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Crystallization inhibition of an amorphous sucrose system using raffinose*

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Abstract: The shelf life of pure amorphous sucrose systems, such as cotton candy, can be very short. Previous studies have shown that amorphous sucrose systems held above the glass transition temperature will collapse and crystallize. One study, however, showed that adding a small percent of another type of sugar, such as trehalose, to sucrose can extend the shelf life of the amorphous system by slowing crystallization. This study explores the hypothesis that raffinose increases the stability of an amorphous sucrose system. Cotton candy at 5 wt% raffinose and 95 wt% sucrose was made and stored at room temperature and three different relative humidities (%RH) 11%RH, 33%RH, and 43%RH. XRD patterns, and glass transition temperatures were obtained to determine the stability as a function of %RH. The data collected showed that raffinose slows sucrose crystallization in a low moisture amorphous state above the glass transition temperature and therefore improves the stability of amorphous sucrose systems.

Key words: Crystallization, Amorphous sucrose system, Raffinose
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INTRODUCTION

A recent paper by physicists who have now begun to look at foods touting the use of "soft condensed matter physics" as an approach would be valuable for understanding stability (Mezzenga *et al*., 2005). One method to study such soft condensed matter is that of the glass transition between a brittle or glassy-like material and that of a ductile or rubbery material (Labuza *et al*., 2004). The quality of many foods is dependent upon the physical state of sucrose such as soft cookies. Another of these foods is cotton candy which is a useful tool for demonstrating the principles of soft condensed matter. Cotton candy (candy floss in many parts of the world) exists in an amorphous glassy state with sugar (sucrose) making up almost 100% of the structure. On hot, humid days, cotton candy can collapse and crystallize into a hard lump of sucrose crystals imbedded in a glass structure. Because of this, it is difficult to mass produce, distribute and sell quality cotton candy products at grocery stores or over the internet. Labuza and Labuza (2004) extensively studied the stability of cotton candy as an example of a pure amorphous solid at room temperature and stored at different relative humidities (%RH). They found that cotton candy stored at room temperature and at either ~0%RH or 11%RH stayed amorphous for ≥2 years. Cotton candy samples stored at room temperature and 33%RH collapsed and crystallized in 3 d, while those at 45%RH, 54%RH, or 75%RH collapsed and crystallized in less than 1 d, actually in 6 h at 45%RH and 1 h at 75%RH. The samples that crystallized did so because they were held at or above the glass transition temperature of sucrose corresponding to the given relative humidity.

Studies have been done on increasing the stability of an amorphous sucrose system by adding a small percent of another sugar to form a mixture. Roe and Labuza (2006) conducted such a study to observe the

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effects of trehalose on the crystallization of sucrose in cotton candy and a freeze dried sucrose/trehalose mixture. It was thought that trehalose would interrupt the crystallization of sucrose because trehalose has a higher glass transition temperature as compared to sucrose. Roe and Labuza (2006) found that 100% sucrose system crystallized after 11 d when stored at room temperature and 33%RH. Cotton candy made with 25% trehalose and 75% sucrose stored at room temperature and 33%RH collapsed, but did not become crystalline even after 26 d. It was also found that at room temperature and 54%RH, after 46 h, the system containing 25% trehalose and 75% sucrose was not crystalline, but that the 100% sucrose system was fully crystallized. It was concluded that the crystallization of the sucrose systems was slowed by trehalose but no mechanism was proffered.

Raffinose is a tri-saccharide composed of glucose, fructose and galactose (α-D-galactopyranosyl-(1-6)-α-D-glucopyranosyl-α-D-fructofuranoside) and is present in many foods of plant origin especially beans and melons. The 1st 2 monosaccharides in the structure are sucrose. It is not digestible by humans, who lack the necessary α-galactosidase enzyme. It has been evaluated by the Japanese as a functional food intended to promote bowel health (Nagura *et al*., 1999). Its presence is a nuisance in the manufacturing of crystalline sucrose from sugar beets as fine needles form rather than the typical sucrose crystal found in table sugar. The mechanism of inhibition is believed to be the attachment of the sucrose portion of raffinose on the major planar growing surface of the crystal. This only slows crystallization on one face so long fine needles still grow since raffinose does not attach to the other surfaces. In addition this attachment does not induce any raffinose XRD peaks (Vaccari *et al*., 1986; Mantovani *et al*., 1977; 1983; Mathlouthi and Reiser, 1995). Smythe (1967) and Iglesias *et al*.(2000) also found that raffinose slows the crystallization of sucrose in aqueous solutions and that the optimal equilibrium state of crystalline raffinose is as a pentahydrate form, therefore, a relatively large amount of water is needed to completely crystallize it. Pure raffinose also has a higher glass transition temperature as compared to pure sucrose and may work in the same way trehalose inhibited crystallization of sucrose as found by Roe and Labuza (2006).

The objective of this study was to determine whether raffinose would inhibit or slow the crystallization of sucrose from the amorphous solid state of a glassy material, cotton candy, when held above and below the glass transition temperature.

MATERIALS AND METHODS

Cotton candy was prepared with 5 wt% of raffinose pentahydrate and 95 wt% crystalline sucrose (5%-R:95%-S). The cotton candy was made using a Gold Medal Products, Co. Model 3017 cotton candy machine. Because raffinose has a higher melting point than is capable by the typical cotton candy machine, a space heater placed over the ingredient reservoir helped to liquefy the raffinose/sucrose mixture. After preparation, the cotton candy was placed into open jars and then immediately stored at room temperature (~23 °C) in three relative humidity tanks containing saturated salt solutions (11%RH lithium chloride; 33%RH, magnesium chloride; and 43%RH, potassium carbonate).

The crystallization of sucrose and raffinose in the samples was monitored by powder XRD using a Siemens D5005 small angle powder X-ray diffractor. The samples were put into 20 mm pans (~1.5 g) and then the surface was scrapped evenly. Scans were taken over the 10 to 27 2θ degrees (Bragg angle) range at a step of 0.04 degrees with a 4 second dwell at each step.

A Perkin Elmer differential scanning calorimeter, Model-DSC7 was used to obtain the glass transition temperatures of both pure sucrose cotton candy and the 5%-R:95%-S mixture at the three relative humidities. Glass transition temperatures were obtained using samples that were not crystallized. The samples were scanned at a rate of 10 °C/min starting at –30 °C and stopping once the melting peak was reached.

RESULTS

The glass transition temperatures of the pure sucrose and 5%-R:95%-S mixture are tabulated in Table 1 along with one dataset (midpoint) from that in literature (Sun *et al*., 1996) for pure sucrose. See Roe

Table 1 Glass transition temperature (onset and endpoint) of sucrose and 5% raffinose/95% sucrose as a function of %RH as compared to the values of Sun *et al*.(1996) for pure sucrose

System	T_g		
	Onset (°C)	End (°C)	Sun *et al*.(1996)
11%RH, 100% sucrose	52	65	~ 52
11%RH, 5% raffinose and 95% sucrose	52	67	
33%RH, 100% sucrose	19	27	~26 to 27
33%RH, 5% raffinose and 95% sucrose	22	30	
43%RH, 100% sucrose	7	4	~15
43%RH, 5% raffinose and 95% sucrose	<−20	<−20	

and Labuza (2006) for a tabulation of sucrose values showing that raffinose had very little effect on changing the T_g at 11%RH and 33%RH as compared to pure sucrose, the differences are not meaningful. Note that Roe and Labuza (2006) found that trehalose raised the T_g of the mixtures albeit being added at a higher percent. The glass transition temperature for the 5%-R:95%-S mixture at the 43%RH chamber was not detectable perhaps because of the lower sensitivity at 10 °C/min rate.

As shown by Labuza and Labuza (2004) these data can be used to indicate at which humidity an amorphous system can begin to crystallize at room temperature, in this case crystallization occurred at 33%RH at ~23 °C for both systems. They also found that a 100% sucrose system stored at room temperature and 11%RH which is below the T_g curve at 23 °C did not crystallize for at least 24 months like the Makower and Dye (1956) samples although they began to detect crystallization at ~200 d for amorphous sucrose at 16%RH. Labuza and Labuza (2004) samples kept in our lab for 3 years did not show crystallinity by XRD.

The XRD patterns during storage can confirm crystallization as sugars have very distinct and different patterns. Fig.1 indicated that the XRD pattern for crystalline raffinose pentahydrate shows there are three distinct peaks at ~10.3, 13.2 and 20.7 degrees. Relevant literature reports sucrose has distinct peaks at 11.6, 13.1, 18.8, 19.6 and 24.6 degrees, which can be easily discerned from raffinose crystals. Fig.2a of the XRD pattern of the 5%-R:95%-S mixture at 11%RH stored for 32 d shows that the typical amorphous glass halo pattern has several peaks representing isolated sucrose crystals that probably did not melt during the preparation of the cotton candy. Labuza and Labuza (2004) found that at room temperature and 33%RH, a 100% sucrose system crystallized within 3 d; however, as shown in Fig.2b, the 5%-R:95%-S mixture at the same conditions did not crystallize at 72 h although there were a few random and small sucrose peaks. Product stored for 37 d shown by Fig.2c, also did not crystallize, indicating sucrose crystallization inhibition by the raffinose. Finally, Labuza and Labuza (2004) found that storage at 45%RH resulted in collapse and crystallization within 6 h based on a T_g of about –7 °C to –8 °C, ie, much below room temperature. As noted, the T_g of this raffinose system could not be determined perhaps because the ice formation exotherm about it was obviously much less than 23 °C. As seen in Fig.2d, there was no crystallization at ≤24 h, although it did occur at 48 h (Fig.2e) six times longer than for pure sucrose.

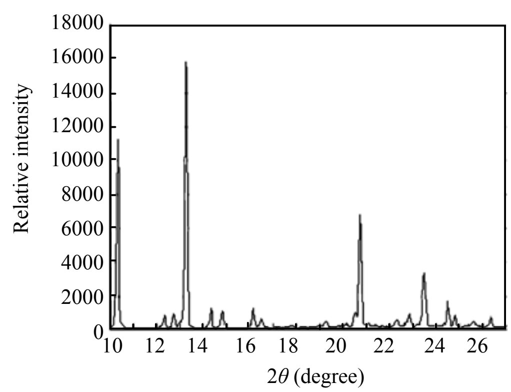

Fig.1 XRD of raffinose pentahydrate showing relative intensities as a function of Bragg angle

CONCLUSION

In conclusion, raffinose decreases the rate of

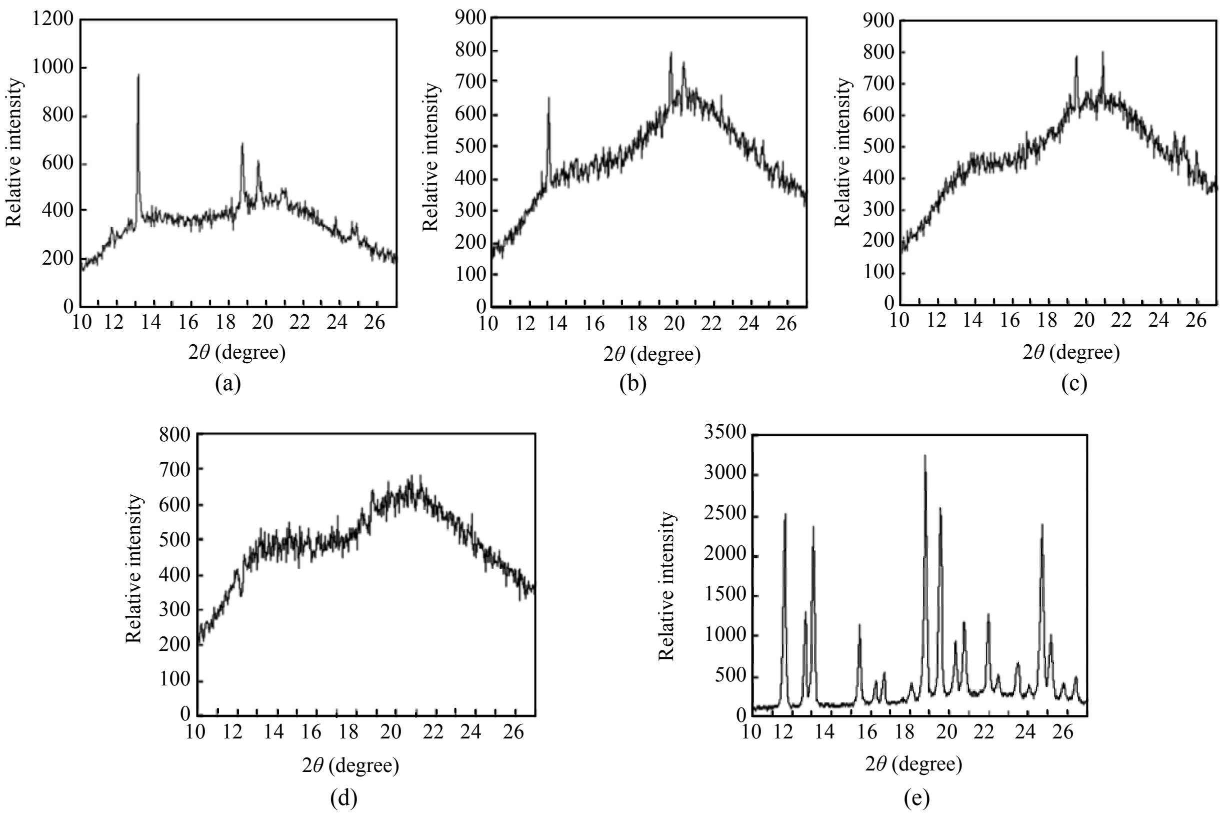

Fig.2 XRD of 5% raffinose and 95% sucrose system (a) after about 5 weeks stored at room temperature and 11%RH, (b) after 72 h stored at room temperature and 32%RH, (c) after 37 d stored at room temperature and 33%RH, (d) after 24 h stored at room temperature and 43%RH and (e) after 48 h stored at room temperature and 43%RH showing relative intensity vs Bragg angle

crystallization of an amorphous sucrose system held above its glass transition temperature. The mechanism of the retardation of the rate of crystallization based on lowering of the T_g by addition of 5 raffinose can be ruled out. Thus the actual mechanism is most likely the attachment of the sucrose part of raffinose on the major growing face of the already formed sucrose crystal. The economic benefit of increasing the shelf life of cotton candy is not significant; although, this science may be used to increase the shelf life of other foods such as sugar containing cookies which harden in a very short time due to sucrose crystallization (Labuza *et al*., 2004). Increasing the shelf life of a major food product like cookies by 2~3 d could be of large economic benefit for the food service industry and consumers. This work illustrates that understanding the properties of soft condensed matter (foods) can lead to potential solutions related to instability.

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