

## Thermal behaviour of confectionary sweeteners' blends

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The present research investigates the glass transition and melting of sucrose and some of the most commonly used in the confectionary industry sweeteners – erythritol, sorbitol, maltitol and isomalt. A comparison between the thermal properties of the studied sweeteners and the sucrose is done. It is found that the glass transition temperature and the melting temperature of the sucrose are the highest. The parameters of the maltitol were the closest to these of the sucrose probably due to their common disaccharide chemical structure. The erythritol is characterized as the sweetener with the lowest glass transition temperature and the highest enthalpy of melting. Based on the glass transition behaviour of the sugar mixtures, a miscibility between sucrose/erythritol, sucrose/sorbitol, maltitol/erythritol, maltitol/sorbitol, maltitol/isomalt, erythritol/sorbitol, erythritol/isomalt and sorbitol/isomalt was established. Intermolecular hydrogen bonding between sucrose/maltitol, sucrose/isomalt and maltitol/isomalt were demonstrated.

**Keywords:** sucrose, sweeteners, glass transition, melting, miscibility, differential scanning calorimetry

### INTRODUCTION

Understanding and controlling the state of sugars and sweeteners is critical for making high-quality confectioneries and many other food products. The sugars and sweeteners play the main role to attaining the desired characteristics, from appearance to texture. They may be found dissolved in the water in a food, dispersed as a crystalline phase, immobilized in the amorphous or glassy state, or various combinations of these states [1]. During processing, the sugars and sweeteners in the confectionery formulations typically go through one or more phase transition, depending on the nature of the product. Changes in phase behaviour may also occur during storage, usually with a negative effect on shelf life. Therefore knowledge about the thermal behaviour of sugars and sweeteners could help in technology optimization and finding the best storage conditions. The most important transitions for the sugars and sweeteners are the melting (crystallization) and the glass transition.

The melting is endothermic first order transition wherein the crystal structure is destroyed and material goes to liquid state. Crystalline sugars melt, when they are heated to or above their melting temperature. The sugars do not have sharp melting temperatures and their melting proceeds over a temperature range. For this reason, melting endotherms are fairly broad. The melting temperatures of the sugars are sensitive to water, impurities and crystallinity [2]. Some sugars may caramelize and become brown concomitantly with

the melting process and they may also decompose before melting [3].

Solid confections can either be in a crystalline state or in a thermodynamically unstable amorphous state [4]. The amorphous state can exist either as a viscous fluid-like rubbery state or as a high-viscosity glassy state with low molecular mobility [3]. The amorphous glasses are characterized by a random arrangement of the molecules with no long-scale ordering. The glass transition occurs when the glassy state converts to the rubbery state (or vice versa), with the temperature of this transition being called the glass transition temperature ( $T_g$ ) [5]. The glass transition is a second-order state transition that results in changes in various material properties, including specific heat, dielectric constant, viscosity, molecular mobility, and mechanical properties [6]. Thus, the glass transition can be measured by tracking changes in these properties.

The sugar glasses are not completely static or unchanging [7]. Many exhibit a phenomenon known as enthalpic relaxation [8], which might loosely be defined as rearrangements of the sugar molecules while in the glassy state.

The glassy state is metastable due to the limited molecular mobility so that diffusion-based chemical reactions and physical changes (such as crystallization) are severely limited.  $T_g$  is governed by the molecular composition, the degree of polymer cross-linking, and the plasticizer (such as water) concentration [9]. Among the disaccharides,  $T_g$  varies from 65 °C to 70 °C for sucrose to over 100 °C for lactose, whereas the monosaccharides glucose and fructose have  $T_g$  values of about 31 °C and 5 °C to 10 °C, respectively. Note the

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significantly lower  $T_g$  for most, but not all, polyols. Maltitol and isomalt, in particular, have  $T_g$  values above room temperature, making them suitable for use in sugar-free hard candies.

The present work aims to investigate the thermal behaviour of sweetener's blends in respect to their miscibility.

## EXPERIMENTAL DETAILS

### Sample preparation

Analytical grade crystalline sucrose and sweeteners – isomalt, erythritol, sorbitol and maltitol, were purchased from Sigma-Aldrich. They were dehydrated in vacuum oven at 60 °C for 5 hours and then stored at room temperature in an exicator at 0% relative humidity (RH) (above  $P_2O_5$  desiccant).

The sample mixtures were prepared by dissolving the particular sugar in distilled water (solid-water ratio 1:9). Solutions from each two sugars were mixed in weight ratios 1:3, 1:1 and 3:1 and freeze-dried to solids. The solutions were firstly frozen at -30 °C for 24 hours and then dried under vacuum (5 Pa) for more than 48 hours using TOPT-10B mini Vacuum Freeze Dryer. Subsequently dry powders were obtained. They were stored in an exicator at 0% relative humidity (RH) (above  $P_2O_5$  desiccant) until being used.

### Thermal analysis

A differential scanning calorimeter DSC 204 F1 Phoenix (NETZSCH, Germany) equipped with intracooler was used. The DSC was calibrated with indium. In order to avoid condensation of water, argon gas was used to purge the furnace chamber at 20 ml/min. Dry sample (5-10 mg) was weighed into 40  $\mu$ l aluminium standard crucible and hermetically sealed with aluminium standard lead. Melting and glass transitions were analysed using Proteus® Software. All experiments were run in triplicates.

The temperature profile of the DSC experiments is illustrated in Fig.1 [10]. All the investigated samples were initially melted in a DSC pan by heating from room temperature ( $T_1 = 25$  °C) to  $T_0 = 200$  °C at a heating rate of 20 °C/min. The temperature and the enthalpy of melting were determined from the first heating run. The molten sample was cooled at a cooling rate of 20 °C/min to a temperature that was about 60 °C below its glass transition temperature  $T_g$ , which was defined as inflection point in the specific heat capacity – temperature dependence, in order to form an amorphous glass. The sample was then reheated at 4 °C/min to a temperature about 40 °C above  $T_g$ . Through the experiments, the glass transition

temperatures and the relaxation enthalpy were determined.

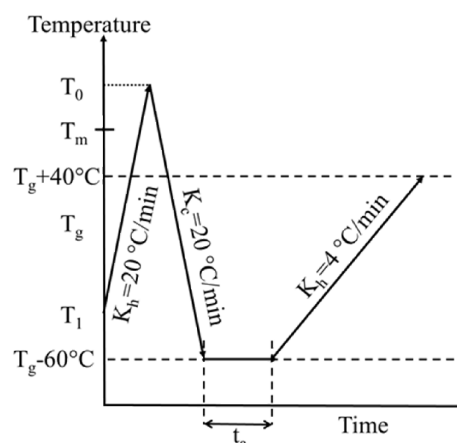


Fig.1. DSC temperature profile

## RESULTS AND DISCUSSION

### Melting

The results about melting behaviour of the sucrose and the investigated sweeteners are presented in Fig.2 and Table 1. They are in good agreement with previously reported data [11, 12].

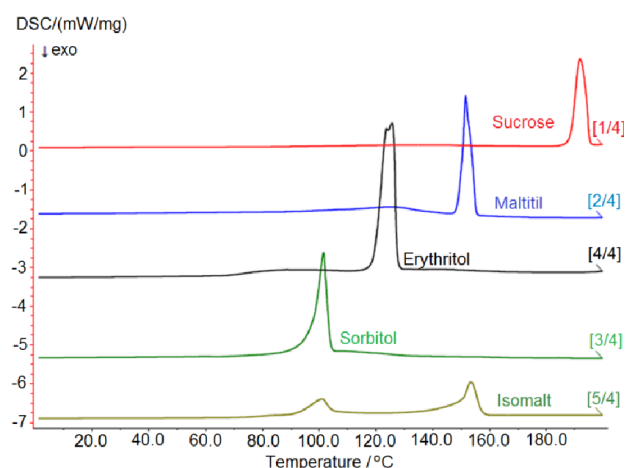


Fig.2. Melting temperatures of sugars

Table 1. Melting point and enthalpy of fusion of the investigated sugars

Sugar/ sweetener	Glass transition $T_g$ , °C	Melting point $T_m$ , °C	Enthalpy $\Delta H_f$ , J/g
Sucrose	61.93	189.1	126.4
Maltitol	43.10	149.6	160.8
Isomalt	32.00	98.0/155.0	143.0
Sorbitol	-9.20	97.4	187.4
Erythritol	-42.50	119.6/125.7	313.0

It is interesting to note that the sucrose, which is a disaccharide, possesses the highest melting temperature and the lowest enthalpy of fusion. The melting temperature of maltitol – the other disaccharide, is the closest to that of the sucrose,

but its enthalpy of fusion is about 27 % higher than the sucrose enthalpy of fusion. The other tree sweeteners, which are sugar alcohols, are characterized with lower melting temperatures. The erythritol is found to be the sweetener with the highest enthalpy of fusion. The double melting peak of the erythritol could be due to different crystal size and a crystal size distribution [13]. As far as isomalt is a mixture of two sugar alcohols - gluco-mannitol and gluco-sorbitol, it is characterized with two melting temperatures – 98 °C and 155 °C respectively. The differences, which are found in the melting behavior of the investigated sugars, are interesting in the terms of their application in the food industry and are related to the optimization of the treatment processes.

#### Glass transition

The glass transition temperatures  $T_g$  of the sucrose and the investigated sweeteners are presented in Table 1. The disaccharides – sucrose and maltitol – are characterized with the highest values of  $T_g$  (61.93 °C and 43.10 °C respectively), and the glass transitions of the alcohols vary in a wide temperature range – from -42.5 °C to 32 °C. The received data are similar to these reported in the literature [12].

Usually the glass transition of a mixture is between the glass transition temperatures of the components and can be expressed by Gordon-Taylor equation:

$$T_g = \frac{\omega_1 T_{g1} + K \omega_2 T_{g2}}{\omega_1 + K \omega_2}, \quad (1)$$

Here  $T_g$ ,  $T_{g1}$ ,  $T_{g2}$  are the glass transition temperatures of the binary mixture, component 1, and component 2 respectively,  $\omega_1$  and  $\omega_2$  are the weight fractions of component 1 and component 2 respectively,  $K$  is a constant, which according to

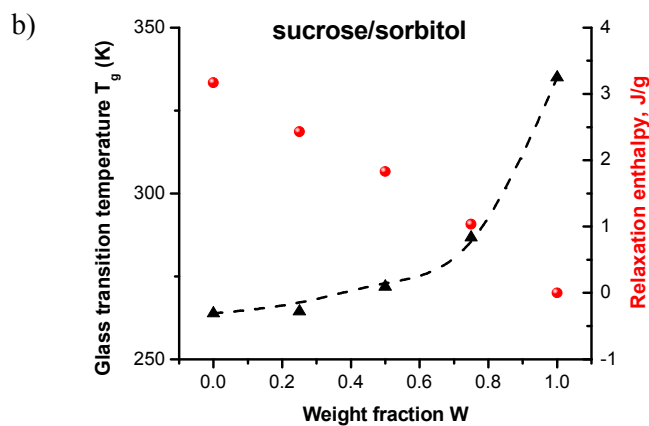
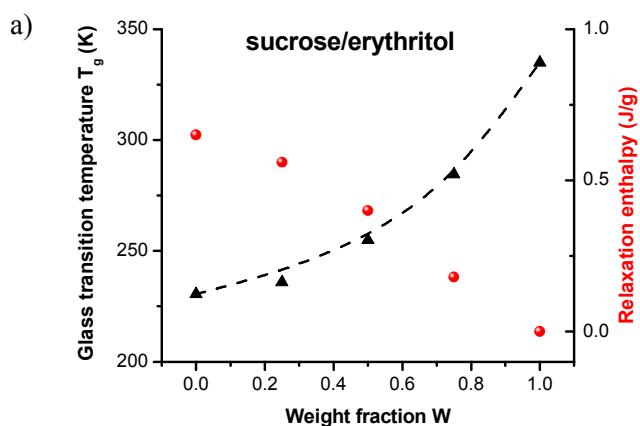
the free volume theory is related to the free volumes of the two components [14] and can be calculated using Simha-Bouer rule [15]:

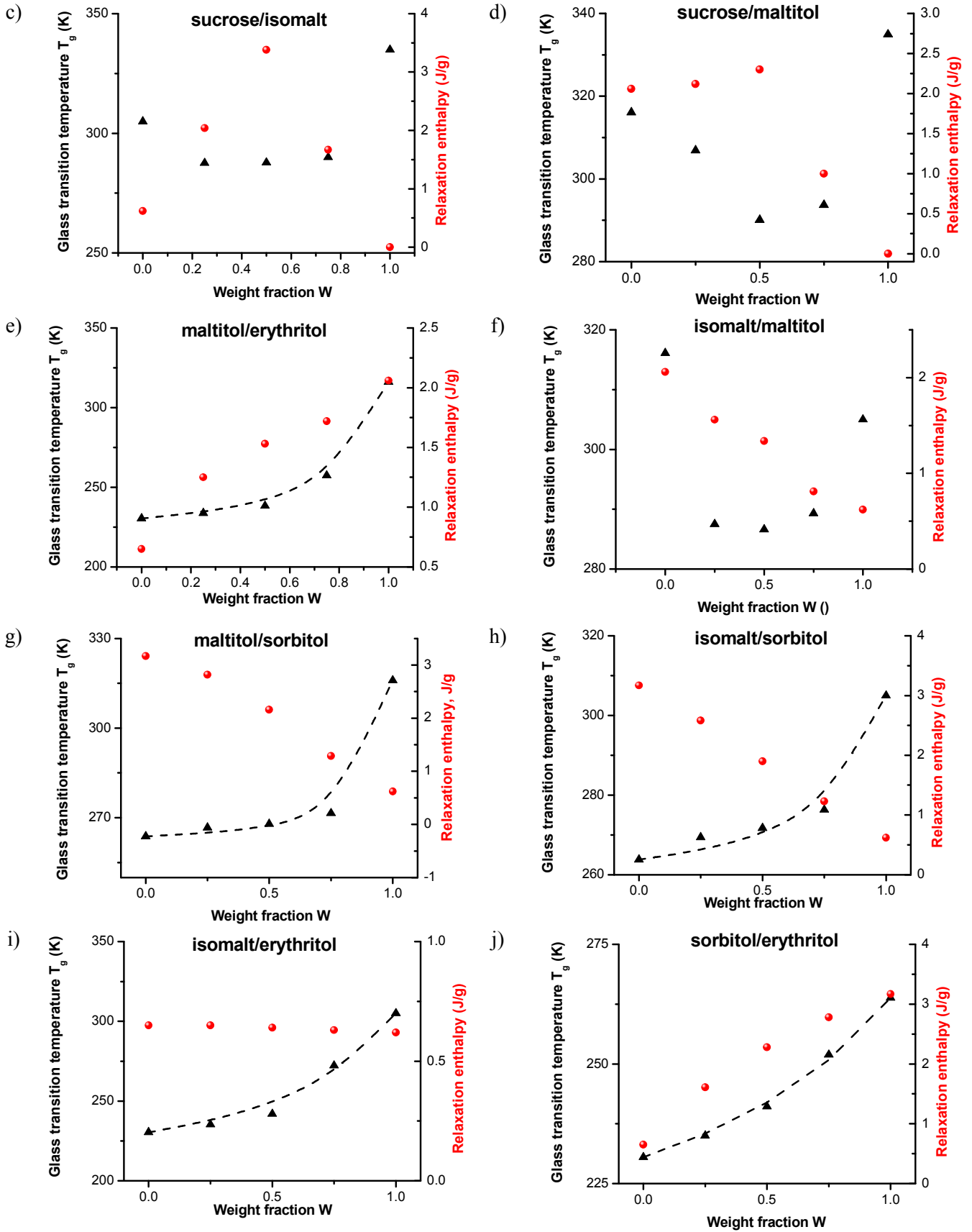
$$K \approx \frac{T_{g1} \cdot \rho_1}{T_{g2} \cdot \rho_2}, \quad (2)$$

where  $\rho$  is the density of each component.

Figures 3(a) – 3(j) show the glass transition temperatures of the sugar mixtures. Each mixture shows a single glass transition temperature, which means that the components are miscible in the mixture. The free volume theory predicted the mixing of most of the sugar pairs – sucrose/erythritol, sucrose/sorbitol, maltitol/erythritol, maltitol/sorbitol, isomalt/sorbitol, isomalt/erythritol and sorbitol/erythritol. The values of the  $K$  constant were calculated in these cases using the regression of the experimental data by the equation (1). These values are shown in Table 2. In cases of sugar mixtures between sucrose/isomalt, sucrose/maltitol and isomalt/maltitol, the glass transition temperatures of the mixtures are lower than these of the pure sugars.

It is interesting to note that the glass transition temperatures of sugars whose mixtures do not obey the Gordon-Taylor equation, are very close to each other and their ratio is near to one. These results are similar to the behaviour of co-lyophilized binary mixtures of sucrose and another component – amorphous tapioca starch syrup [10], lactose, dextran [16], etc. where the  $T_g$  values of the mixtures are lower than the values, predicted from the free volume theory. The differences could be attributed to non-uniform distribution of the free volume between the components or to interaction between the components through hydrogen bonding and formation of new network [17].





**Fig.3.** Glass transitions temperatures and relaxation enthalpies of sugar mixtures:  $\blacktriangle$  - experimental data for the glass transition temperature, ----- theoretical model for glass transition temperatures of the sweeteners' blends,  $\bullet$  - experimental data for the relaxation enthalpy at glass transition

It is known from the literature [18, 19] that the maltitol and isomalt show in aqueous solutions a fully extended conformation without intramolecular hydrogen bonds. All hydroxyl groups are involved in intermolecular hydrogen-bond. It could be assumed that the maltitol and isomalt interact with the sucrose and each other to form hydrogen bond network. Therefore the blends sucrose/maltitol, sucrose/isomalt and maltitol/isomalt disobey the Gordon-Taylor equation.

**Table 2.** K values of the sweeteners' blends

Mixture	K	$\frac{T_{g1}}{T_{g2}}$
Sucrose/erythritol	3.09	1.45
Sucros/sorbitol	6.80	1.27
Sucrose/isomalt	-	1.09
Sucrose/ maltitol	-	1.06
Maltitol/erythritol	6.8	1.37
Maltitol/isomalt	-	1.04
Maltitol/sorbitol	15.68	1.20
Isomalt/sorbitol	5.68	1.16
Isomalt/erythritol	3.16	1.32
Sorbitol/erythritol	1.91	1.14

The relaxation enthalpy at the glass transition was calculated for the pure and mixed sugars – Fig.3. It was found out that the sucrose does not undergo any relaxation process at glass transition and the relaxation enthalpy is zero. All the sweeteners tend to approach towards the most stable state and undergo through structural relaxation. The relaxation enthalpy of binary mixtures changes almost linearly except in the cases of mixtures between the sucrose and maltitol and sucrose and isomalt. In these cases the relaxation enthalpy of the mixtures is higher than the relaxation enthalpies of the pure sugars and it coincides with glass transition temperatures, which are lower than the predicted from the theory. The phenomena might be due to a bit net loss of hydrogen bonding that resulted in a loose glassy structure. However further studies need to be done in support of this assumption.

## CONCLUSION

Thermal properties of confectionary sugars were investigated in respect to characterize their behaviour during processing and to clarify their miscibility. Among the investigated sugars the sucrose possesses the highest glass transition and melting temperature and the lowest enthalpy of fusion. The glass transition undergoes without relaxation process. The thermal transitions of the investigated sweeteners vary in a wide temperature

range and their enthalpies of fusion are higher than sucrose's. Therefore different process conditions should be developed for product with replaced sucrose. Based on the single glass transition of the sweeteners' blends a miscibility between sucrose/erythritol, sucrose/ sorbitol, maltitol/ erythritol, maltitol/ sorbitol, maltitol/ isomalt, erythritol/ sorbitol, erythritol/ isomalt and sorbitol/ isomalt was confirmed. Intermolecular interactions were found to exist between sucrose/maltitol, sucrose/isomalt and maltitol/isomalt and as a result the thermal behaviour of these blends does not match the Gordon-Taylor.

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