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GLASS TRANSITION TEMPERATURE BEHAVIOR OF A MODEL BLEND OF CARBOHYDRATES

COMPORTAMIENTO DE LA TEMPERATURA DE TRANSICIÓN VÍTREA DE UNA MEZCLA MODELO DE CARBOHIDRATOS

COMPORTAMENTO DA TEMPERATURA DE TRANSICIÓN VÍTREA DUNHA MEZCLA MODELO DE CARBOHIDRATOS

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Abstract

The glass transition of amorphous food materials in processing and storage of foods is important. The effect of a quaternary model mixture from glucose, fructose, sucrose and water on the glass transition temperature was determined. State and phase diagrams were elaborated as well solubility curves of these mixtures. The measurements of glass transition temperature of mixtures and pure components were carried out on a differential scanning calorimeter. An empirical model was created to involve the mixture behavior. The carbohydrates present in the mixture had influence between them in the glass transition temperature determination. The solubility of glucose and sucrose showed a linear behavior with a change of first order. The solubility of fructose pointed out the presence of eutectics to high and low concentration of fructose, having a high change in the molecular arrangement between 140 and 150°C, as a result the fructose had molecular rejection to glucose and sucrose.

Keywords: Carbohydrates, glass transition, solubility.

Resumen

La transición vítrea de materiales alimentarios heterogéneos en el procesado y almacenaje de alimentos es importante. En este estudio se determinó el efecto de una mezcla modelo cuaternaria de glucosa, fructosa, sacarosa y agua sobre la temperatura de transición vítrea. Se elaboraron diagramas de fase y estado, así como curvas de solubilidad de las mezclas. Las medidas de temperatura de transición vítrea de las mezclas y componentes puros se realizaron con un calorímetro diferencial de barrido. Se desarrolló un modelo empírico para definir el comportamiento de las mezclas. Los carbohidratos presentes en las mezclas tuvieron influencia sobre la temperatura de transición vítrea. La solubilidad de glucosa y sacarosa mostró un comportamiento lineal con cambios de primer orden. La solubilidad de fructosa apuntó la presencia de eutécnicos de concentración alta y baja de fructosa, teniendo un gran cambio en su conformación molecular entre 140ºC y 150ºC, con el resultado de que la fructosa mostró un rechazo hacia la glucosa y sacarosa.

Palabras clave: Carbohidratos, transición vítrea, solubilidad.

Resumo

A transición vítrea de materiais alimentarios heteroxéneos no procesado e almacenaxe de alimentos é importante. Neste estudio determinóu-se o efecto dunha mezcla modelo cuaternaria de glucosa, fructosa, sacarosa e auga sobre a temperatura de transición vítrea. Elaboráron-se diagramas de fase e estado, así como curvas de solubilidade das mezclas. As medidas de temperatura de transición vítrea das mezclas e compoñentes puros realizáron-se cun calorímetro diferencial de barrido. Desenrolou-se un modelo empírico para defini-lo comportamento das mezclas. Os carbohidratos presentes nas mezclas tiveron influencia sobre a temperatura de transición vítrea. A solubilidade de glucosa e sacarosa amosou un comportamento lineal con cambios de primeiro orde. A solubilidade de fructosa apuntou a presencia de eutécnicos de concentración alta e baixa de fructosa, tendo un gran cambio na súa conformación molecular entre 140ºC e 150ºC, co resultado de que a fructosa amosou un rechazo cara a glucosa e sacarosa.

Palabras chave: Carbohidratos, transición vítrea, solubilidade.

INTRODUCTION

Many processes used in the preparation of food products such as dehydration, concentration, extrusion, or melting transform the crystalline sugar components into amorphous sugars. The sugars present in foods can have from low to high molecular weight. The soluble sugars can be in disorder state know that amorphous sugars. The amorphous sugars in food products are in metastable non-equilibrium state and can be subject to physical aging during their shelf life. The physical aging produces unfavorable changes in some properties, density, hardness and brittleness, which in turn affect the quality and the stability of the food products (Wungtanagorn and Schmidt, 2001). Evaluation about thermodynamic properties that reflects the physical state of amorphous foods would probably useful in evaluation of glassy foods and food components.

Glass transition temperature (T_g) is a physical important parameter in food processing. It explains the physical and chemical behavior such as the softness in snack products, sugar cristallization in amorphous solids, and the stickiness and caking in food products (Chuy and Labuza, 1994).

Below the glass transition temperature (T_g), the material is in a rigid state, having a high internal viscosity, Over T_g, the *glassy* material became soft and gummy, showing a viscosity decrease and mobility increase.

Glass transition temperature can be defined as the temperature under an amorphous system changes from glassy state to rubbery state (Karmas *et al.*, 1992). The determination of glass transition temperature is complicated with food products because of their chemical and microstructural complexity (Le Meste *et al.*, 2002). The most natural composition of carbohydrates in fruits and vegetables is a blend of glucose, fructose and sucrose in an aqueous environment. There are a lack of know about thermodynamic behavior of this type of blend.

In a literature review there are not reports about glass transition temperature in quaternary blends of carbohydrates. Thus the objective of this work was to evaluate the influence of the three carbohydrates on the glass transition temperature of the aqueous blend.

MATERIALS AND METHODS

Quaternary mixtures

Mixtures made of glucose (Sigma Aldrich, St. Louis, Mo.), fructose and sucrose (Chemical products Monterrey), and distilled water were used. Table 1 shows the composition of the quaternary mixtures.

The carbohydrates were melted and then mixed with two purposes, a) to obtain homogeneity and b) to eliminate thermal memory according to procedure reported by Foubert *et al.* (2003). Weighed samples from 3.5 to 4 mg were placed on aluminum pans of 7 mm diameter to be read on the differential scanning calorimeter.

Table 1.- Concentration in molar fractions of carbohydrates blends used in this experiment.

Blend	Glucose	Fructose	Sucrose	Water
1	1	0	0	0
2	0.70	0.10	0.10	0.10
3	0.55	0.15	0.15	0.15
4	0.40	0.20	0.20	0.20
5	0.25	0.25	0.25	0.25
6	0.10	0.30	0.30	0.30
7	0	1	0	0
8	0.10	0.70	0.10	0.10
9	0.15	0.55	0.15	0.15
10	0.20	0.40	0.20	0.20
11	0.25	0.25	0.25	0.25
12	0.30	0.10	0.30	0.30
13	0	0	1	0
14	0.10	0.10	0.70	0.10
15	0.15	0.15	0.55	0.15
16	0.20	0.20	0.40	0.20
17	0.25	0.25	0.25	0.25
18	0.30	0.30	0.10	0.30
19	0	0	0	1
20	0.10	0.10	0.10	0.70
21	0.15	0.15	0.15	0.55
22	0.20	0.20	0.20	0.40
23	0.25	0.25	0.25	0.25
24	0.30	0.30	0.30	0.10

Glass transition temperature

The T_g onset values of the quaternary mixtures were obtained using a differential scanning calorimetry (DSC). A DSC 550 ISI equipped with an intracooler was used for all the measurements with a sealed empty pan as the reference material. Liquid nitrogen was used as flushing agent over the head. The instrument was calibrated with indium at range temperature from 25 to 200°C, heating velocity of 20°C/min and 2 min as residence time. The glass transition temperature onset was measured on three pure carbohydrates and 20 mixtures. Measurements were made in duplicate. Results were analyzed by ANOVA test (pd»0.05) using software Statistica (StatSoft V.5.1, Tulsa, OK).

Solubility curves

The solubility curves were made by the chemical potential of pure solute following the next equation:

$$\ln x_B = -\left(\Delta H_{fus,m} / R\right)\left\{\left(1/T\right) - \left(1/T^*\right)\right\} \qquad (1)$$

where:

X_B	Solute molar fraction
T	Temperature
T*	Solute melting point
R	Gas constant
? H	Entalphy

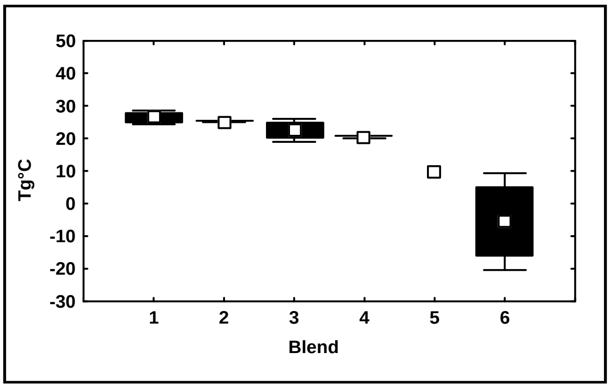

Figure 1. Tg behavior in function of glucose. (Code for blend see Table 1).

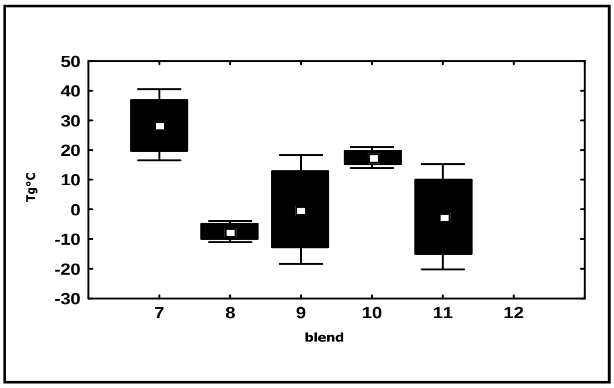

Figure 2. Effect of fructose on Tg.

This expression is valid if the system is in equilibrium and pressure is constant and the solution is ideal (Fairley *et al.*, 1994).

Fragility index was calculated as followed equation 2.

m = - Ea/ (2.303RT_g onset) (2)

Where Ea is activation energy from Arrhenius plot, R is gas constant, and T_g onset is the onset of glass transition. This term is controversial because Simatos *et al*. (1995) reported that T_g used should be obtained by inflection of The Adam-Gibbs model. But Smidova *et al.* (2003) reported that the use of T_g onset done better results that the method proposed by Simatos *et al.* (1995).

Phase Diagrams were built by graphing the blend concentration vs melting temperature of component in higher concentration on the mixture.

Experimental results were analyzed by multiple regression approach for Arrhenius behavior Anova and Tuckey test were employed to evaluate influence of carbohydrates into the systems. Significance was defined at pd» 0.05. It was used Statistica v.5.2 as software package (StatSoft, Tulsa, OK).

RESULTS AND DISCUSSION

Glucose influence on glass transition temperature in the quaternary mixture of carbohydrates

Isothermal curves for pure glucose and quaternary mixture where the main component is glucose were obtained. It is important to note that in both type of systems (pure and blends), thermograms with only one peak were observed, but the shape of the peak were different and the values obtained too. Thus the blend was obtained and the components were incorporated into the blend changing the behavior of the simple compounds. From Figure 1, it can be observed that when glucose decrease, t_g onset also decrease, pure glucose have a t_g onset of 26°C (±1°C) this value is according to range reported by Smidova *et al*. (2003). It was used tg onset because t_g in food systems is not a value is a range of value (Smidova *et al.*, 2003) and the glucose at 0.1 M shows t_g onset of -5°C (±10°C), differences between t_g onset values were confirmed by ANOVA test. Similar behavior has been observed by Collares *et al.* (2003) for the carbohydrates blend. When an addition of a component into a carbohydrate blend occurs, the glass transition temperature decrease for the blend. From Figure 1, it is possible to see that the level of standard error was increasing with the increase of the number and quantity of another compounds in the blend (i. e. more complex system), this phenomena may be to implicate that molecular interactions increase in the blends and then the error rising.

Fructose influence on glass transition temperature in the quaternary mixture of carbohydrates

Typical isothermal curves for pure fructose and quaternary mixture where the main component is fructose, were obtained. In Figure 2 it can be seen that this mixture has an irregular behavior probably due to the molecular mobility of this carbohydrate. The large difference in melting temperature of the blends caused a portion of the fructose component in the mixtures to decompose before the glucose was completely melted. The decomposition of fructose may be responsible for the differences on the entalphy change. The fructose liquid obtained on fusion is initially not in the equilibrium state. Slow relaxation processes can occur in the liquid above T_g onset due to the coexists of at least six structurally distinct conformers of the fructose molecule; i.e two anomer forms (Finegold *et al.*, 1989; Jiang and Angell, 1995). Each conformer has a different level of energy. The composition of the conformers, the rate of tautomerization, and the equilibrium state of the liquid are a function of temperature with different time scales for equilibration.

Sucrose influence on glass transition temperature in the quaternary mixture of carbohydrates

Typical isothermal curves for pure sucrose and quaternary mixture where the main component was obtained. It can be seen that this mixture present a simple behavior like to glucose but not similar (Figure 3). Maybe due to the sucrose is formed by glucose and fructose.
According to Hartel *et al.* (1993), just on the temperature of glass transition, the sugar solution is plastic, as a result, there is a mobility in this temperature range, although the

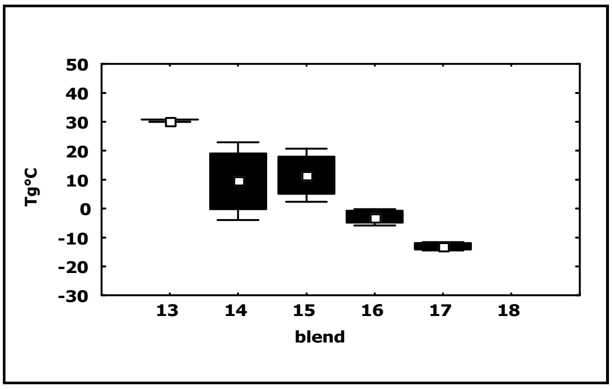

Figure 3. Effect of sucrose on Tg.

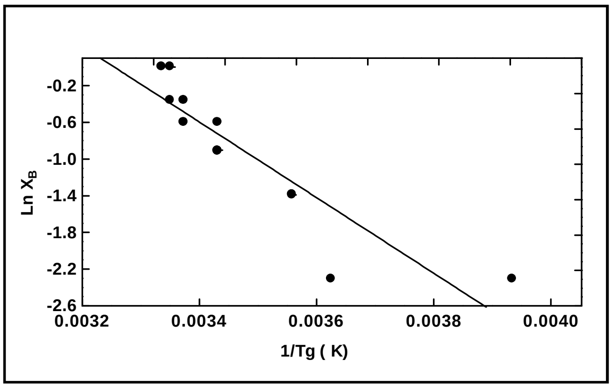

Figure 4. Solubility of glucose.

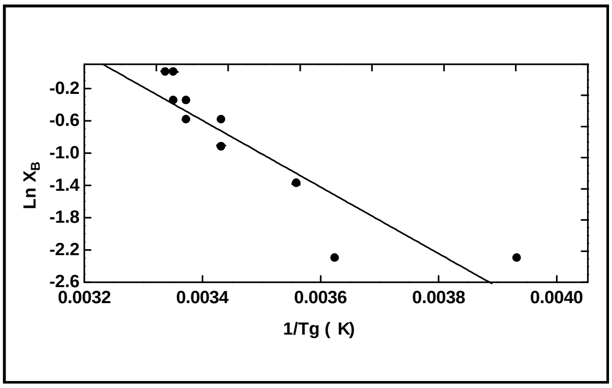

Figure 5. Solubility of fructose.

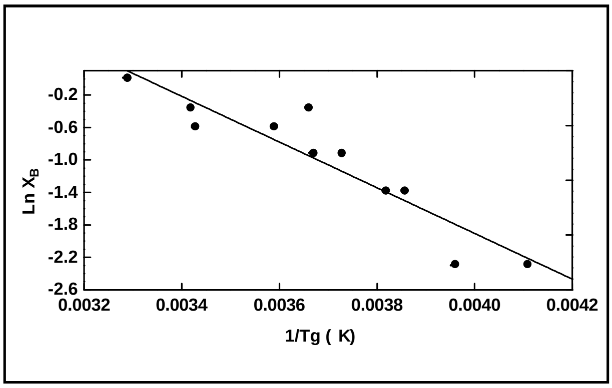

Figure 6. Solubility of sucrose.

solution can not freely flow. However, the behavior is simple and of the linear nature but contraire to glucose behavior the levels of standard error were higher at low amounts of another compound, this behavior maybe caused for the nature of the sucrose (two monomers).

The experimental results indicated the presence of an eutectic behavior. This phenomenon is complicated due to the supersaturated solutions frequently are melted before the eutectic crystallization occurs. In this kind of mixtures, the eutectic behavior and the eutectic crystallization are affected by the mixture components (Ross, 1995). Crystal formation occurs below melting temperature. At temperatures below the eutectic temperature, the solute and solvent are in crystalline state.

Figure 4 shows the solubility graph for glucose. Its value of r^2 was 0.813, the reason of relatively low value of correlation was result of extreme data, when the minor data showed on the figure was excluded r^2 was 0.963. From the above results it can be concluded that at higher concentrations of glucose was shows higher solubility, this is atypical behavior of ideal systems (Toro-Vazquez and Gallegos-Infante, 1996). It is interesting to note that only at higher concentrations is observed this behavior usually at higher concentration there are interactions between molecules, this behavior produce deviations of the ideal behavior. However, several organic compounds shows different trends, Adeyemi *et al.* (1991) reported that blends of fatty acids shows non ideal behavior at low concentrations. The reason about this phenomenon presented not only in fatty acids or in glucose is not clear at its beyond of the objective of this work.

Figure 5 shows the solubility graph for fructose. The value of r^2 obtained was 0.0174. This low correlation indicated deviations from ideal behavior, this deviations could be observed by the presence of eutectics at high and low concentration of fructose. A higher change in the molecular order can be observed between 140 and 150°C. Fructose tends to present a molecular reject to glucose and sucrose.

Figure 6 shows the solubility graph for sucrose. The r^2 value was 0.88, this value is good in comparison that obtained for fructose. From the above results it can be seen that the sucrose behavior is similar to that found for glucose, at highest sucrose concentration, highest solubility. Similar trend was observed for glucose.

The «strong/fragile liquid» classification for liquids was proposed by Angell *et al.* (1994). They used this concept to classify supercooled materials into «strong» and «fragile» liquids according to the change in their properties in the temperature range above T_g onset. This classification is an indicator of the sensitivity of the structure to temperature changes. The concept of fragility was simplified for systems near T_g onset by introduction a parameter called the fragility index. Is defined as the slope at the T_g onset of the T_g onset Arrhenius plot of any property ie viscosity in logarithmic form.

The fragility index obtained for glucose mixtures and calculated following method of Simatos *et al.* (1995) was 1884 (±22.3) (in function of solubility), for sucrose was 1222 (±19.6), for fructose the value was 172.8 (±9.2). Thus the fragility index values decreased to 1884 for glucose and 172.8 for fructose indicating that glucose was more fragile than sucrose and fructose. Similar trends were found by Wungtanagorn *et al.* (2001) finding that glucose was more fragile than fructose. Unfortunately in this experimental work the problem with fructose was that the fructose mixtures were not Arrhenius and thus it is impossible calculate fragility index. But according with Wungtanagorn *et al.* (2001), the strong liquids exhibit Arrhenius temperature dependent behavior. On the other hand, fragile liquids exhibit non-Arrhenius temperature dependent behavior. In this sense, the addition of fructose increased fragile liquid nature.

CONCLUSIONS

It can be concluded that all the components in the quaternary mixture of carbohydrates decreased the glass transition temperature onset. The glucose and sucrose showed Arrhenius temperature dependence, but fructose not. Saccharose was more strong liquid that glucose and the addition of fructose at the mixture increased the fragility of the blend.

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