



Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

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

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ARTICLE INFO

Article history:

Received 2 May 2017

Received in revised form

7 July 2017

Accepted 10 July 2017

Available online xxx

Keywords:

Glass transition

Confections

Polyols

Carbohydrates

Sugar replacement

Couchman-Karaszc equation

ABSTRACT

Our objectives were to compare the Couchman-Karaszc-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-Karaszc equation fit the data better than the modified equation; although both generally overestimated T_{gm} . Blends containing sorbitol had the largest ΔT_{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 ($\overline{R}^2 = 0.984$) 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 ($\overline{R}^2 = 0.998$), but adequately described by a more generalizable linear model ($\overline{R}^2 = 0.979$). Application of an empirical correction based on moisture content or cook temperature and T_{CK} of dry ingredients reduced the average ΔT_{gm}^{CK} from 20.1°C and 11.3°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; ΔC_p , change in specific heat; T_m , melting temperature; T_{CK} , T_g value calculated via the Couchman-Karaszc equation; T_{gm} , T_g of mixture; ΔT_{gm}^{CK} , difference between calculated T_{CK} and measured T_{gm} ; ΔT_{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_{CK}^{LT} , T_g value calculated via a linear empirical equation based on T_{CK} and sample cook temperature; $\Delta T_{gm}^{CK^{MC}}$, difference between calculated T_{CK}^{MC} and measured T_{gm} ; $\Delta T_{gm}^{CK^{CT}}$, difference between calculated T_{CK}^{CT} or T_{CK}^{LT} and measured T_{gm} ; C, cane sucrose; I, isomalt; M, maltitol; S, sorbitol; CS, corn syrup solids.

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<http://dx.doi.org/10.1016/j.jfoodeng.2017.07.007>

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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 (ΔC_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 ΔC_p is independent of temperature (Katkov and Levine, 2004). The notation ΔC_{pi} is used to refer to the ΔC_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 ΔC_p is proportional to temperature (Equation (3)). The invalidity of the assumption of independence between ΔC_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 ΔT_{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 ΔT_{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

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