



# Glass transition prediction strategies based on the Couchman-Karasz equation in model confectionary systems



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## ABSTRACT

Our objectives were to compare the Couchman-Karasz-predicted glass transition temperature,  $T_{CK}$ , to the measured glass transition temperature of a mixture,  $T_{gm}$ , of model confectionary systems and develop an empirical correction to improve the accuracy of prediction. Results showed that the original Couchman-Karasz equation fit the data better than the modified equation; although both generally overestimated  $T_{gm}$ . Blends containing sorbitol had the largest  $\Delta T_{gm}^{CK}$ , where  $\Delta T_{gm}^{CK} = T_{CK} - T_{gm}$ . While  $T_{gm}$  varied with composition, the increase in  $T_{gm}$  with decreasing moisture content was linear ( $R^2 = 0.984$ ) and consistent across blends ( $4.5 \pm 0.9^\circ\text{C}/1\%$  moisture, wb). The increase in  $T_{gm}$  with increasing cook temperature was best described by a polynomial model ( $R^2 = 0.998$ ), but adequately described by a more generalizable linear model ( $R^2 = 0.979$ ). Application of an empirical correction based on moisture content or cook temperature and  $T_{CK}$  of dry ingredients reduced the average  $\Delta T_{gm}^{CK}$  from  $20.1^\circ\text{C}$  and  $11.3^\circ\text{C}$  for modified and original equations, respectively, to  $<5.6^\circ\text{C}$ .

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## 1. Introduction

Thermal properties of confectionary products, including the melting temperature ( $T_m$ ) of crystalline components and glass transition temperature ( $T_g$ ) of amorphous components, as well as the crystalline to amorphous ratio, significantly impact system texture and stability (Levine and Slade, 1986). Predominantly amorphous (non-crystalline, disordered solid) candies are formed by heating ingredients to a set temperature and then quickly cooling the resultant supersaturated sugar solution to below the temperature range in which recrystallization of sugars can occur,

between  $T_g$  and  $T_m$  of the material (Hartel et al., 2011; Roos, 1995). The transition from an amorphous glass to a rubber is associated with a decrease in viscosity and an increase in mobility (Roos and Karel, 1991a). Therefore, amorphous food materials held above their  $T_g$  are said to be rubbery and have leathery to soft/sticky properties, while amorphous materials below their  $T_g$  are said to be glassy or crisp and are less susceptible to stickiness, deformation, crystallization or structural instability than their rubbery counterparts (Katz and Labuza, 1981; Levine and Slade, 1986; Mendenhall and Hartel, 2014; Roos and Karel, 1991a; Slade et al., 1991).

The glassy amorphous state is a metastable, non-equilibrium state, and the temperature at which a material undergoes the glass transition is positively related to the molecular weight of the material or material ingredients (Hartel et al., 2011; Roos, 1995; Slade et al., 1991). In addition to composition,  $T_g$  is impacted by moisture content and the thermal history of the sample (Abiad et al., 2009; Lee et al., 2011b). Caramelization can occur during the processing of confectionary products, significantly altering the thermal profile, as smaller molecular fragments decrease  $T_g$ , while polymerization increases  $T_g$  (Vanhal and Blond, 1999). In this context, caramelization refers to the series of decomposition and polymerization reactions of sugar molecules, which occurs when a time-temperature combination sufficient to cause decomposition

**Abbreviations:**  $T_g$ , glass transition temperature;  $\Delta C_p$ , change in specific heat;  $T_m$ , melting temperature;  $T_{CK}$ ,  $T_g$  value calculated via the Couchman-Karasz equation;  $T_{gm}$ ,  $T_g$  of mixture;  $\Delta T_{gm}^{CK}$ , difference between calculated  $T_{CK}$  and measured  $T_{gm}$ ;  $\Delta T_{gm}^{MC}$ ,  $T_g$  value calculated via an empirical equation based on  $T_{CK}$  and sample moisture content;  $T_{CK}^{CT}$ ,  $T_g$  value calculated via a polynomial empirical equation based on  $T_{CK}$  and sample cook temperature;  $T_{gm}^{CT}$ ,  $T_g$  value calculated via a linear empirical equation based on  $T_{CK}$  and sample cook temperature;  $\Delta T_{gm}^{CKMC}$ , difference between calculated  $T_{CK}^{MC}$  and measured  $T_{gm}$ ;  $\Delta T_{gm}^{CKCT}$ , difference between calculated  $T_{CK}^{CT}$  or  $T_{gm}^{CT}$  and measured  $T_{gm}$ ; C, cane sucrose; I, isomalt; M, maltitol; S, sorbitol; CS, corn syrup solids.

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of the sugar is applied (Lee et al., 2011a). Because  $T_g$  plays a significant role in product texture and stability, accurate prediction of  $T_g$  based on formulation and processing conditions is valuable for both formula development and process control (Abiad et al., 2009; Slade et al., 1991).

Numerous models have been developed to predict the  $T_g$  of mixtures,  $T_{gm}$ , based on the properties of the components of the mixture. The Gordon–Taylor (Gordon and Taylor, 1952) and Couchman–Karasz (Couchman and Karasz, 1978) models are two of the most ubiquitous, particularly in food and food ingredient research (Arvanitoyannis and Biliaderis, 1999; Chaudhary et al., 2011; Liu et al., 2007; Orford et al., 1990; Pouplin et al., 1999; Roos, 1992; Ruiz-Cabrera and Schmidt, 2015). Gordon-Taylor and Couchman-Karasz predicted  $T_g$  values will hereafter be written as  $T_{GT}$  and  $T_{CK}$ , respectively. The Gordon-Taylor equation (Equation (1)), in which  $x_i$  is the molar or weight fraction of component  $i$ ,  $T_{gi}$  is the  $T_g$  of component  $i$ , and  $K$  is a constant that is specific to the components in the mixture and related to the coefficient of expansion of the components as they undergo the glass transition, was developed to predict the  $T_g$  of polymer blends (Gordon and Taylor, 1952; Truong et al., 2002).

$$T_{GT} = \frac{x_1 T_{g1} + K x_2 T_{g2}}{x_1 + K x_2} \quad (1)$$

While the Gordon-Taylor equation is generally reliable in the prediction of  $T_g$  for polymer blends and polymer-plasticizer blends, it is less accurate in the prediction of  $T_g$  for systems with low molecular weight solutes (Katkov and Levine, 2004). The Couchman-Karasz equation, which is based on the assumption that the glass transition is a thermodynamic event, weights the  $T_g$  of components by the change in heat capacity ( $\Delta C_p$ ) instead of the change in volume at the glass transition (Abiad et al., 2009; Couchman and Karasz, 1978). The original form of the Couchman-Karasz equation (2) includes the assumption that  $\Delta C_p$  is independent of temperature (Katkov and Levine, 2004). The notation  $\Delta C_{pi}$  is used to refer to the  $\Delta C_p$  at the glass transition for component  $i$ .

$$\ln(T_{CK}) = \frac{\Delta C_{p1} x_1 \ln(T_{g1}) + \Delta C_{p2} x_2 \ln(T_{g2})}{\Delta C_{p1} x_1 + \Delta C_{p2} x_2} \quad (2)$$

A modified version of Equation (2) was also presented by Couchman and Karasz (1978), which assumes, instead of independence, that  $\Delta C_p$  is proportional to temperature (Equation (3)). The invalidity of the assumption of independence between  $\Delta C_p$  and temperature was argued, and use of the modified Equation (3) was advocated, by ten Brinke et al. (1983); Equation (3) is the most commonly used form of the Couchman-Karasz equation.

$$T_{CK} = \frac{\Delta C_{p1} x_1 T_{g1} + \Delta C_{p2} x_2 T_{g2}}{\Delta C_{p1} x_1 + \Delta C_{p2} x_2} \quad (3)$$

The Couchman-Karasz equation is frequently extended to ternary or quaternary systems, which can be expressed in simplified form (Equation (4)) or treated as a binary mixture of solids and water (Equation (5)) (Katkov and Levine, 2004; Truong et al., 2002).

$$T_{CK} = \frac{\sum \Delta C_{pi} x_i T_{gi}}{\sum \Delta C_{pi} x_i} \quad (4)$$

$$T_{CK} = \frac{\Delta C_{p \text{ solids}} x_{\text{solids}} T_{g \text{ solids}} + \Delta C_{p \text{ water}} x_{\text{water}} T_{g \text{ water}}}{\Delta C_{p \text{ solids}} x_{\text{solids}} + \Delta C_{p \text{ water}} x_{\text{water}}} \quad (5)$$

More complex modifications to the Couchman-Karasz equation have been made, including the modifications by Pinal (2008), which accounts for the entropy of mixing of the components in the blend, and by Kwei (1984), which added a term to account for hydrogen bonding interaction between polymeric components; however, exploration of these models is beyond the scope of this work.

To date, most evaluations of the Couchman-Karasz equation for prediction of  $T_g$  within the food realm have focused on binary or ternary mixtures of carbohydrates, proteins, and water (Arvanitoyannis et al., 1993; Gontard and Ring, 1996; Kalichevsky et al., 1993, 1992; Kalichevsky and Blanshard, 1993; Liu et al., 2007; Matveev et al., 2000; Orford et al., 1990; Pouplin et al., 1999; Saavedra-Leos et al., 2012), though Roos (1992) has also published an investigation of the  $T_g$  of strawberries and horseradish at various moisture content and  $a_w$  values. Amorphous mixtures are generally prepared by freeze drying or dehydration of a solution (Arvanitoyannis et al., 1993; Kawai and Hagura, 2012; Liu et al., 2007; Roos and Karel, 1991b) or by melting and quick-cooling, often via DSC, (Orford et al., 1990; Ruiz-Cabrera and Schmidt, 2015; Simatos et al., 1996; Wungtanagorn and Schmidt, 2001). This study aims to provide a realistic assessment of the reliability of Couchman-Karasz models for use in full- and reduced-sugar confectionary systems, employing a method of amorphization which approximates the cooking process employed for the production of confectionary products.

One persistent challenge in use of Couchman-Karasz or other models to predict  $T_g$  is the determination of moisture content. In order to predict the  $T_g$  for model confectionary systems, our first objective was to estimate the moisture content of model confectionary systems cooked to 120, 130, 140, and 150 °C, which correspond to the firm ball, hard ball, soft crack, and hard crack stages of sugar cooking, respectively. Moisture content was estimated through the generation of boiling point elevation curves and compared to moisture content values measured via Karl Fischer titration for a subset of samples. We hypothesized that moisture content at a given final cook temperature would increase with increasing moles of solute, due to the increase in the boiling point of the solution caused by the increase in moles of solute.

Our second objective was to assess the fit of the original and modified Couchman-Karasz model for model confectionary systems. We hypothesized that the Couchman-Karasz model would overestimate  $T_g$  and that  $\Delta T_{gm}^{CK}$ , or the difference between the measured and Couchman-Karasz predicted  $T_g$ , would increase with increasing final cook temperature, due to the heat-induced decomposition of ingredients. Finally, our third objective was to develop an empirical model to predict the  $T_g$  of model confectionary systems from the initial composition of the blend and final cook temperature. We hypothesized that the application of this empirical correction would result in a reduction of the average  $\Delta T_{gm}^{CK}$ .

## 2. Materials and methods

### 2.1. Carbohydrate blend ingredients and formulation

Simplified model confectionary systems, comprised only of carbohydrates and water, were developed. Carbohydrate ingredients utilized include cane sucrose (C & H Sugar, ASR Group, West Palm Beach, FL), corn syrup solids (Dextrose Equivalent 49–55, supplier requests nondisclosure), isomalt (CK Products, LLC, Fort Wayne, IN), maltitol (supplier requests nondisclosure), and

sorbitol (supplier requests nondisclosure). The typical carbohydrate profile of the corn syrup solids were as follows: 8% dextrose, 56% maltose, 16% maltotriose, and 20% higher saccharides.

Sugar alcohols were introduced into the carbohydrate blends at 20 and 40% of the total carbohydrate mass, usage levels which are similar to 25 and 50% replacement of sugars in confectionary systems. One sugar alcohol at most was used in each blend. The specific sugar alcohol used and the usage level is abbreviated in sample naming schemes as follows: C0 for control or no sugar alcohol used, I for isomalt, M for maltitol, S for sorbitol, 20 for 20% sugar alcohol by total solids mass, and 40 for 40% sugar alcohol by total solids mass. Three sucrose to corn syrup ratios were utilized: 1 to 0, 3 to 1, and 1 to 1. These ratios are indicated in formula names by the abbreviation CS and the numbers 0, 25, or 50, which describe the percentage of corn syrup out of the total mass of corn syrup and sucrose. All combinations of sugar alcohol, sugar alcohol usage level, and corn syrup solids usage level were produced with the exception of the 100% sucrose formula. The percent composition and sample code names for carbohydrate blend formulas are displayed in Table 1.

## 2.2. Model confectionary system ingredients and preparation

To prepare the samples, carbohydrate ingredients in the ratios described in Table 1 and totaling 500 g per batch were weighed and mixed with 200 g of filtered water in a stainless steel saucepan. The temperature of the mixture was monitored with a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.) and stirred continuously as it was heated on a gas range. A consistent heat setting was applied in the preparation of each batch to affect a relatively consistent heating rate across batches; batches reached 120 °C after approximately 25 min of heating and 150 °C after approximately 5 additional minutes, or 30 total minutes of heating. Approximately 50 g of material was removed from the pan at 120, 130, 140, and 150 °C and deposited in droplets on an aluminum foil grid, for use in thermal analysis, and poured into a silicon mold (WOOTOP, Shenzhen, Guangdong, China), for use in moisture analysis. Droplets were sealed in pans for thermal analysis within 2 h of sample preparation in order to minimize changes to the moisture content of the material prior to analysis. Material reserved for moisture content analysis was sealed in plastic cups with lids (Solo Cup Company, Inc., Chicago, IL, U.S.A.) and stored in a freezer at −15 °C to preserve the physical state and moisture content of the samples. Each formula was produced once, with the exception of three representative samples, I40-CS25, M40-CS25, and S40-CS25, which were produced twice in

order to evaluate the reproducibility of the preparation process. Data from both batches of representative samples, I40-CS25, M40-CS25, and S40-CS25, were used exclusively in sections 3.3, 3.4, and 3.5; data from the first batch of all samples was used in sections 3.2 and 3.6.

## 2.3. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was conducted to characterize the glass transition behavior of carbohydrate ingredients and model confectionary systems. All runs were conducted using a DSC Q2000 instrument with an autosampler (TA Instruments, New Castle, DE, U.S.A.) and a refrigerated cooling system (RCS 90). The instrument was calibrated using an indium reference (known melting temperature of 156.6 °C; known enthalpy of 28.71 J/g) prior to analysis. All samples were massed in Tzero pans and sealed with hermetic lids (TA Instruments, New Castle, DE, U.S.A.), and runs were carried out under a dry nitrogen purge gas at a flowrate of 50 mL/min. Glass transition temperature ( $T_g$ ) onset, midpoint, and endpoint values, as well as change in specific heat capacity at the glass transition ( $\Delta c_p$ ) were determined from DSC thermograms using the Glass/Step Change function with Manual Tangent Selection within Universal Analysis software (Version 4.4A, TA Instruments New Castle, DE, U.S.A.). Manual tangent selection was used to prevent errors in  $T_g$  analysis caused by the presence of a physical aging peak. The temperature at the half-height of the glass transition was designated as the  $T_g$  midpoint; this method of  $T_g$  midpoint determination reduces the sensitivity of the parameter to differences in glass transition width.

With the exception of the corn syrup solids, all carbohydrate ingredients were originally in the crystalline state. Therefore, prior to analysis of  $T_g$  properties, crystalline carbohydrate ingredients were made amorphous using a melting and quick cooling protocol in the DSC. Crystalline ingredient samples ( $8.9 \pm 0.8$  mg) were heated at a rate of 10 °C/min until just melted, to a temperature of 200 °C, 160 °C, 155 °C, and 105 °C, for cane sucrose, isomalt, maltitol, and sorbitol, respectively. Melted sucrose, isomalt, maltitol, and sorbitol samples were then quickly cooled to −50 °C and heated again at 10 °C/min to 220 °C, 180 °C, 175 °C, and 125 °C, respectively, to capture the glass transition and confirm the complete amorphization of samples. The glass transition parameters of the corn syrup solids ingredient were measured by equilibrating the already amorphous sample ( $8.2 \pm 0.2$  mg) at −60 °C and then scanning at a rate of 10 °C/min to 95 °C. The  $T_g$  of isomalt, maltitol, sorbitol, and corn syrup solids was measured in duplicate, and the  $T_g$  of sucrose was measured in triplicate.

**Table 1**

Relative composition of ingredients and sample code names for model confectionary blends. Formulas are organized by % of the total mass contributed by sugar alcohol, as noted in the top row, and ratio of sucrose to corn syrup solids (CS), as noted in the second row.

Ingredient	Full Sugar Formulas		20% Sugar Alcohol Formulas			40% Sugar Alcohol Formulas		
	Sucrose: CS ratio 3:1	1:1	No CS	3:1	1:1	No CS	3:1	1:1
		% Composition	% Composition			% Composition		
Sucrose	75	50	80	60	40	60	45	30
Corn syrup solids	25	50	0	20	40	0	15	30
Sugar alcohol	0	0	20	20	20	40	40	40
Sugar Alcohol		Sample Code Name						
Control (none used)	C0-CS25	C0-CS50	Not Applicable			Not Applicable		
Isomalt			I20-CS0	I20-CS25	I20-CS50	I40-CS0	I40-CS25	I40-CS25
Maltitol	Not Applicable		M20-CS0	M20-CS25	M20-CS50	M40-CS0	M40-CS25	M40-CS25
Sorbitol			S20-CS0	S20-CS25	S20-CS50	S40-CS0	S40-CS25	S40-CS25

Model confectionary systems were made amorphous by the cooking process described in section 2.2. To facilitate loading of samples, which were often sticky and hard to handle, into Tzero pans, samples droplets were deposited onto  $5 \times 5$  mm squares on a sheet of aluminum foil. The foil squares were then cut out using a precision blade, and samples were loaded with foil into pans. The mass of a  $0.25 \text{ mm}^2$  square of foil was taken into account in the determination of sample mass, and a reference pan containing a  $0.25 \text{ mm}^2$  square of foil was used to produce the baseline for all sample runs. The  $T_g$  parameters of model confectionary samples ( $10.7 \pm 5.7 \text{ mg}$ ) cooked to 120, 130, 140, and  $150^\circ\text{C}$  were measured in duplicate using a protocol of equilibration at  $-60^\circ\text{C}$ , after which samples were heated at a rate of  $10^\circ\text{C}/\text{min}$  to  $95^\circ\text{C}$ .

#### 2.4. Model confectionary system boiling point elevation curve generation

Boiling point elevation curves were generated for each ratio of sucrose, corn syrup solids, and sugar alcohol previously described in Table 1. A total of 60 g of solids was combined with 40 g of filtered water in a 100 ml beaker. The beaker and contents were heated on a Corning PC-420D hot plate (Corning Inc., Corning, New York, U.S.A.). The mixture was stirred continuously with a spatula and the temperature was monitored with a high accuracy Traceable<sup>®</sup> thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.). The initial mass of the beaker was tared and the mass was recorded with a Mettler PM6000 scale (Mettler Toledo, Columbus, Ohio, U.S.A.) at increments of  $2^\circ\text{C}$  starting at  $100^\circ\text{C}$  and continuing until the mass of the mixture reached the mass of the initial solids content (60 g). This process was completed once for every formula, and repeated a second time for three representative samples (I40-CS25, M40-CS25, S40-CS25) to evaluate the reproducibility of the method.

The initial solids mass fraction in each test was 0.60. All mass lost during heating was assumed to be water, and the solids mass fraction was calculated as the quotient of the initial mass of solids (60 g) divided by the total mass of solids and water at a given temperature. Following data collection, boiling point elevation curves showing the change in boiling point over a range of solid mass fraction values for individual formulas and averaged curves for aggregated data of like-formulas were produced in Microsoft excel (Microsoft Corporation, Seattle, WA, U.S.A.). Curves for formulas with like corn syrup solids composition represent an average of 6 curves for CS0 or 7 curves for CS25 and CS50, while curves for formulas with like sugar alcohol composition represent an average of 3 curves each.

#### 2.5. Karl Fischer titration

Moisture content values for a representative subset of the samples (I40-CS25, M40-CS25, S40-CS25) were determined by volumetric Karl Fischer titration (EMD, Aquastar AQV21). The analysis was conducted by DonLevy Laboratories (Crown Point, Indiana, U.S.A.), and measurements were made in duplicate for each final cook temperature (120, 130, 140, and  $150^\circ\text{C}$ ) for two batches of each of the three formulas. A 50% formamide, 50% methanol solvent system was used for all testing. Samples were stirred continuously in the solvent system for 5 min to dissolve the sample; then the solution was titrated for approximately 10 min. The analysis was conducted at ambient conditions of 20.0% relative humidity and  $23.0^\circ\text{C}$ .

#### 2.6. Analysis and modeling of glass transition data

Measured  $T_{gm}$  values of samples from 2 batches of 3 sample

formulas (I40-CS25, M40-CS25, S40-CS25) were statistically compared to  $T_{CK}$  values calculated using both the original and modified versions of the Couchman-Karas equation and using batch-specific moisture content values measured via Karl Fischer titration. Two-tailed, one sample t-tests were conducted separately for each batch of a given sample using XLSTAT (Addinsoft, New York, NY, U.S.A.). Measured  $T_{gm}$  values were deemed significantly different from corresponding  $T_{CK}$  values when  $p < 0.05$ .

Linear and polynomial empirical models relating sample  $T_g$  to sample moisture content and cook temperature, as well as  $R^2$  values for each model, were generated from  $T_g$  and moisture content data from the first batch or trial of each model confectionary formula using Microsoft excel (Microsoft Corporation, Seattle, WA, U.S.A.).

### 3. Results and discussion

#### 3.1. Glass transition properties of ingredients

The average measured  $T_g$  onset, midpoint, and endpoint values, as well as the  $\Delta c_p$ , of carbohydrate ingredients used in this study are reported in Table 2. In general, the expected positive correlation between molar mass and  $T_g$  is observed. The exception to this trend is seen for corn syrup solids, which have a higher average molar mass than sucrose, but a lower  $T_g$ . This may be due to plasticization of higher molecular weight carbohydrates in the corn syrup solids by monosaccharides and small amounts of residual water not removed in the manufacturing process. The measured  $T_g$  midpoint of sucrose,  $70.4^\circ\text{C}$ , falls in the range of previously reported  $T_g$  values also measured at  $10^\circ\text{C}/\text{min}$  ( $69.7^\circ\text{C}$  to  $72.2^\circ\text{C}$ ) (Lee et al., 2011b; Liu et al., 2007; Orford et al., 1990; Vanhal and Blond, 1999). Measured  $T_g$  midpoint values were lower than some previously reported literature values for isomalt [measured  $43.2^\circ\text{C}$ , literature  $59.5^\circ\text{C}$  (Cammenga and Zielasko, 1996)], maltitol [measured  $40.0^\circ\text{C}$ , literature  $50.3^\circ\text{C}$  (Lappalainen and Pitkänen, 2006)], and sorbitol [measured  $-4.6^\circ\text{C}$ , literature  $-1.6^\circ\text{C}$  (Yu et al., 1998)]. Differences in measured and previously reported  $T_g$  values for sugar alcohol ingredients may be due to differences in ingredient processing and properties between suppliers, such as ingredient purity, isomeric ratio (in the case of isomalt), and residual moisture content.

In order to most accurately reflect the glass transition properties of the specific ingredients used, the experimentally measured midpoint  $T_g$  and  $\Delta c_p$  values shown in Table 2 were used throughout for the calculation of  $T_{CK}$ . Glass transition properties for water were obtained from the literature. The values of  $T_g$  reported in the literature for water range from 135 K to 143 K (Hallbrucker et al., 1989; Macfarlane and Angell, 1984; Sugisaki et al., 1968); in this study, a  $T_g$  of 136 K ( $-137^\circ\text{C}$ ) and a  $\Delta c_p$  of  $1.94 \text{ J/g}^\circ\text{C}$  were used for all calculations (Katkov and Levine, 2004).

**Table 2**

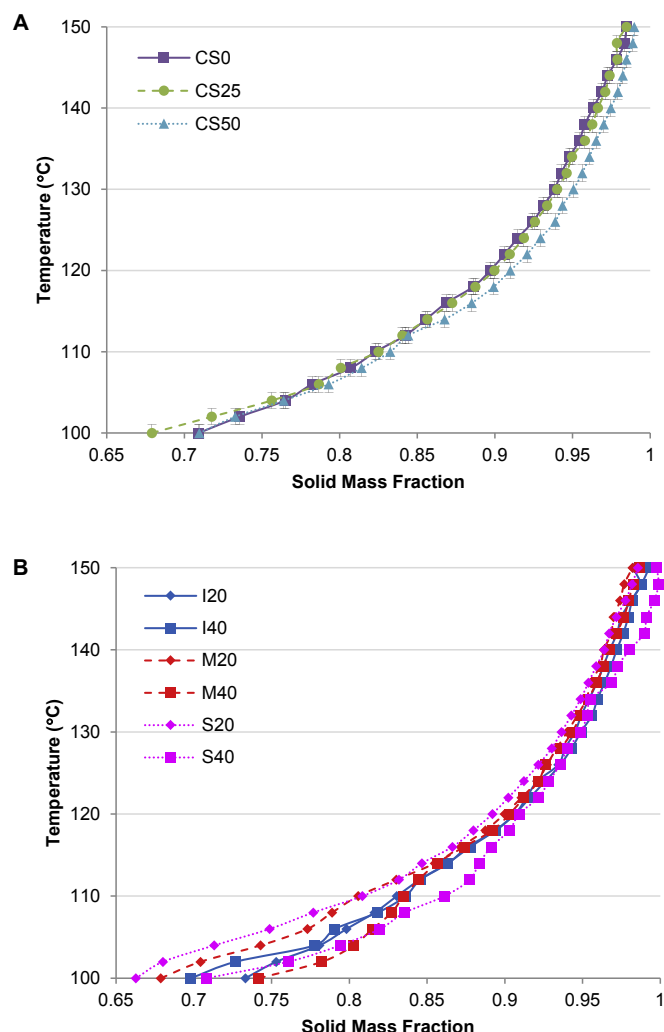
Molar mass, measured  $T_g$  onset, midpoint, and endpoint, and data  $\Delta c_p$  values for carbohydrate ingredients, and literature values for water.

Ingredient	Molar Mass (g/mol)	$T_g$ onset ( $^\circ\text{C}$ )	$T_g$ midpoint ( $^\circ\text{C}$ )	$T_g$ endpoint ( $^\circ\text{C}$ )	$\Delta c_p$ (J/g $^\circ\text{C}$ )
C&H cane sucrose	342.3	66.9	70.4	73.7	0.73
Corn syrup solids	420.1 <sup>a</sup>	57.1	59.0	60.9	0.76
Isomalt	344.3	38.7	43.2	47.3	0.96
Maltitol	344.3	35.9	40.0	43.9	0.74
Sorbitol	182.2	-7.9	-4.6	-1.9	1.16
Water	18.0		-137.2 <sup>b</sup>		1.94 <sup>b</sup>

<sup>a</sup> Average molar mass estimated from manufacturer composition specifications.

<sup>b</sup> Literature values from Katkov and Levine (2004).





**Fig. 1.** Boiling point elevation curves representing the average relationship between the temperature to which the mixture had been cooked and the solids mass fraction of the mixture, aggregated for samples with like corn syrup solids composition (A) and sugar alcohol composition (B). Formula code names are defined in Table 1.

### 3.2. Boiling point elevation curves

Fig. 1A shows that boiling point elevation in the model confectionary systems studied was inversely related to corn syrup concentration. Differences between CS0 and CS25 formulas were minimal, but moisture content of CS0 formulas exceeded that of CS50 formulas by an average of 1.1% (wet basis) at a given temperature. This relationship is intuitive, as boiling point is a colligative property, and higher usage levels of corn syrup solids, which have a higher average molecular weight than the other carbohydrates studied, would result in fewer total moles of solute and less elevation of the boiling point. This trend also agrees with previously published comparisons of boiling point elevation curves for corn syrup and sucrose solutions (Hartel et al., 2011).

When average boiling point elevation curves for each sugar alcohol treatment (Fig. 1B) were compared, however, consistent trends did not emerge. Because isomalt and maltitol have similar molecular weights to sucrose, while the molecular weight of sorbitol is approximately half that of sucrose, the expectation was that samples containing sorbitol would exhibit greater boiling point elevation than blends containing isomalt or maltitol, and that the samples composed of 40% sorbitol would exhibit greater

boiling point elevation than the samples containing only 20% sorbitol. Instead, while the S20 samples did exhibit the greatest degree of average boiling point elevation, the averaged S40 samples exhibited a relatively low degree of boiling point elevation. While this result is counterintuitive, it is important to note that no clear separation of boiling point elevation curves by sugar alcohol treatment is observed. Some spread can be seen at lower temperatures, but curves tended to converge after 120 °C. Between temperatures of 120 °C and 150 °C, the maximum difference in average moisture content between samples of different sugar alcohol treatments was 1.7% (wet basis). While the variation in boiling point observed between formulas was relatively small, a 1% difference in moisture content can have a significant impact on  $T_g$ , as well as other material properties. Further study and isolation of single formula variables should be conducted to confirm and explain trends in boiling point elevation of model confectionary systems.

### 3.3. Moisture content of model confectionary samples

Generation of boiling point elevation (BPE) curves provided a simple means of estimating moisture content, but does not give a direct measurement of sample moisture content. Karl Fischer (KF) titration is generally considered the most accurate method of moisture content determination for low-moisture food materials, due to its relatively low limits of detection, and for carbohydrate materials, which are prone to decomposition during heating, and therefore, prone to systematic error when gravimetric methods are used (Ruiz, 2005). In order to assess the accuracy of the BPE estimation method, KF titration was performed and measured moisture content was compared to estimated values for a representative subset of samples, I40-CS25, M40-CS25, and S40-CS25 (Table 3).

In general, BPE-estimated and KF-measured moisture content values fell within 1% moisture content, wet basis (wb), of each other for samples cooked to 120 or 130 °C, but values diverged for samples cooked to 140 or 150 °C. For all samples, KF-measured moisture content values were higher than BPE-estimated values for the two higher final cook temperatures. In I40-CS25 and S40-CS25 samples cooked to 150 °C, the difference between KF-measured and BPE-estimated moisture content values was close to 3%, wb. Since the difference in moisture content values between the methods increases with cook temperature, it is probable that the difference is due to non-water volatile losses during the heating of samples in the BPE method. It is worth noting that while consistent

**Table 3**

Estimated moisture content from an average of two boiling point elevation (BPE) curves and average measured moisture content from 2 Karl Fischer (KF) measurements on each of two batches of I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150 °C. Moisture content values are reported in percent wet basis (% wb). Reported standard deviation values (SD) reflect the variation in boiling point elevation curves and variation between batch averages of Karl Fischer measurements. Formula code names are defined in Table 1.

Final Cook Temperature (°C)		I40-CS25		M40-CS25		S40-CS25	
		BPE % wb	KF % wb	BPE % wb	KF % wb	BPE % wb	KF % wb
120	Mean	9.87	9.00	10.60	9.07	10.04	9.71
	SD	0.23	0.57	1.13	0.63	2.57	0.05
130	Mean	5.32	6.19	6.50	6.01	6.55	6.49
	SD	0.17	0.65	0.51	0.47	2.15	0.31
140	Mean	2.71	4.49	3.73	3.88	2.98	4.30
	SD	0.41	0.01	0.87	0.58	2.87	0.30
150	Mean	0.61	3.29	1.68	2.93	0.47	3.42
	SD	0.04	0.17	0.91	0.60	0.67	0.08

differences are found between moisture content values determined by the KF and BPE methods, only minor differences are found for KF-measured moisture content values between samples. KF measured moisture content values for S40-CS25 samples exceed values for I40-CS25 and M40-CS25 samples by an average of 0.67, 0.39, 0.12, and 0.31% wb, when heated to 120, 130, 140, and 150 °C, respectively.

### 3.4. Glass transition properties of model confectionary systems

Representative DSC thermograms for I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150 °C are presented in Fig. 2. The small endothermic peak in Fig. 2A can be attributed to enthalpic relaxation that occurred in the I40-CS25 sample cooked to 150 °C between sample production and DSC analysis. Comparison between plots shows a decrease in  $T_g$  from I40-CS25 to M40-CS25 to S40-CS25, corresponding to the decrease in  $T_g$  from isomalt to maltitol to sorbitol (Table 2). Comparison of thermograms within each plot shows a consistent increase in  $T_g$  with increasing cook temperature, which is intuitive due to the decrease in moisture content with increasing cook temperature. These effects of cook temperature and sugar alcohol treatment were maintained across all samples; however, corn syrup solids content had an inconsistent effect on  $T_g$ . DSC data for all samples can be found in the Appendix (Table A.1).

### 3.5. Assessment of fit of Couchman-Karasz equations to experimental $T_{gm}$

Experimental  $T_{gm}$  data for I40-CS25, M40-CS25, and S40-CS25 samples are plotted alongside  $T_{CK}$  values calculated via the original and modified Couchman-Karasz equations at a range of solids weight fraction values (Fig. 3). Comparison of  $T_{CK}$  for both versions of the Couchman-Karasz equation shows that the models are nearly identical when the solids weight fraction approaches 1, but diverge as the solids weight fraction decreases. This visual juxtaposition of experimental data with  $T_{CK}$  from the original and modified Couchman-Karasz equations, Equation (2) and Equation (3), respectively, allows for a comparative assessment of fit for both models. The modified  $T_{CK}$  overestimates  $T_{gm}$  for all three samples, while the original  $T_{CK}$  overestimates  $T_{gm}$  for S40-CS25 samples, but comes close to  $T_{gm}$  for I40-CS25 and M40-CS25 samples ( $\pm 5$  °C). Table 4 provides numerical values for  $T_{gm}$  and the difference between  $T_{gm}$  and  $T_{CK}$ , calculated using the original and modified Couchman-Karasz equations. When the original Couchman-Karasz equation was used, mean values of  $T_{gm}$  for I40-CS25 and M40-CS25 fell within 5.5 °C of the calculated  $T_{CK}$  values. However, though the original Couchman-Karasz comes close to  $T_{gm}$  for I40-CS25 and M40-CS25 samples, it overestimated mean values of  $T_{gm}$  for S40-CS25 samples by 10–12 °C. Further, though the original Couchman-Karasz equation  $T_{CK}$  is within 5.5 °C of  $T_{gm}$  for the range

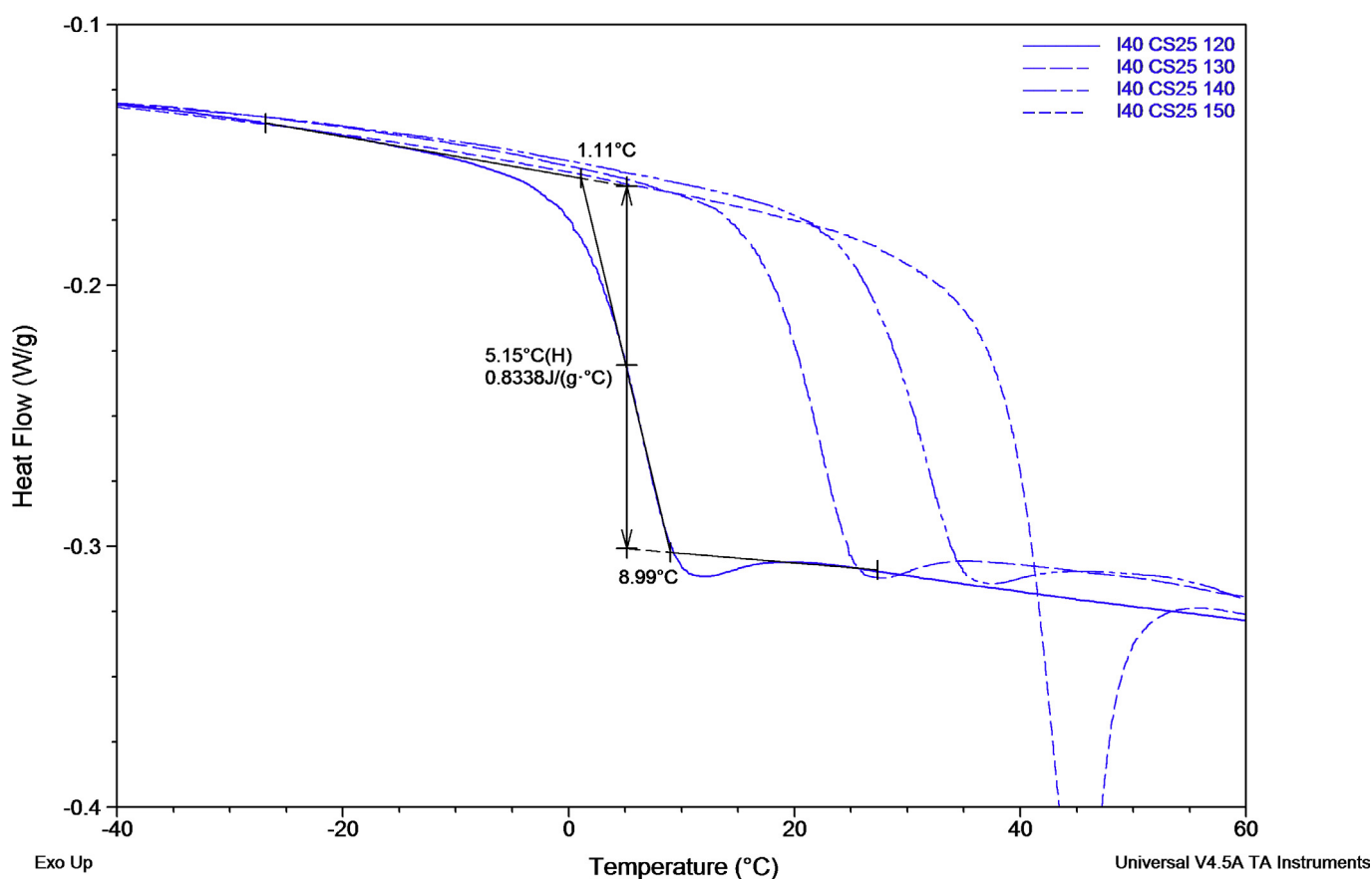


Fig. 2. Differential scanning calorimetry (DSC) thermograms showing the glass transition region for I40-CS25 (A), M40-CS25 (B), and S40-CS25 (C) samples heated to 120, 130, 140, and 150 °C. A demonstration of the method of  $T_g$  analysis is given in Fig. 1A. Samples identities are indicated in the legends by the formula name followed by the temperature to which the sample was cooked in °C. Formula code names are defined in Table 1.

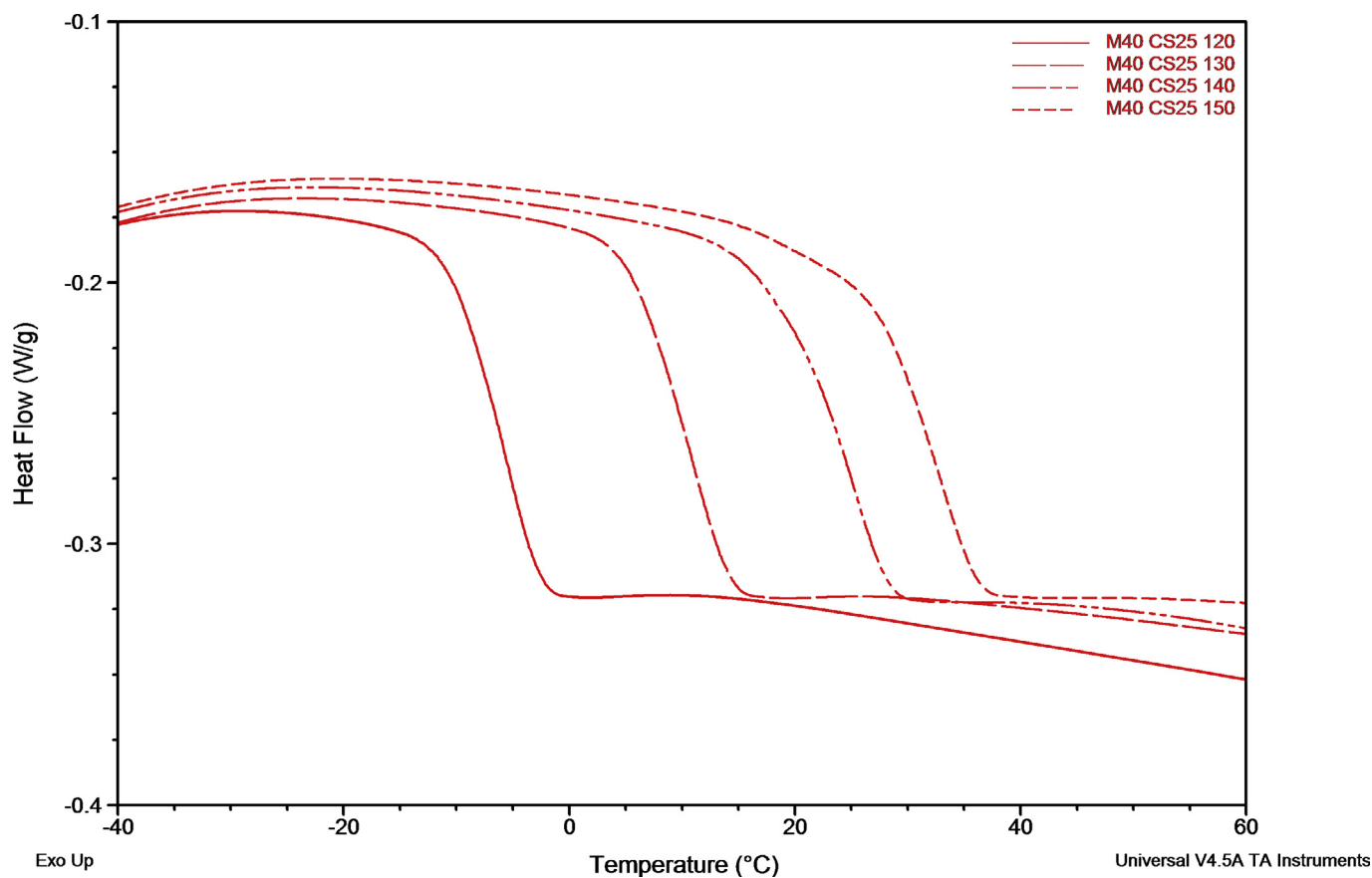


Fig. 2. (continued).

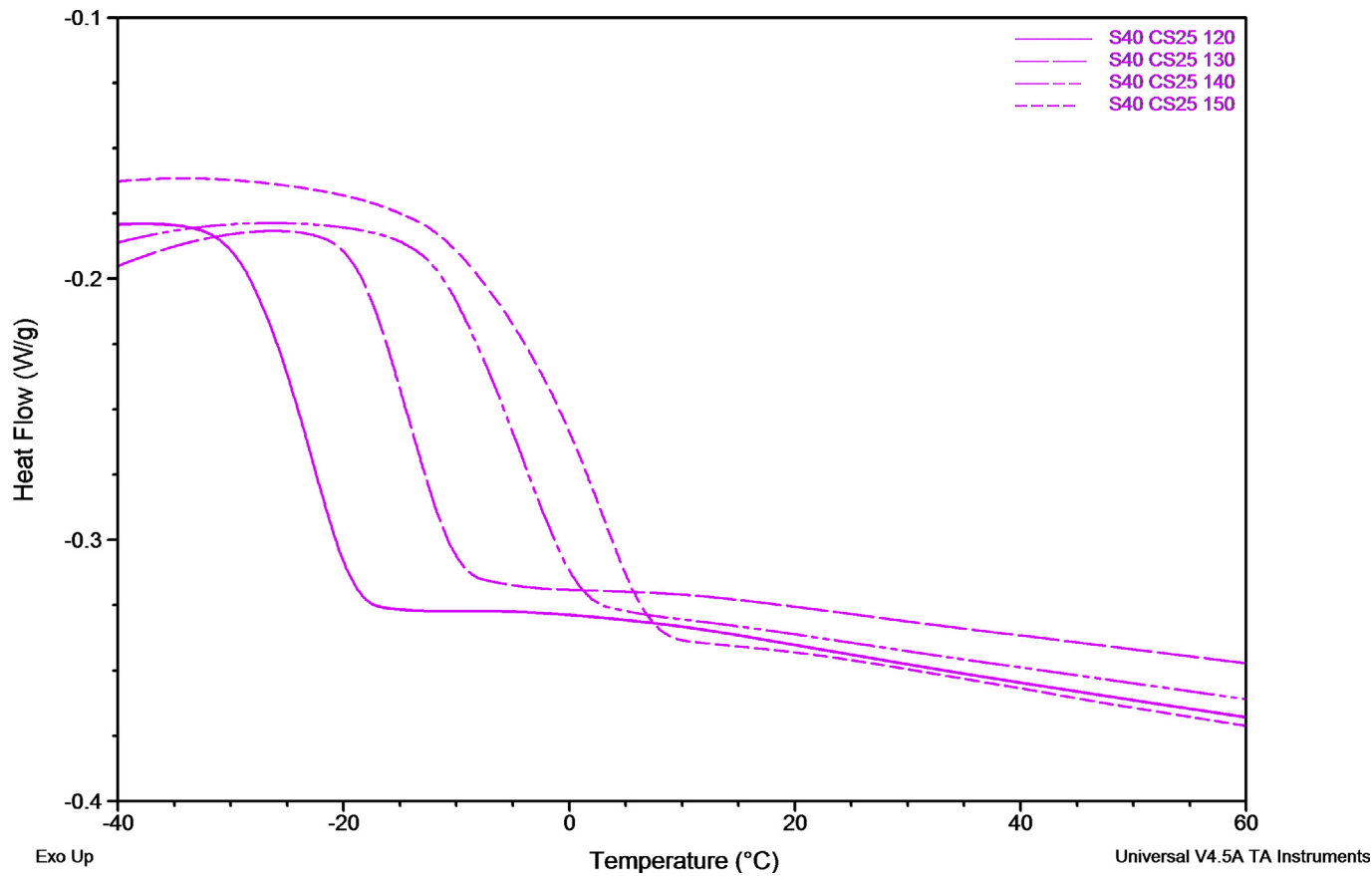
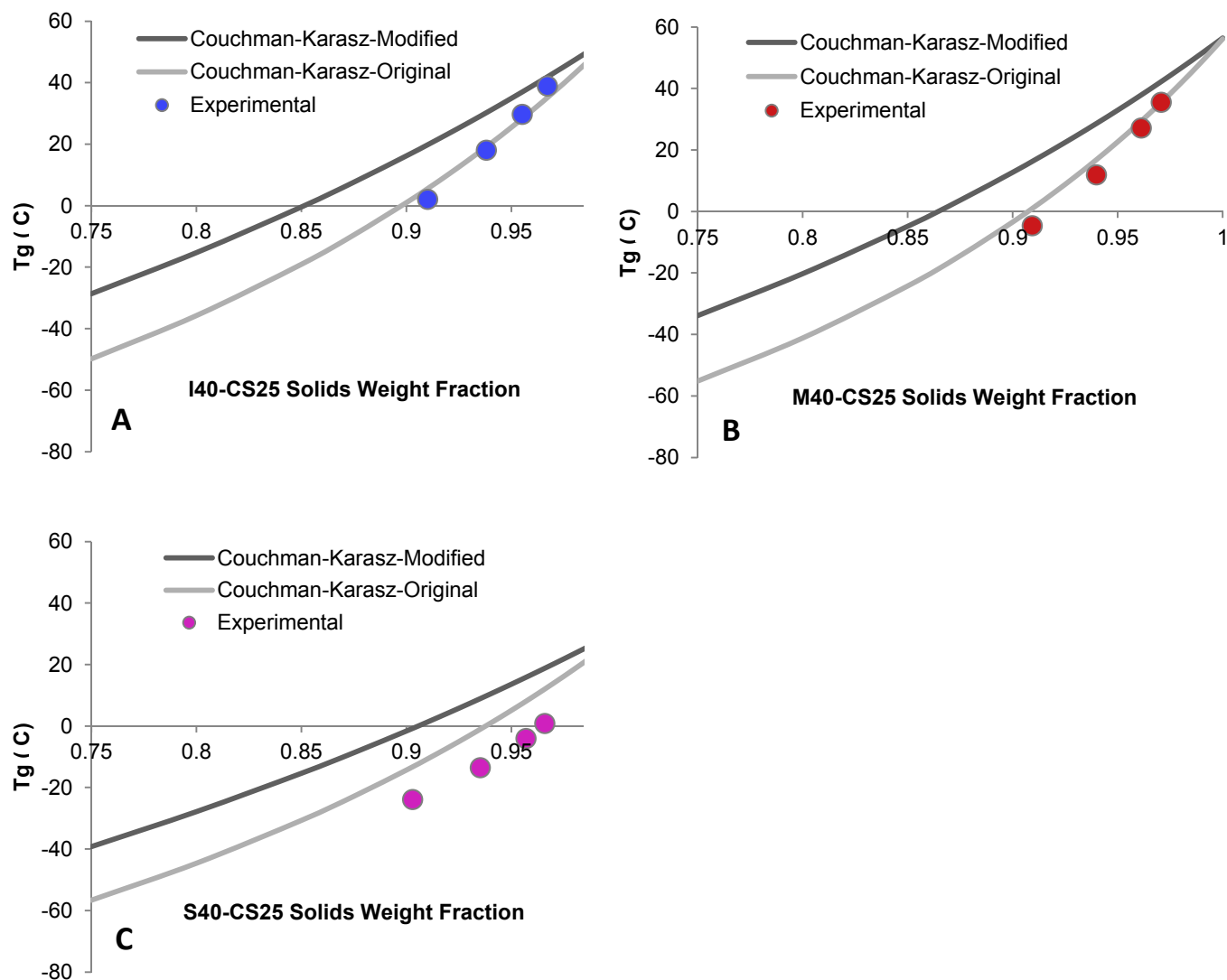


Fig. 2. (continued).



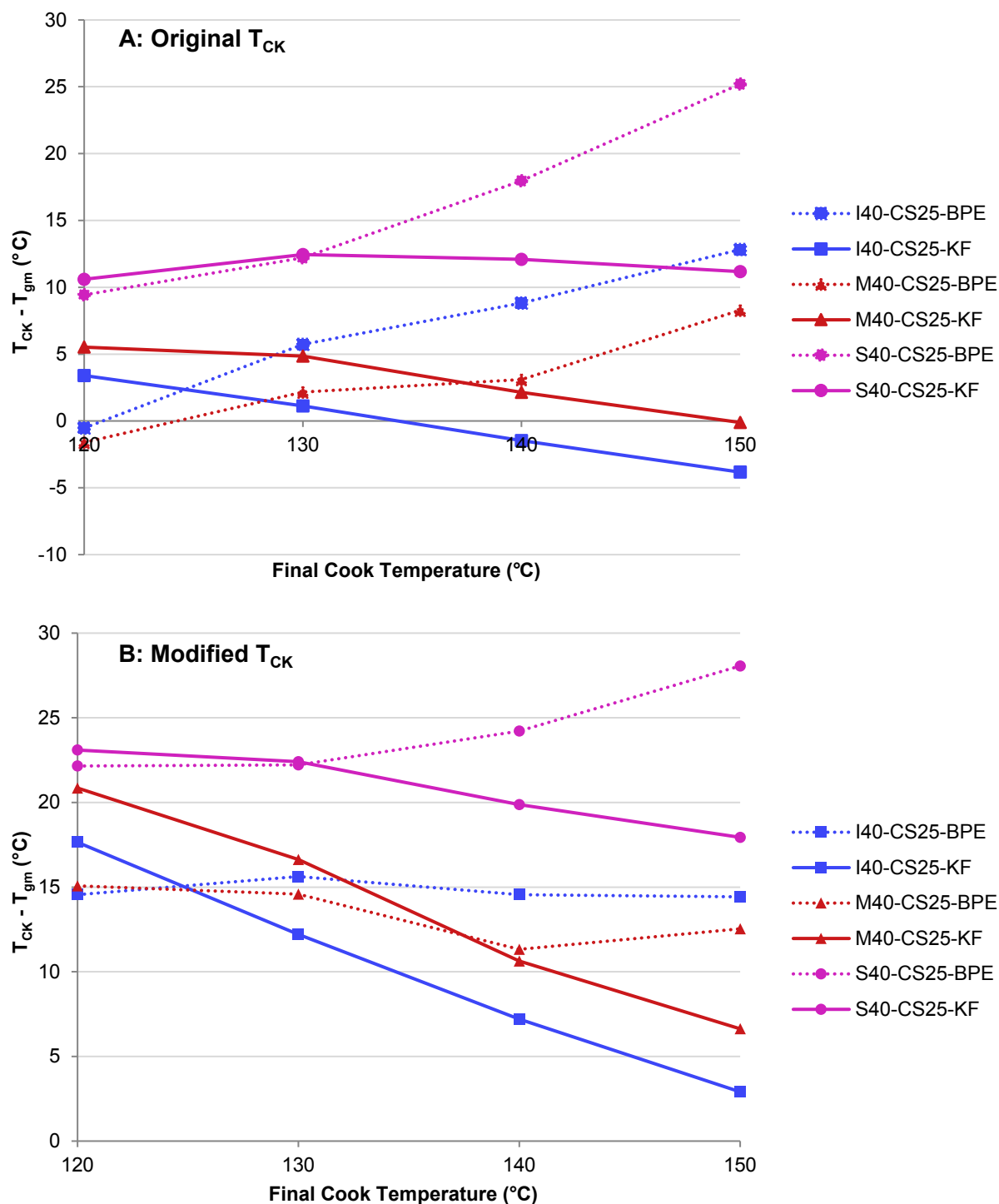
**Fig. 3.** Average experimentally measured  $T_{gm}$  values plotted against average solids weight fraction, calculated as the total weight minus the weight fraction of water measured via Karl Fischer titration, across both batches for I40-CS25 (A), M40-CS25 (B), and S40-CS25 (C) samples. Experimental data is plotted with predicted  $T_{CK}$  curves obtained using both the original and modified Couchman-Karasz equations for the given formulas and at solid weight fraction values between 0.75 and 1.0. Formula code names are defined in Table 1.

**Table 4**  
Mean experimental  $T_{gm}$  midpoint values, followed by bracketed standard deviation (SD) values, and original and modified  $\Delta T_{gm}^{CK}$  values, calculated using Karl Fischer mean moisture content values, for I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150 °C.  $T_{gm}$  values presented are averages of two batches for each model confectionary formula, but statistical comparisons were conducted within batch only.\*† Formula code names are defined in Table 1.

Formula	Final Cook Temperature (°C)	Experimental $T_g$	Comparison to $T_{CK}$	
		$T_{gm}$ (SD) (°C)	Original $T_{CK} - T_{gm}$ (°C)	Modified $T_{CK} - T_{gm}$ (°C)
I40-CS25	120	2.12 (3.98)	3.41†	17.67*†
	130	18.04 (3.87)	1.15	12.21*†
	140	29.76 (0.47)	-1.47*†	7.21*†
	150	38.96 (0.86)	-3.83*†	2.92†
M40-CS25	120	-4.59 (2.24)	5.54*†	20.85*†
	130	11.97 (2.36)	4.87*†	16.63*†
	140	27.24 (4.46)	2.17†	10.65*†
	150	35.57 (5.01)	-0.08*†	6.67*†
S40-CS25	120	-23.88 (0.21)	10.60*†	23.10*†
	130	-13.50 (1.05)	12.45*†	22.41*†
	140	-4.00 (1.67)	12.09*†	19.86*†
	150	0.83 (0.67)	11.17*†	17.95*†

\*Batch 1  $T_{gm}$  is significantly different from  $T_{CK}$  at an  $\alpha = 0.05$  significance level; †Batch 2  $T_{gm}$  is significantly different from  $T_{CK}$  at an  $\alpha = 0.05$  significance level.





**Fig. 4.** Difference between calculated  $T_{CK}$  and experimentally measured  $T_{gm}$ , by both original (A) and the modified (B) Couchman-Karas equation and using moisture content values estimated from boiling point elevation (BPE) curves and measured via Karl Fischer (KF) titration for I40-CS25, M40-CS25, and S40-CS25 samples plotted by final cook temperature. Formula code names are defined in Table 1.

of solid mass fraction values studied, it is evident that the measured  $T_{gm}$  decreases with increasing moisture content at a greater rate than predicted by either equation.

Fig. 4 provides a visual representation of this trend. We originally hypothesized that  $\Delta T_{gm}^{CK}$  would increase with increasing cook temperature, as heat-induced decomposition of carbohydrates has

been shown to result in a lowering of the average molecular weight and  $T_g$  of the sample (Jiang et al., 2008). However, as Fig. 4 shows, the opposite effect of cook temperature on  $\Delta T_{gm}^{CK}$  is observed: the degree to which  $T_{CK}$  overestimates  $T_{gm}$  decreases with increasing cook temperature. While this result was at first surprising, it agrees with past research which found that the plasticizing effect of water

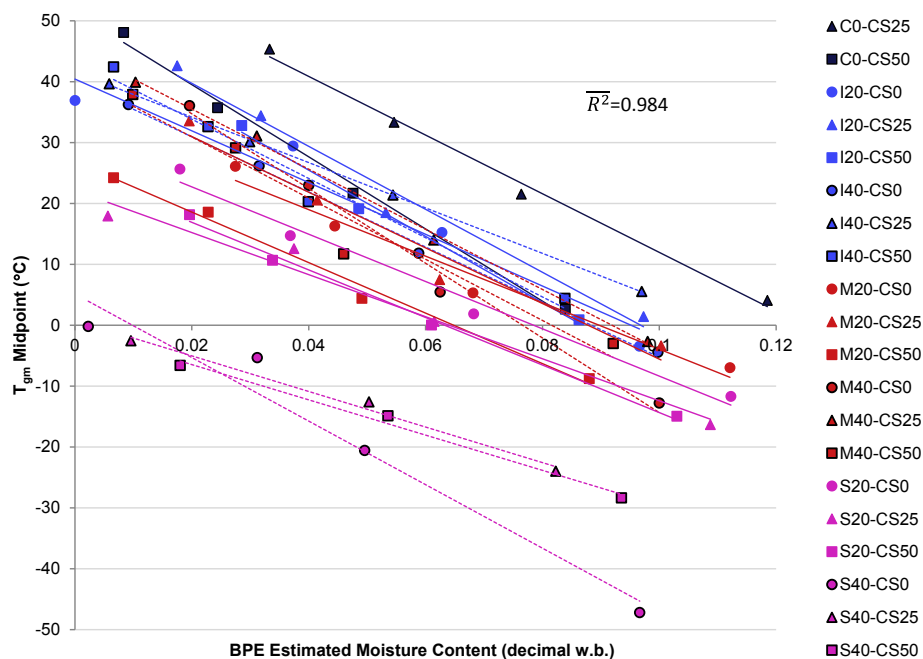


Fig. 5. Plot of average measured  $T_{gm}$  midpoint values versus boiling point elevation (BPE) estimated moisture content, wet basis (wb), for all samples. The average  $R^2$  for the linear trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 1.

is not directly proportional to moisture content. Instead, the degree of plasticization due to water increases more rapidly at higher water concentrations due to an increase in free volume and mobility in the system (Abiad et al., 2009; Lechuga-Ballesteros

et al., 2002). It can be concluded, then, that the effect of decomposition due to cooking has a small effect on  $T_{gm}$  relative to the plasticizing effect of water in these systems.

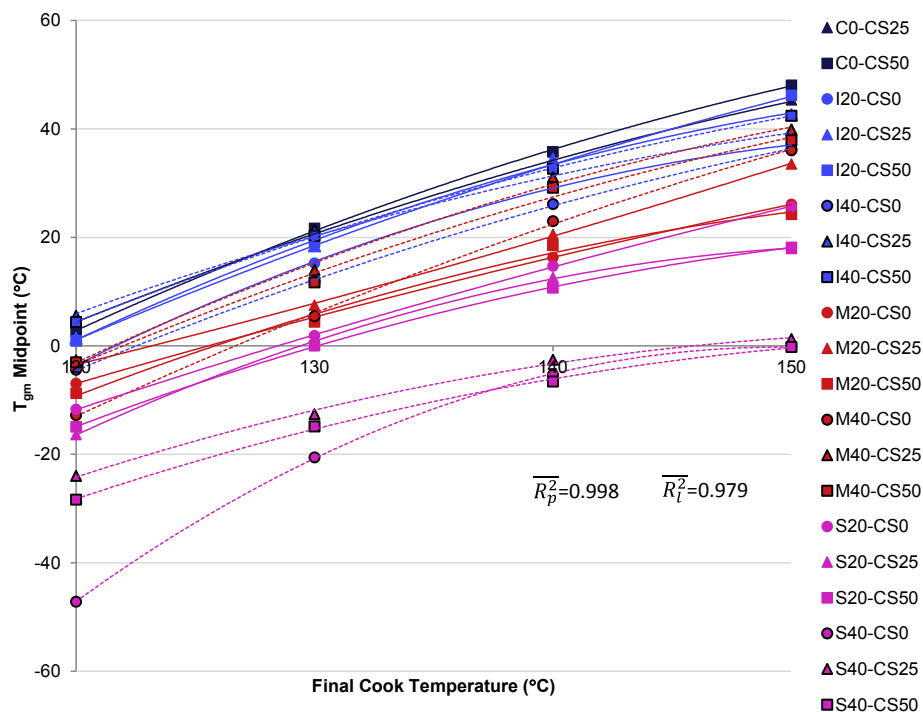


Fig. 6. Plot of average measured  $T_{gm}$  midpoint values versus final cook temperature for all samples. Polynomial trendlines are used in this figure; an alternate figure with linear trendlines is available in Figure C.1. The average  $R^2$  for the polynomial ( $R_p^2$ ) and linear ( $R_l^2$ ) trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 1.

### 3.6. Development of empirical corrections to Couchman-Karaszc equation

The modified Couchman-Karaszc equation (Equation (3)), the most commonly used form of the equation (Katkov and Levine, 2004), failed to reliably predict  $T_{gm}$  of the model confectionary systems studied. The original Couchman-Karaszc equation (Equation (2)) came close for some, but not all, samples, and showed a systematic shift from under to overestimation of  $T_{gm}$  as moisture content increased. In order to develop an empirical model that can predict  $T_{gm}$  with greater reliability for this sample set, experimental  $T_{gm}$  values were compared to both estimated sample moisture content (Fig. 5) and final cook temperature (Fig. 6).

Fig. 5 shows that  $T_{gm}$  decreases linearly with increasing moisture content ( $R^2 = 0.984$ ) at a fairly consistent rate of  $4.5 \pm 0.9$  °C for every 1.0% change in moisture content (wb). The linear equations and  $R^2$  values for each individual formula are given in Table B.1. Because the slope of the relationship between  $T_{gm}$  and moisture content appears to be relatively independent of formula, it is reasonable to develop a standardized empirical model for the estimation of  $T_{gm}$  by moisture content. While the rate of change in  $T_{gm}$  with moisture content was formula-independent, the absolute  $T_{gm}$  at a given moisture content was strongly dependent on formula. It was therefore logical to develop the empirical model as a correction to the Couchman-Karaszc equation, using the calculated  $T_{CK}$  value for solids and applying the empirical relationship between  $T_{gm}$  and moisture to adjust for changes in moisture content. The resultant equation (Equation (6)), in which  $x$  is equal to the % moisture (wb) and  $T_{CKsolids}$  is the calculated  $T_g$  for only the non-water components of the sample, can be used to calculate a new  $T_{CK}^{MC}$ . The superscript MC refers to the input variable, Moisture Content, in this empirical equation. Since the original and modified versions of the Couchman-Karaszc equation give nearly identical results when moisture content approaches 0, the more commonly-used and mathematically simpler modified version was used to calculate  $T_{CKsolids}$ .

$$T_{CK}^{MC} = T_{CKsolids} - 4.48x - 19 \quad (6)$$

Comparison of  $T_{CK}^{MC}$  to measured  $T_{gm}$  values showed that the use of the empirical correction improved the overall accuracy of the Couchman-Karaszc equation, from an average  $\Delta T_{gm}^{CK}$  of 20.1 °C and 11.3 °C for the modified and original equations, respectively, to an average  $\Delta T_{gm}^{CK^{MC}}$  of 5.5 °C across all samples. This improvement was promising, but calculation of  $T_{CK}^{MC}$  still requires measurement of moisture content, which can be challenging for model confectionary systems or other carbohydrate-based systems. To address this challenge, a second approach to the development of an empirical correction was taken, this time using final cook temperature instead of moisture content as the empirical input variable. As Fig. 6 shows, the absolute  $T_{gm}$  for a given cook temperature is again dependent on formula, while the increase in  $T_{gm}$  with increasing cook temperature is fairly consistent across samples. However, while the relationship between  $T_{gm}$  and cook temperature is consistent, it does not appear to be linear. The non-linear nature of the relationship between cook temperature and  $T_{gm}$  makes intuitive sense; reduction in moisture content with increasing cook temperature is the driving

force for the increase in  $T_{gm}$ , and moisture loss with cook temperature is likewise non-linear.

A second order polynomial equation was fit to the data and described the relationship between  $T_{gm}$  and cook temperature very well, with an average  $R^2$  of 0.998. However, there was a considerable range in coefficients of the polynomial equation between samples. For this reason, a linear equation was also generated for the data (Figure C.1). The linear models did not show as good a fit to the experimental data, but the average  $R^2$  was still quite high (0.979) and the slope of the linear trendline was more consistent across samples ( $1.28 \pm 0.21$  °C). Polynomial and linear equations and  $R^2$  values for individual formulas are given in Table B.2.

The averaged polynomial and linear relationship between cook temperature and  $T_{gm}$  were used to construct Equations (7) and (8), respectively, in which  $T_{CKsolids}$  is again the calculated  $T_g$  for non-water components of the sample formula, and  $x$  is now equal to the temperature (T), in °C, above 120 °C to which the sample has been heated ( $x = T - 120$  °C).

$$T_{CK}^{CTp} = T_{CKsolids} - 0.0175x^2 + 1.81x - 62 \quad (7)$$

$$T_{CK}^{CTl} = T_{CKsolids} + 1.28x - 60 \quad (8)$$

The superscript CT in Equations (7) and (8) refers to the new input variable, Cook Temperature, and the subscripts on CT refer to the use of either a polynomial (p) or linear (l) model. Applying these empirical corrections results in a reduction of  $\Delta T_{gm}^{CK}$ ; the average  $\Delta T_{gm}^{CT}$  when Equations (7) or (8) is used is 5.24 and 5.33 °C, respectively.

## 4. Conclusions

Experimental  $T_{gm}$  values aligned more closely to the original Couchman-Karaszc model than to the modified Couchman-Karaszc model for the model confectionary systems studied, though both models overestimated  $T_{gm}$  in sorbitol-containing samples and at higher moisture content ranges. The empirical corrections developed herein provided enhanced prediction of model confectionary system  $T_g$  relative to the modified and original Couchman-Karaszc equations alone. To our knowledge, this study includes the first reported empirical model for the prediction of  $T_g$  based on a processing parameter, cook temperature. The average increase in  $T_{gm}$  with decreasing moisture content or increasing cook temperature, which were found to be fairly uniform across the confectionary model systems, could provide a useful “rule of thumb” in the planning of changes to formulation or processing parameters. The empirical models presented are meant to supplement, not replace the Couchman-Karaszc equation, and are limited by the finite number of temperatures (4), ingredients (5), ingredients in a single mixture (3), batch size (1), and cooking protocols (1) used to construct them. This applicability of the developed empirical models to systems beyond those described in this study is unknown; however, the approach utilized could easily be extended to other types of food systems.

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## Appendix A. Model confectionary systems differential scanning calorimetry data

**Table A.1**

Differential scanning calorimetry data, including glass transition ( $T_g$ ) onset, midpoint, and endpoint values, and change in specific heat capacity at the glass transition ( $\Delta c_p$ ) from the first batch of each model confectionary system cooked to 120, 130, 140, and 150 °C. Two replicates were conducted for each sample at each final cook temperature. Formula code names are defined in Table 1.

Formula	Final Cook Temperature (°C)	Replicate	$T_g$ onset (°C)	$T_g$ midpoint (°C)	$T_g$ endpoint (°C)	$\Delta c_p$ (J/g/°C)
C0-CS25	120	1	−0.61	3.74	7.93	0.8144
		2	−0.20	4.44	8.91	0.8305
	130	1	16.90	21.84	26.59	0.8043
		2	16.97	21.23	25.48	0.7991
	140	1	29.42	33.34	36.90	0.7975
		2	29.66	33.32	36.97	0.8169
	150	1	43.09	45.48	47.76	0.7698
		2	42.86	45.25	47.58	0.7209
C0-CS50	120	1	−2.60	2.68	7.78	0.7825
		2	−2.79	2.66	7.73	0.8040
	130	1	17.05	21.75	26.36	0.7665
		2	16.18	21.58	26.68	0.8002
	140	1	31.38	35.58	39.49	0.8084
		2	32.00	35.91	39.60	0.8056
	150	1	45.59	48.04	50.50	0.7655
		2	45.58	48.10	50.53	0.7585
I20-CS0	120	1	−7.59	−3.38	0.64	0.8651
		2	−7.48	−3.52	0.31	0.8553
	130	1	10.61	15.34	19.78	0.8858
		2	10.50	15.14	19.54	0.8988
	140	1	24.83	29.29	33.43	0.8596
		2	25.16	29.55	33.77	0.8376
	150	1	33.94	36.57	39.14	0.7243
		2	34.40	37.30	40.01	0.7954
I20-CS25	120	1	−2.59	1.51	5.45	0.8190
		2	−3.38	1.35	5.77	0.8402
	130	1	13.81	18.39	22.75	0.7780
		2	13.64	18.59	23.16	0.7881
	140	1	30.32	35.18	39.70	0.7939
		2	27.98	33.66	38.96	0.7995
	150	1	39.09	42.12	44.90	0.7499
		2	39.93	43.12	45.96	0.7947
I20-CS50	120	1	−5.12	−0.86	3.32	0.7929
		2	−1.72	2.65	7.01	0.8118
	130	1	14.96	19.34	23.67	0.7861
		2	14.42	18.93	23.35	0.8249
	140	1	28.58	32.88	36.93	0.8495
		2	27.86	32.75	37.31	0.8697
	150	1	43.31	45.58	47.90	0.7759
		2	44.35	46.79	49.13	0.7821
I40-CS0	120	1	−7.89	−4.19	−0.62	0.9398
		2	−8.72	−4.62	−0.83	0.9559
	130	1	6.88	11.77	16.32	0.9314
		2	7.66	11.93	16.06	0.9379
	140	1	22.01	26.09	30.05	0.7589
		2	21.99	26.23	30.34	0.8942
	150	1	33.32	35.99	38.69	0.9146
		2	33.83	36.50	39.28	0.9193
I40-CS25	120	1	1.29	5.87	10.17	0.8491
		2	0.96	5.23	9.31	0.8756
	130	1	17.16	21.80	26.18	0.8203
		2	16.90	20.95	24.89	0.8092
	140	1	25.35	30.14	34.60	0.8082
		2	25.82	30.18	34.34	0.8031
	150	1	37.42	39.90	42.30	0.7974
		2	37.36	39.44	41.82	0.7839
I40-CS50	120	1	−0.21	4.51	8.96	0.8765
		2	0.05	4.29	8.42	0.8773
	130	1	14.50	19.89	25.06	0.8556
		2	15.95	20.74	25.42	0.8098

Table A.1 (continued)

Formula	Final Cook Temperature (°C)	Replicate	T <sub>g</sub> onset (°C)	T <sub>g</sub> midpoint (°C)	T <sub>g</sub> endpoint (°C)	Δc <sub>p</sub> (J/g/°C)
	140	1	28.77	32.76	36.48	0.8291
		2	28.65	32.51	36.23	0.8830
	150	1	39.68	41.99	44.20	0.8144
		2	40.31	42.84	45.27	0.8067
M20-CS0	120	1	−11.09	−7.14	−3.22	0.8386
		2	−10.93	−6.76	−2.62	0.6997
	130	1	−0.83	5.34	11.00	0.9122
		2	0.27	5.30	10.20	0.7318
	140	1	11.37	16.25	21.04	0.8463
		2	11.75	16.36	20.80	0.7599
	150	1	20.86	25.65	30.42	0.9076
		2	22.08	26.52	30.77	0.7927
M20-CS25	120	1	−8.30	−3.52	0.96	0.7805
		2	−8.13	−3.20	1.57	0.7797
	130	1	2.30	7.21	11.82	0.8324
		2	2.87	7.79	12.34	0.7865
	140	1	15.58	20.53	25.33	0.7700
		2	15.29	20.62	25.67	0.7911
	150	1	31.46	34.32	36.95	1.1960
		2	28.28	32.78	37.17	0.6774
M20-CS50	120	1	−12.87	−8.44	−4.03	0.7818
		2	−13.98	−9.06	−4.28	0.8540
	130	1	−0.55	4.75	9.93	0.7612
		2	−1.53	4.07	9.52	0.8367
	140	1	12.01	18.50	24.74	0.8472
		2	12.96	18.64	24.17	0.7957
	150	1	18.72	24.64	30.38	0.7908
		2	18.66	23.80	28.92	0.7848
M40-CS0	120	1	−16.79	−13.01	−9.35	0.8430
		2	−16.90	−12.57	−8.43	0.8676
	130	1	1.15	5.47	9.60	0.8178
		2	1.82	5.46	9.11	0.7868
	140	1	17.51	22.26	26.92	0.8265
		2	18.44	23.74	28.73	0.7651
	150	1	33.80	36.35	38.78	0.7890
		2	33.06	35.75	38.24	0.7155
M40-CS25	120	1	−7.23	−2.75	1.48	0.8339
		2	−6.44	−2.55	1.27	0.8607
	130	1	8.48	13.62	18.52	0.8514
		2	9.32	14.36	19.20	0.7954
	140	1	26.42	31.00	35.32	0.8302
		2	26.35	31.19	35.59	0.8104
	150	1	37.34	39.95	42.32	0.7516
		2	37.58	39.87	42.08	0.7452
M40-CS50	120	1	−7.93	−3.00	1.75	0.8288
		2	−7.44	−3.03	1.25	0.7754
	130	1	6.37	11.49	16.35	0.7915
		2	7.34	11.95	16.35	0.7536
	140	1	23.35	29.30	35.06	0.7399
		2	23.06	28.99	34.58	0.7631
	150	1	35.01	37.58	40.66	0.6916
		2	34.85	38.21	41.48	0.7283
S20-CS0	120	1	−16.94	−11.81	−6.79	0.7115
		2	−17.04	−11.58	−6.37	0.6120
	130	1	−5.36	1.27	7.62	0.8458
		2	−2.85	2.45	7.69	0.7211
	140	1	9.32	15.03	20.55	0.7445
		2	8.68	14.42	19.96	0.8210
	150	1	19.34	25.34	31.12	0.8413
		2	20.98	25.99	30.84	0.8349
S20-CS25	120	1	−21.46	−16.57	−11.77	0.8013
		2	−20.49	−16.13	−11.84	0.7557
	130	1	−5.48	0.35	6.01	0.7856
		2	−4.42	0.91	6.14	0.7675
	140	1	6.77	12.58	18.27	0.8045
		2	6.40	12.61	18.61	0.8356
	150	1	11.16	17.21	23.12	0.7868
		2	13.12	18.68	24.14	0.7228
S20-CS50	120	1	−21.16	−15.67	−10.20	0.7234

(continued on next page)



**Table A.1** (continued)

Formula	Final Cook Temperature (°C)	Replicate	T <sub>g</sub> onset (°C)	T <sub>g</sub> midpoint (°C)	T <sub>g</sub> endpoint (°C)	Δc <sub>p</sub> (J/g/°C)
	130	2	−20.14	−14.23	−8.50	0.7852
		1	−6.92	−0.05	6.60	0.8030
	140	2	−6.46	0.11	6.30	0.7998
		1	3.64	9.03	14.77	1.3990
	150	2	4.73	12.32	19.69	0.7945
		1	10.08	17.63	24.82	0.7732
S40-CS0	120	2	11.15	18.73	26.19	0.7752
		1	−51.82	−48.03	−44.48	0.5313
	130	2	−50.57	−46.33	−42.33	0.5334
		1	−36.74	−22.60	−9.21	0.7761
	140	2	−27.24	−18.54	−10.40	0.8218
		1	−11.56	−5.26	0.79	0.9048
	150	2	−12.99	−5.39	1.98	0.9190
		1	−8.92	−0.27	7.78	0.9155
		2	−7.38	−0.09	6.80	0.7897
		1	−29.29	−23.73	−18.40	0.9246
S40-CS25	120	2	−29.75	−24.18	−18.82	0.9112
		1	−18.57	−12.60	−6.92	0.9082
	130	2	−18.46	−12.58	−7.01	0.8960
		1	−9.70	−2.69	3.91	0.9257
	140	2	−9.58	−2.43	4.35	0.9173
		1	−6.39	1.33	8.66	0.9155
	150	2	−6.21	1.21	8.33	0.9028
		1	−35.15	−29.11	−23.31	0.9371
	120	2	−33.53	−27.63	−21.95	0.9017
		1	−20.86	−14.85	−9.05	0.8843
S40-CS50	130	2	−20.97	−14.88	−9.01	0.9114
		1	−13.06	−6.67	−0.32	0.8886
	140	2	−13.89	−6.49	0.59	0.9147
		1	−8.39	−0.31	7.34	0.9306
	150	2	−8.66	−0.11	7.82	0.8818

## Appendix B. Empirical linear and polynomial equation coefficients and R<sup>2</sup> values

**Table B.1**

Linear equation coefficients, where  $y = mx + b$ , and R<sup>2</sup> values, describing the relationship between moisture content (x) and T<sub>gm</sub> (y) and corresponding to Fig. 5, for each individual sample. Formula code names are defined in Table 1.

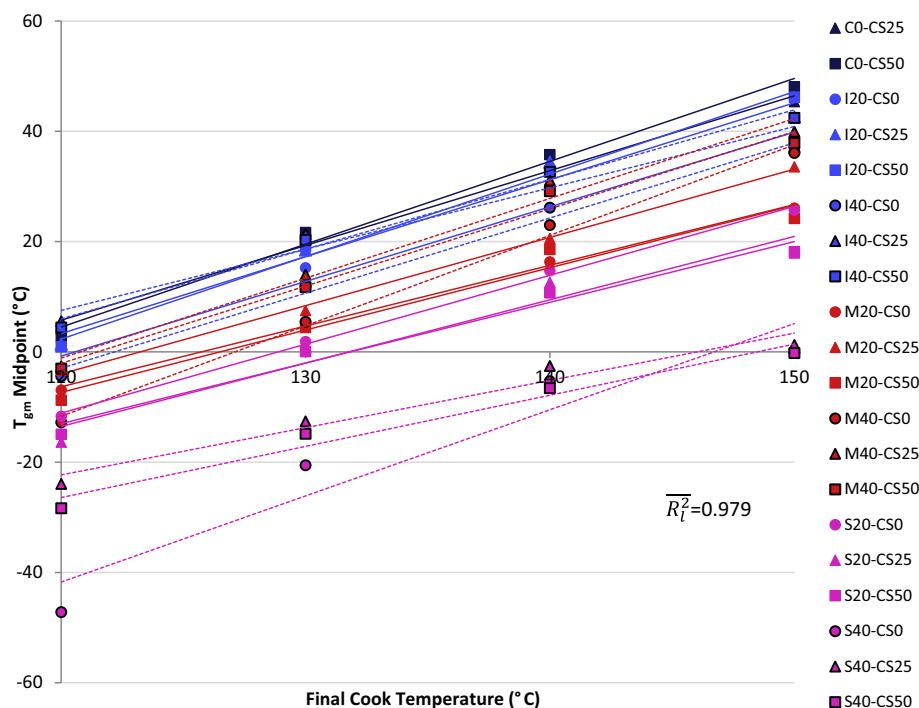
Formula	m	b	R <sup>2</sup>
C0-CS25	−4.82	60.1	0.993
C0-CS50	−5.93	51.4	0.994
I20-CS0	−4.25	40.4	0.952
I20-CS25	−5.17	50.1	0.977
I20-CS50	−5.44	47.2	0.992
I40-CS0	−4.53	40.0	0.997
I40-CS25	−3.73	41.6	1.00
I40-CS50	−4.87	43.6	0.973
M20-CS0	−3.82	34.3	0.971
M20-CS25	−4.57	40.1	0.963
M20-CS50	−4.15	26.9	0.990
M40-CS0	−6.13	47.0	0.990
M40-CS25	−4.94	45.4	0.998
M40-CS50	−5.02	41.0	0.949
S20-CS0	−3.89	30.5	0.983
S20-CS25	−3.45	22.1	0.975
S20-CS50	−3.91	24.7	0.995
S40-CS0	−5.22	5.13	0.959
S40-CS25	−2.92	0.808	0.989
S40-CS50	−2.89	−0.678	0.989

**Table B.2**

Polynomial equation coefficients, where  $y = ax^2 + bx + c$ , linear equation coefficients, where  $y = mx + b$ , and R<sup>2</sup> values, describing the relationship between cook temperature minus 120 °C (x) and T<sub>gm</sub> (y) and corresponding to Fig. 6, for each individual sample. Formula code names are defined in Table 1.

Formula	Polynomial Model				Linear Model		
	a	b	c	R <sup>2</sup>	m	b	R <sup>2</sup>
C0-CS25	−0.0135	1.76	4.38	0.998	1.36	5.74	0.990
C0-CS50	−0.0167	2.00	2.83	1.00	1.50	4.50	0.990
I20-CS0	−0.0279	2.19	−3.56	1.00	1.35	−0.764	0.967
I20-CS25	−0.0222	2.06	1.10	0.998	1.40	3.32	0.978
I20-CS50	−0.0122	1.86	1.11	0.999	1.50	2.33	0.994
I40-CS0	−0.0154	1.83	−4.52	1.00	1.36	−2.98	0.990
I40-CS25	−0.0158	1.59	5.94	0.995	1.11	7.52	0.979
I40-CS50	−0.0153	1.72	4.45	1.00	1.26	5.99	0.988
M20-CS0	−0.00620	1.29	−6.95	1.00	1.10	−6.32	0.997
M20-CS25	0.00530	1.08	−3.48	1.00	1.24	−4.00	0.998
M20-CS50	−0.0188	1.69	−9.23	0.993	1.13	−7.35	0.972
M40-CS0	−0.0130	2.03	−13.0	1.00	1.64	−11.7	0.995
M40-CS25	−0.0196	2.03	−3.09	0.996	1.45	−1.13	0.982
M40-CS50	−0.0150	1.85	−3.58	0.994	1.40	−2.09	0.985
S20-CS0	−0.0065	1.45	−11.8	1.00	1.25	−11.1	0.998
S20-CS25	−0.0291	2.02	−16.4	1.00	1.15	−13.5	0.951
S20-CS50	−0.0187	1.66	−14.9	1.00	1.10	−13.0	0.977
S40-CS0	−0.0537	3.17	−47.1	1.00	1.56	−41.8	0.914
S40-CS25	−0.0188	1.42	−24.2	0.997	0.857	−22.3	0.960
S40-CS50	−0.0178	1.46	−28.2	0.999	0.928	−26.4	0.970

### Appendix C. Linear trendlines for $T_{gm}$ vs final cook temperature



**Fig. C.1.** Plot of average measured  $T_{gm}$  midpoint values versus final cook temperature for all samples with linear trendlines. The average  $R^2$  for the linear ( $R^2_i$ ) trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 1.

### References

- Abiad, M.G., Carvajal, M.T., Campanella, O.H., 2009. A review on methods and theories to describe the glass transition phenomenon: applications in food and pharmaceutical products. *Food Eng. Rev.* 1, 105–132. <http://dx.doi.org/10.1007/s12393-009-9009-1>.
- Arvanitoyannis, I., Biliaderis, C.G., 1999. Physical properties of polyol-plasticized edible blends made of methyl cellulose and soluble starch. *Carbohydr. Polym.* 38, 47–58. [http://dx.doi.org/10.1016/S0144-8617\(98\)00087-3](http://dx.doi.org/10.1016/S0144-8617(98)00087-3).
- Arvanitoyannis, I., Blanshard, J.M.V., Ablett, S., Izzard, M.J., Lillford, P.J., 1993. Calorimetric study of the glass transition occurring in fructose solutions. *Carbohydr. Res.* 246, 13–22.
- Cammenga, H.K., Zielasko, B., 1996. Thermal behaviour of isomalt. *Thermochim. Acta* 271, 149–153. [http://dx.doi.org/10.1016/0040-6031\(95\)02560-X](http://dx.doi.org/10.1016/0040-6031(95)02560-X).
- Chaudhary, D.S., Adhikari, B.P., Kasapis, S., 2011. Glass-transition behaviour of plasticized starch biopolymer system - a modified Gordon-Taylor approach. *Food Hydrocoll.* 25, 114–121. <http://dx.doi.org/10.1016/j.foodhyd.2010.06.002>.
- Couchman, P.R., Karasz, F.E., 1978. A classical thermodynamic discussion of the effect of composition on glass-transition temperatures. *Macromolecules* 11, 117–119. <http://dx.doi.org/10.1021/ma60061a021>.
- Gontard, N., Ring, S., 1996. Edible wheat gluten film: influence of water content on glass transition temperature. *J. Agric. Food Chem.* 44, 3474–3478. <http://dx.doi.org/10.1021/jf960230q>.
- Gordon, M., Taylor, J.S., 1952. Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. *J. Appl. Chem.* 2, 493–500. <http://dx.doi.org/10.1002/jctb.5010020901>.
- Hallbrucker, A., Mayer, E., Johari, G.P., 1989. Glass-liquid transition and the enthalpy of devitrification of annealed vapor-deposited amorphous solid water: a comparison with hyperquenched glassy water. *J. Phys. Chem.* 93, 4986–4990. <http://dx.doi.org/10.1021/j100349a061>.
- Hartel, R.W., Ergun, R., Vogel, S., 2011. Phase/state transitions of confectionery sweeteners: thermodynamic and kinetic aspects. *Compr. Rev. Food Sci. Food Saf.* 10, 17–32. <http://dx.doi.org/10.1111/j.1541-4337.2010.00136.x>.
- Jiang, B., Liu, Y.T., Bhandari, B., Zhou, W.B., 2008. Impact of caramelization on the glass transition temperature of several caramelized sugars. Part 1: chemical analyses. *J. Agric. Food Chem.* 56, 5138–5147. <http://dx.doi.org/10.1021/jf703792x>.
- Kalichevsky, M.T., Blanshard, J.M.V., 1993. The effect of fructose and water on the glass transition of amylopectin. *Carbohydr. Polym.* 20, 107–113. [http://dx.doi.org/10.1016/0144-8617\(93\)90085-1](http://dx.doi.org/10.1016/0144-8617(93)90085-1).
- Kalichevsky, M.T., Jaroszkiewicz, E.M., Ablett, S., Blanshard, J.M.V., Lillford, P.J., 1992. The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydr. Polym.* 18, 77–88. [http://dx.doi.org/10.1016/0144-8617\(92\)90129-E](http://dx.doi.org/10.1016/0144-8617(92)90129-E).
- Kalichevsky, M.T., Jaroszkiewicz, E.M., Blanshard, J.M.V., 1993. A study of the glass transition of amylopectin-sugar mixtures. *Polym. Guildf.* 34, 346–358. [http://dx.doi.org/10.1016/0032-3861\(93\)90088-R](http://dx.doi.org/10.1016/0032-3861(93)90088-R).
- Katkov, I.I., Levine, F., 2004. Prediction of the glass transition temperature of water solutions: comparison of different models. *Cryobiology* 49, 62–82. <http://dx.doi.org/10.1016/j.cryobiol.2004.05.004>.
- Katz, E.E., Labuza, T.P., 1981. Effect of water activity on the sensory crispness and mechanical deformation of snack food products. *J. Food Sci.* 46, 403–409. <http://dx.doi.org/10.1111/j.1365-2621.1981.tb04871.x>.
- Kawai, K., Hagura, Y., 2012. Discontinuous and heterogeneous glass transition behavior of carbohydrate polymer-plasticizer systems. *Carbohydr. Polym.* 89, 836–841. <http://dx.doi.org/10.1016/j.carbpol.2012.04.018>.
- Kwei, T.K., 1984. The effect of hydrogen bonding on the glass transition of polymer mixtures. *J. Polym. Sci.* 22, 307–313. <http://dx.doi.org/10.1002/pol.1984.130220603>.
- Lappalainen, M., Pitkänen, I., 2006. Quantification of amorphous content in maltitol by StepScan DSC. *J. Therm. Anal. Calorim.* 84, 345–353. <http://dx.doi.org/10.1007/s10973-006-7520-7>.
- Lechuga-Ballesteros, D., Miller, D.P., Zhang, J., 2002. Residual water in amorphous solids: measurement and effects on stability. In: Levine, H. (Ed.), *Amorphous Food and Pharmaceutical Systems*. The Royal Society of Chemistry, Athenaeum, Manchester, UK, pp. 275–316.
- Lee, J.W., Thomas, L.C., Jerrell, J., Feng, H., Cadwallader, K.R., Schmidt, S.J., 2011a. Investigation of thermal decomposition as the kinetic process that causes the loss of crystalline structure in sucrose using a chemical analysis approach (Part II). *J. Agric. Food Chem.* 59, 702–712. <http://dx.doi.org/10.1021/jf104235d>.
- Lee, J.W., Thomas, L.C., Schmidt, S.J., 2011b. Effects of heating conditions on the glass transition parameters of amorphous sucrose produced by melt-quenching. *J. Agric. Food Chem.* 59, 3311–3319. <http://dx.doi.org/10.1021/jf104853s>.
- Levine, H., Slade, L., 1986. A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPs). *Carbohydr. Polym.* 6, 213–244. [http://dx.doi.org/10.1016/0144-8617\(86\)90021-4](http://dx.doi.org/10.1016/0144-8617(86)90021-4).
- Liu, Y., Bhandari, B., Zhou, W., 2007. Study of glass transition and enthalpy relaxation of mixtures of amorphous sucrose and amorphous tapioca starch syrup

- solid by differential scanning calorimetry (DSC). *J. Food Eng.* 81, 599–610. <http://dx.doi.org/10.1016/j.jfoodeng.2006.12.017>.
- Macfarlane, D.R., Angell, C.A., 1984. Nonexistent glass transition for amorphous solid water. *Society* 159–162.
- 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 Hydrocoll.* 14, 425–437. [http://dx.doi.org/10.1016/S0268-005X\(00\)00020-5](http://dx.doi.org/10.1016/S0268-005X(00)00020-5).
- Mendenhall, H., Hartel, R., 2014. Control of caramel texture through formulation. *Manuf. Confect.* 94, 57–67.
- Orford, P.D., Parker, R., Ring, S.G., 1990. Aspects of the glass transition behaviour of mixtures of carbohydrates of low molecular weight. *Carbohydr. Res.* 196, 11–18.
- Pinal, R., 2008. Entropy of mixing and the glass transition of amorphous mixtures. *Entropy* 10, 207–223. <http://dx.doi.org/10.3390/entropy-e10030207>.
- Pouplin, M., Redl, A., Gontard, N., 1999. Glass transition of wheat gluten plasticized with water, glycerol, or sorbitol. *J. Agric. Food Chem.* 47, 538–543. <http://dx.doi.org/10.1021/jf980697w>.
- Roos, Y., Karel, M., 1991a. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *J. Food Sci.* 56, 38–43. <http://dx.doi.org/10.1111/j.1365-2621.1991.tb07970.x>.
- Roos, Y., Karel, M., 1991b. Phase transitions of mixtures of amorphous polysaccharides and sugars. *Biotechnol. Prog.* 7, 49–53. <http://dx.doi.org/10.1021/bp00007a008>.
- Roos, Y.H., 1995. Physical state and molecular mobility. In: Roos, Y.H. (Ed.), *Phase Transitions in Foods*. Academic Press, San Diego, pp. 19–48. <http://dx.doi.org/10.1016/B978-0-12-595340-5.50002-X>.
- Roos, Y.H., 1992. Water activity and physical state effects on amorphous food stability. *J. Food Process Preserv.* 16, 433–447.
- Ruiz-Cabrera, M.A., Schmidt, S.J., 2015. Determination of glass transition temperatures during cooling and heating of low-moisture amorphous sugar mixtures. *J. Food Eng.* 146, 36–43. <http://dx.doi.org/10.1016/j.jfoodeng.2014.08.023>.
- Ruiz, R.P., 2005. Karl fischer titration. In: Wrolstad, R.E., Acree, T.E., Decker, E.A., Penner, M.H., Reid, D.S., Schwart, S.J., Shoemaker, C.F., Smith, D.M., Sporns, P. (Eds.), *Handbook of Food Analytical Chemistry*. John Wiley & Sons, Hoboken, pp. 13–16.
- Saavedra-Leos, M.Z., Grajales-Lagunes, A., González-García, R., Toxqui-Terán, A., Pérez-García, S.A., Abud-Archila, M.A., Ruiz-Cabrera, M.A., 2012. Glass transition study in model food systems prepared with mixtures of fructose, glucose, and sucrose. *J. Food Sci.* 77, E118–E126. <http://dx.doi.org/10.1111/j.1750-3841.2012.02678.x>.
- Simatos, D., Blond, G., Roudaut, G., Champion, D., Perez, J., Faivre, A.L., 1996. Influence of heating and cooling rates on the glass transition temperature and the fragility parameter of sorbitol and fructose as measured by DSC. *J. Therm. Anal.* 47, 1419–1436. <http://dx.doi.org/10.1007/BF01992837>.
- Slade, L., Levine, H., Reid, D.S., 1991. Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. *Crit. Rev. Food Sci. Nutr.* 30, 115–360. <http://dx.doi.org/10.1080/10408399109527543>.
- Sugisaki, M., Suga, H., Seki, S., 1968. Calorimetric study of the glassy state. IV. Heat capacities of glassy water and cubic ice. *Bull. Chem. Soc. Jpn.* 41, 2591–2599.
- ten Brinke, G., Karasz, F.E., Ellis, T.S., 1983. Depression of glass transition temperatures of polymer networks by diluents. *Macromolecules* 16, 244–249. <http://dx.doi.org/10.1021/ma00236a017>.
- Truong, V., Bhandari, B.R., Howes, T., Adhikari, B., 2002. Analytical model for the prediction of glass transition temperature of food systems. In: Levine, H. (Ed.), *Amorphous Food and Pharmaceutical Systems*. The Royal Society of Chemistry, Cambridge, pp. 31–47.
- Vanhal, I., Blond, G., 1999. Impact of melting conditions of sucrose on its glass transition temperature. *J. Agric. Food Chem.* 47, 4285–4290. <http://dx.doi.org/10.1021/jf981411q>.
- Wungtanagorn, R., Schmidt, S.J., 2001. Thermodynamic properties and kinetics of the physical ageing of amorphous glucose, fructose, and their mixture. *J. Therm. Anal. Calorim.* 65, 9–35.
- Yu, L., Mishra, D.S., Riggsbee, D.R., 1998. Determination of the glass properties of D-mannitol using sorbitol as an impurity. *J. Pharm. Sci.* 87, 774–777. <http://dx.doi.org/10.1021/js970224o>.