize the effect of the addition of a short-chained polysaccharide, such as inulin, on the physicochemical characteristics of waxy maize starch by comparing their moisture sorption characteristics and glass transition temperatures under limited moisture environments.

2. Materials and methods

2.1. Sample preparation

Waxy maize starch (WMS, constituted by 98% amylopectin, obtained as Amioca™ from National Starch, Bridgewater, NJ) and inulin (Raftiline® HP, >99.5% pure, donated by Orafti, Malvern, PA) were used. Inulin was suspended in distilled de-ionized water at a concentration of 40% (w/w, w.b.) and heated to 90 °C, according to the procedure followed by Zimeri and Kokini (2002). The hot suspension was immediately cooled to −38 °C, in order to avoid inulin from recrystallizing. Samples were then dried and milled into a fine powder using a laboratory mill (Glen Mills, Maywood, NJ). WMS was suspended in distilled de-ionized water at a concentration of 35% (w/w, w.b.) and heated to 121 °C for 15 min in an autoclave in order to eliminate its crystallinity. The resulting gel was immediately cooled down to room temperature, dried and milled into a fine powder, following the same procedure used to prepare inulin samples. In order to obtain mixed samples, inulin was mixed with WMS and water as follows: (a) 10.5% inulin, 24.5% WMS and 65% water (w/w, w.b.), corresponding to an inulin to WMS ratio of 3:7 (d.b.), and (b) 20% inulin, 15% WMS and 65% water (w/w, w.b.), corresponding to an inulin to WMS ratio of 6:4 (d.b.). Mixed samples underwent the same drying and milling treatments as pure WMS samples.

2.2. Equilibration at different storage water activity (A_w) values

Samples were stored in desiccators containing different saturated salt solutions (P_2O_5, LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, and KNO_3), which produced water activity values of 0, 0.11, 0.33, 0.52, 0.75 and 0.93, respectively, at 25 °C (Nyqvist, 1983). The samples were equilibrated for a minimum of 4 weeks.

2.3. Moisture sorption isotherms

The moisture content of the samples was determined by drying in a convection oven at 135 °C for 2 h (AACC method 44-19). The A_w of the samples was measured at room temperature using a Hygroskop DT hygrometer (Rotronic Instrument Corp., Huntington, NY). The moisture sorption isotherms consisted of a plot of moisture content vs. A_w. Samples were analyzed in duplicate. The data were fitted to the Guggenheim–Anderson–DeBoer (GAB) model (Bell & Labuza, 2000; Singh & Singh, 1996).

2.4. X-ray diffraction

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) was operated using Cu Kα radiation ($\lambda = 0.1514$ nm) at 40 kV and 50 mA and a diffraction angle (2θ) fixed at 25°. The length of the scans was 1 h at room temperature. Results consisted of a plot of the diffraction image and the resulting graph of a trace vector plotted through the horizontal. Reported peaks corresponded to rings 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 percentage, following

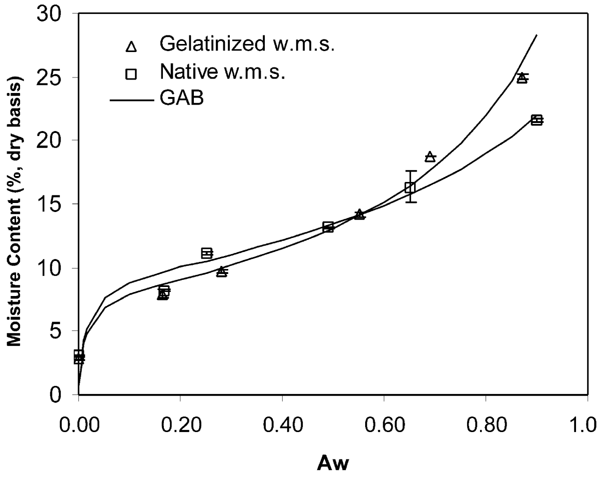

Fig. 1. Moisture sorption isotherms of gelatinized and native WMS (25 °C) fitted to the GAB model.

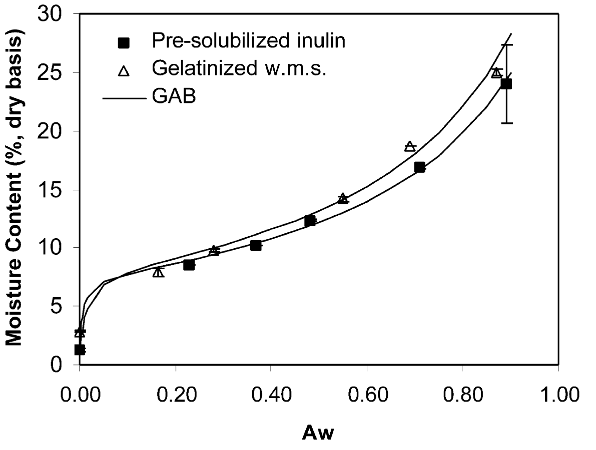

Fig. 2. Moisture sorption isotherms of pre-solubilized inulin and gelatinized WMS fitted to the GAB model.

the procedures detailed by Chinachoti and Steinberg (1986), Kim, Kim, and Shin (1997) and Mizuno, Mitsuiki, and Motoki (1998).

2.5. *Differential scanning calorimetry*

A Perkin–Elmer DSC 7 system (Norwalk, CT) was used, according to the procedure described by Zimeri and Kokini (2002). Calibration was performed using indium as a standard. Experiments were run at a rate of 10 °C/min. Hermetic stainless steel pans were used to avoid moisture loss during heating. Re-scans were immediately performed in order to erase the thermal history of the samples. Measurements were conducted at least in duplicate and an empty stainless steel pan was used 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, complied with the following criteria: it was identified as a step change of heat flow in the DSC thermograms and was observable on the re-scans. The midpoint of the change in slope was identified as the T_g of the system. Melting, a first-order transition, was characterized by an endothermic, non-reversible peak.

2.6. *Glass transition temperature predictive models*

The dependence of T_g on moisture content was predicted using the Gordon and Taylor (1952) equation:

$$T_g = \frac{x_1 T_{g1} + \left(\Delta C_{p2}/\Delta C_{p1}\right) x_2 T_{g2}}{x_1 + \left(\Delta C_{p2}/\Delta C\mathrm{p}_1\right) x_2} \qquad (1)$$

where x_i is the weight fraction of the ith-component, T_{gi}, the glass transition temperature of the ith-component, ΔC_{pi} is the change in heat capacity at T_{gi}. In the present study, T_g and ΔC_p values used to fit the experimental data to Eq. (1) were the following: (a) water −139 °C, 1.94 J/g K (Kalichevsky & Blanshard, 1993); (b) amylopectin: 229 °C, 0.41 J/g K (Kalichevsky & Blanshard, 1993), and (c) inulin: 120 °C, 0.65 J/g K (Zimeri & Kokini, 2002).

3. Results and discussion

3.1. *Moisture sorption properties of waxy maize starch*

The moisture sorption isotherms of gelatinized and native WMS starch at 25 °C are shown in Fig. 1. These materials presented the sigmoid shape (type II isotherm) typical of biological and food materials; similar results were presented by Boki and Ohno (1991) for corn starch and Iglesias and Chirife (1982) for amylopectin. At low A_w values (0–0.60), both starches presented similar behavior. In the higher A_w regime, gelatinized WMS featured a lower A_w than native WMS at any corresponding moisture content, indicating that gelatinized WMS had stronger water binding capacity (Chinachoti & Steinberg, 1986; Roos, 1995). The isotherms were fitted to the GAB model, which is represented by solid lines in the figure. The monolayer values (W_m) for gelatinized and native WMS corresponded to 7.99 and 9.22%, respectively, similar to those previously reported by Bizot et al. (1997).

3.2. *Comparison of waxy maize starch vs. inulin's moisture sorption properties*

The moisture sorption isotherms of pre-solubilized inulin (Zimeri & Kokini, 2002) and gelatinized WMS are compared in Fig. 2. At any moisture content, WMS had a lower A_w than inulin, indicating stronger water-binding capacity. For example, at a moisture content of 10% (d.b.), gelatinized WMS and pre-solubilized inulin presented A_w values of 0.30 and 0.38, respectively, difference which could have a significant effect on the stability of food systems.

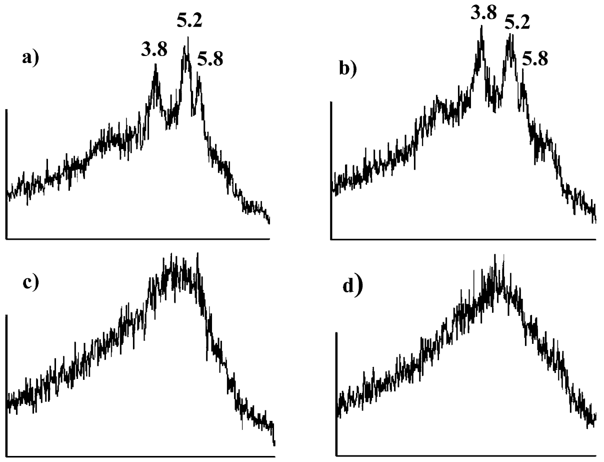

Fig. 3. X-ray diffractograms of native WMS stored at (a) A_w 0; (b) A_w 0.75 and gelatinized WMS stored at (c) A_w 0; (d) A_w 0.75. *d*-spacings given in Å.

3.3. Effect of moisture on the crystallinity of waxy maize starch

Development of crystallinity in WMS samples during storage at 25 °C was determined by X-ray diffraction. Fig. 3a and b correspond to diffractograms of native WMS stored at A_w values of 0 and 0.75, respectively. As expected, native WMS presented an A-type crystallinity pattern with strong peaks at 5.8, 5.2 and 3.8 Å (Zobel, 1988b). Its relative crystallinity (calculated from the ratio of the areas of the peaks vs. the total area) corresponded to ~25%, and remained unchanged, regardless of storage A_w (up to 19% moisture content). According to the literature (Zobel, 1988a), levels of crystallinity in granular starch can range from 14 to 45%.

Fig. 3c and d correspond to gelatinized WMS stored at A_w values of 0 and 0.75, respectively. The existence of a single broad peak is typical of amorphous, fully gelatinized starch (Farhat, Blanshard, Descamps, & Mitchell, 2000). Low relative crystallinity resulted from the experimental treatment of WMS, which consisted in gelatinization and drying. Relative crystallinity in these samples corresponded to ~2% and remained unchanged, regardless of storage A_w. Even at A_w 0.75 (moisture content ~19% at 25 °C), gelatinized WMS remained in the glassy state, conditions at which recrystallization is very difficult to occur due to limited mobility.

3.4. Waxy maize starch's T_g as a function of moisture content

The T_g of gelatinized WMS equilibrated at different A_w values was determined by DSC. Native WMS samples were not examined, since their higher degree of crystallinity would have made the transition very difficult to determine. Fig. 4a–d correspond to DSC thermograms for gelatinized WMS samples at the actual A_w values of 0.30, 0.42, 0.68 and 0.93, respectively. The data were normalized by dividing the heat flow by the sample weight. Both the first scan and re-scan are displayed. The reversibility of T_g, a second-order transition, was observed on the re-scan. Although the onset and endset of the transition occurred within an interval of 20 °C, T_g was identified at the midpoint of the transition.

The ΔC_p values at T_g varied between 0.06 and 0.14 J/g K,

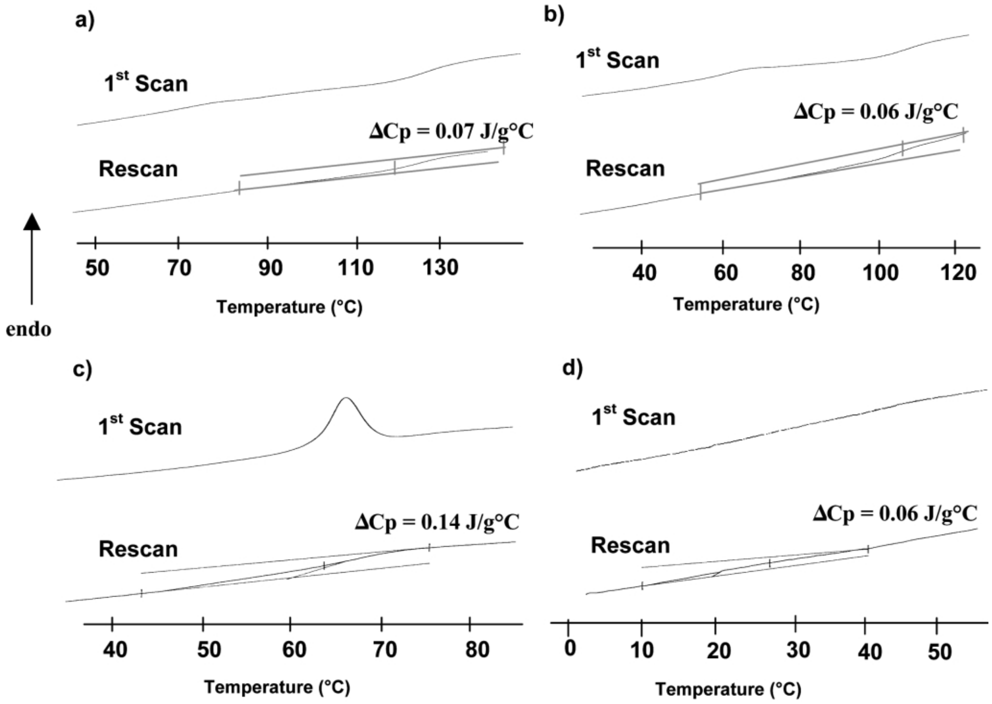

Fig. 4. DSC thermograms of gelatinized WMS at (a) 0.30; (b) 0.42; (c) 0.68; (d) 0.93 A_w values.

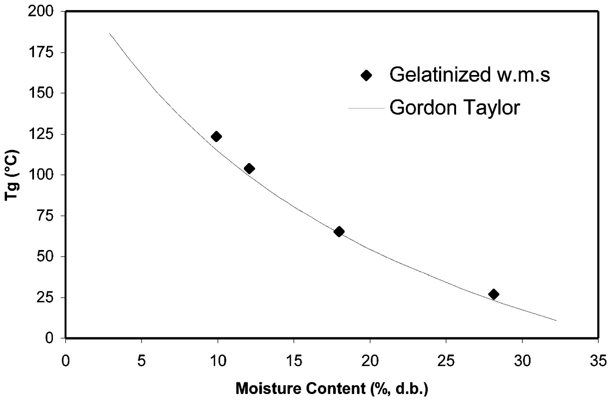

Fig. 5. T_g of gelatinized WMS as a function of moisture content compared to the Gordon–Taylor equation.

indicating a small-magnitude transition; these data confirm the following statement by Biliaderis (1991): the ΔC_p at T_g is not easily detected for most starches due to structural microheterogeneity, which causes a range of non-ordered domains to exist, each one with its own T_g and different plasticization behavior by water.

A sub-T_g endotherm was observed at around 65 °C on the first scan of samples at A_w values of 0.30, 0.42 and 0.68 (Fig. 4a–c). This transition has been identified in the literature as an enthalpy relaxation peak (Shogren, 1992; Thiewes & Steeneken, 1997). Its magnitude increased with A_w, and it was differentiated from T_g because of its lack of reversibility. At A_w 0.93 (Fig. 4d), no enthalpic relaxation was observed since T_g occurred at ~30 °C, lower temperature than that at which the enthalpic relaxation was normally observed (~65 °C).

Fig. 5 shows a plot of gelatinized WMS's T_g vs. moisture content. The data points represent the average of at least two experimental T_g values at each moisture content. Water acted as a plasticizer, as demonstrated by the decrease in T_g with increasing moisture content. The experimental data were fitted to the Gordon–Taylor equation, represented by a solid line in the figure. The ΔC_p for anhydrous WMS, determined by least squares fit following the procedure used by Jouppila and Roos (1997), had a value of 0.43 J/g K, similar to the value of 0.41 J/g K calculated by Kalichevsky and Blanshard (1993) for amylopectin.

As Fig. 5 also indicates, WMS's critical moisture content at which T_g occurs at room temperature, W_{g25}, was approximately 28%, corresponding to an A_w value less than 0.93. Similar values were determined by Mizuno et al. (1998) for potato and wheat starch. Thus, at A_w values below 0.93, WMS samples were found in the glassy state. These results confirm the previously discussed X-ray diffraction results, which showed that gelatinized WMS remained in a highly amorphous state (~2% relative

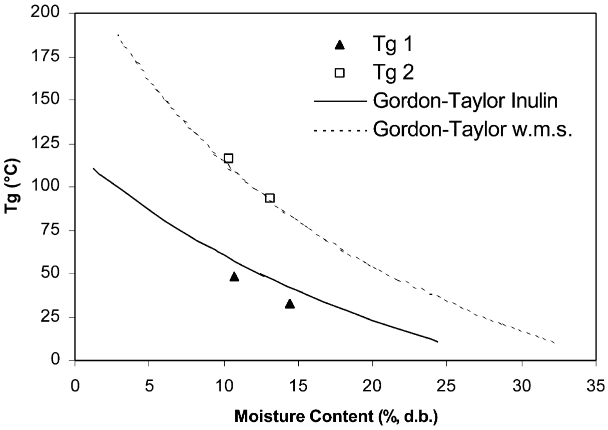

Fig. 7. Two glass transition temperatures in samples containing inulin to WMS ratio of 3:7, determined by DSC and fitted to the Gordon–Taylor equation.

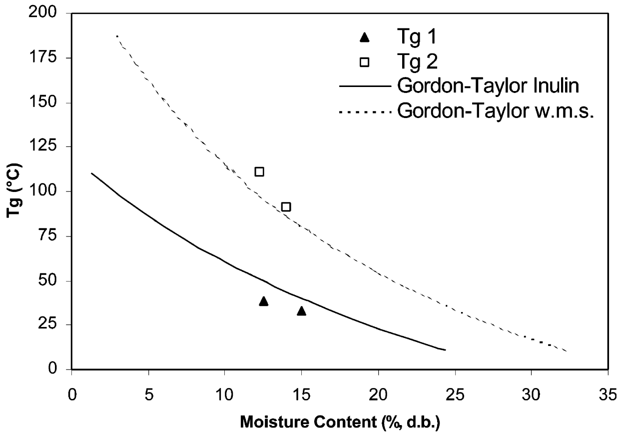

Fig. 8. Two glass transition temperatures in samples containing inulin to WMS ratio of 6:4, determined by DSC and fitted to the Gordon–Taylor equation.

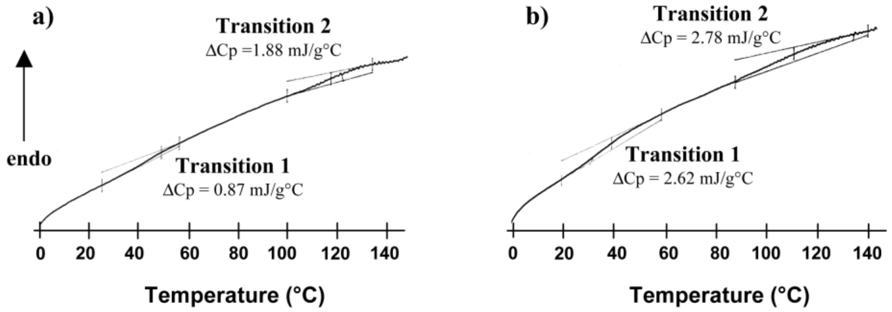

Fig. 6. Two independent T_gs in mixed inulin–WMS systems stored at A_w 0.33 at inulin to WMS ratio of: (a) 3:7 and (b) 6:4.

crystallinity) at moisture contents up to 19% (A_w 0.75), due to limited mobility.

3.5. T_g of mixed inulin–waxy maize starch samples

Fig. 6 shows DSC thermograms (re-scans) of mixed inulin–WMS systems stored at A_w 0.33 with (a) inulin to WMS ratio of 3:7, and (b) inulin to WMS ratio of 6:4.

Two independent reversible endothermic transitions were observed: Transition 1 (lower temperature) and Transition 2 (higher temperature). Similar results were found for mixed samples stored at A_w 0.52 (not shown). Mixed samples at A_ws lower than 0.33 were analyzed, but very high temperatures were needed to obtain T_gs at low moisture contents, leading to sample decomposition. It was not possible to obtain clear glass transitions for mixed samples equilibrated at A_ws above 0.52 due to recrystallization of inulin at high moisture contents. As shown by Zimeri and Kokini (2002), it was not possible to measure T_g for pure inulin samples at high A_w values.

Fig. 7 shows the plot of T_g vs. moisture content for mixed samples containing an inulin to WMS ratio of 3:7 stored at A_ws 0.33 (~11% moisture) and 0.52 (~14% moisture). A dotted line represents the Gordon–Taylor equation plot for pure WMS (shown in Fig. 5), a continuous line represents that of pure inulin (Zimeri & Kokini, 2002), and the symbols represent Transition 1 and Transition 2 observed in mixed inulin–WMS samples. Transition 1 occurred at the same temperature as T_g of pure inulin, and Transition 2 occurred at the same temperature as T_g of pure WMS, at the specific moisture contents shown in the figure. Water plasticized both Transition 1 and Transition 2.

The influence of inulin's addition on the T_g of the system can be determined by comparing Figs. 7 and 8. The latter shows the plot of T_g vs. moisture content for samples containing an inulin to WMS ratio of 6:4; the symbols and lines represent the same data as before. Again, Transition 1 matched the T_g of pure inulin, and Transition 2 matched the T_g of pure WMS. Thus, as the ratio of inulin to WMS increased from 3:7 to 6:4, it did not have any effect on the T_gs of the system. Moreover, the addition of inulin had no plasticizing effects on WMS, i.e. Transitions 1 and 2 occurred at the same temperatures, regardless of the concentration of inulin. The only plasticizer acting in mixed inulin–WMS samples was water.

The compositions at which phase separation was observed are plotted in the form of a ternary state diagram in Fig. 9. (The fact that inulin and WMS were forced to become highly amorphous through sample preparation, in order to measure T_g, should be considered.) Thus, it is clear that phase separation occurred at four different compositions, indicating that the two components were immiscible at moisture contents below 20% (w.b.). At high concentrations used in this study, it was expected for phase separation to occur, since it is well-known that mixing two polymers frequently results in a system in which almost total phase separation occurs (Sperling, 1986). According to Matveev, Grinberg, and Tolstoguzov (2000), in unlike blends of compatible polymers that usually have one T_g, each immiscible polymer retains its own T_g. Biopolymer mixtures usually have, therefore, either two transitions or a single transition in a much broader temperature range. The latter occurs when the individual T_g values are close to one another (Matveev et al., 2000). A similar behavior was observed by Kalichevsky and Blanshard (1993) in mixed samples of fructose and amylopectin. Jurgens (1999a,b) determined that aqueous dispersions containing inulin showed phase separation, observed under light microscopy; phase separation was also observed in inulin-containing low fat spreads after 8 weeks of storage at 5 °C. Issues regarding complete vs. partial phase separation and thermodynamic incompatibility of these biopolymers still need to be addressed.

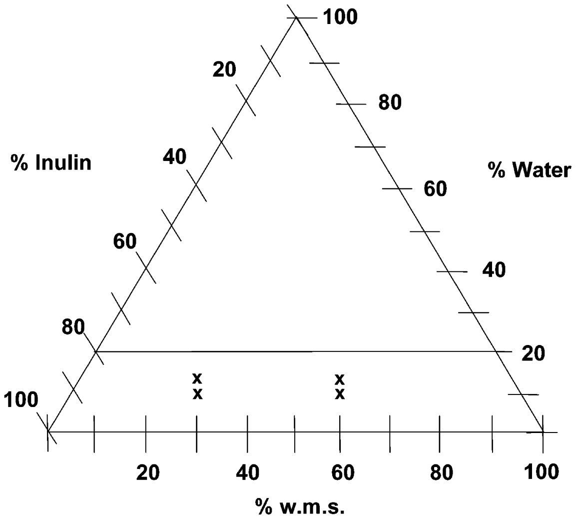

Fig. 9. Ternary state diagram of inulin, WMS and water. Composition of samples at which phase separation was observed is represented by **x**.

4. Conclusion

The glass transition of gelatinized WMS at 25 °C occurred at moisture contents of approximately 28% (w.b.). At the experimental conditions ($A_w \leq 20\%$ w.b.), gelatinized WMS remained in the glassy, amorphous state. Mixed samples of inulin and WMS showed the existence of two T_gs, which corresponded to those of the individual components. It was concluded that phase separation existed at low moisture contents, although the degree and origin of separation was not addressed in this study.

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