Journal of Stored Products Research 59 (2014) 140–145

Contents lists available at ScienceDirect

Journal of Stored Products Research

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

Sorption isotherm and state diagram in evaluating storage stability for sultana raisins

Mariam Esmaiili Bazardeh, Mohsen Esmaiili*

Food Science and Technology Department, Agricultural Faculty, The University of Urmia, P.O.Box 165, Urmia, Iran

ARTICLE INFO

Article history:
Accepted 3 July 2014
Available online

Keywords:
Sultana raisin
Sugaring
Glass transition
Sorption isotherm
State diagram

ABSTRACT

To investigate the optimum storage condition, the interrelation between water activity (a_w) and glass transition temperature (T_g) of sultana raisins were evaluated. Water adsorption isotherms of sultana raisins were measured at 15, 25 and 35 °C using an isopiestic method. The measured data were fitted into BET and GAB models. Thermal transitions of equilibrated raisins and separated crystals of raisins were analyzed using differential scanning calorimetry (DSC). The plasticizing influence of water on glass transition was modeled by Gordon–Taylor, Khalloufi and an empirical model. The state diagram was constructed by adsorption isotherm and the glass line to investigate relation between the two distinct criteria of the raisins stability. The water sorption data provided the monolayer moisture content values of 0.0789 and 0.082 g water/g dry product at 25 °C in the BET and GAB models, respectively. The glass transition temperature of raisins decreased with increasing water contents. According to the state diagram, the predictions of critical water content (C_{wc}) for stability of raisins at 25 °C was underestimated in comparison with the sorption isotherm. Results showed that the state diagram and water adsorption data may be used to predict the stability of sultana raisins and both T_g and a_w should be considered to control sugaring phenomenon in raisins.

1. Introduction

In view of the fact that theory of water activity provides a sole basis for product and process development, the relationship between rate of physicochemical changes in foods and water activity (at a given range) guide the development of food products with prolonged shelf-life and unique quality attributes. Nowadays, these developments have led to the deeper ideas of glass transition. Shelf-life of foods is strongly influenced by water content and temperature. To predict foods stability and calculate the changes of moisture content during storage, moisture sorption isotherms are determined (Gal, 1983). To get a better understanding about the factors governing the stability of foods, it is being recommended that the concept of water activity be added along with the complementary concept of glass transition (Bhandari and Howes, 1999; Roos et al., 1996). However, considerable amount of published data on water activity (a_w) and the glass transition indicate that the relationships between these concepts can be very complex, depending on the complexity of the food system and on the type of stability being studied (Rahman, 2010). For identifying stability of dried foods, the use of the state diagram based on Gordon–Taylor and the GAB (Guggenheim–Andersen–de Boer) sorption models has been proposed (Roos, 1995). The glass transition temperature (T_g) is mainly a function of moisture content, molecular weight and nature of the dry matter compounds in a given substance. As a food material undergoes the glass transition, it changes from a brittle, highly viscous glassy state to a more elastic liquid-like state.

Sultana raisin is one of the important commercial crops in the world. For producing sultana raisins, the ripe seedless grapes are usually dipped in an alkaline emulsion, and then dried by sun (Esmaiili et al., 2007). Crystallization of sugars in raisins (sugaring) is one of the major concerns of exporters and consumers due to an unattractive appearance and disagreeable texture of the raisins. Sugaring usually is seen in a long time stored raisins, when the climate becomes relatively warm and humid (e.g. during May and June). In addition fluctuating storage conditions such as temperature and humidity, excessive handling and abrasion of raisins and high moisture content are known to be important factors in sugaring (Christensen and Peacock, 2000). It is referred that the overall rate of crystallization exhibits a maximum between T_g and equilibrium melting temperature (T_m) (Sperling, 1986). It has to be considered that in dried fruits (e.g. raisins) sugars are a major

* Corresponding author. Tel.: +98 44 3277 5035; fax: +98 44 3277 9558.
E-mail addresses: esmaili_ma@yahoo.com (M.E. Bazardeh), m.esmaiili@urmia.ac.ir, esmaiilim@yahoo.ie (M. Esmaiili).

http://dx.doi.org/10.1016/j.jspr.2014.07.001
0022-474X/

component and knowledge of T_g has generally been accepted as being useful in relation to crystallization rates (Canellas et al., 1993). Time-dependent crystallization of sugars may occur above critical relative humidity. Moisture content has been shown to have the most dramatic effect on glass transition as even a marginal increase in moisture can cause a significant decrease in T_g. The time required for crystallization decrease rapidly with increasing storage relative humidity (RH) (Karel, 1973). Since amorphous sugars are more hygroscopic than crystalline sugars, crystallization may cause releasing water, thereby increasing water content, which can result in accelerated reactions in the remaining material (Kilcast and Subramaniam, 2000). At high RH the crystallized material gained water due to solubilization.

The exact cause of sugaring is not clear and the optimum storage condition for prevention of this phenomenon has not yet been covered in significant details. In this study an attempt is made to examine the interrelationship between the a_w and T_g in evaluating stability of sultana raisins during storage, to get a better understanding about the factors governing the sugaring.

2. Materials and methods

2.1. Materials

Sultana raisins were obtained from the local market in Urmia, West Azerbaijan province, Iran. The adsorption isotherms were determined by static gravimetric method. Raisins with initial moister content of 0.156 (g water/g dry product) were sliced (1 mm thick) to facilitate diffusion of water. Approximately 1 g of samples were distributed into weighing plates and placed in hermetic jars at a known a_w Nine different saturated salt solutions (LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, $Mg[NO_3]_2$, $NaNO_2$, NaCl, KCl, $BaCl_2$) were selected to give different RH in the range of 0.11–0.90. The selected salt solutions and their corresponding RH at different temperatures were taken from data reported by Sablani et al. (2001). The jars were maintained in a temperature controlled cabinet (Heraeus, UT 5050 E, W. Germany, with an accuracy of ±1 °C) at the constant temperatures 15, 25 and 35 °C. Microbial growth at high a_w ($a_w > 0.6$) avoided by using a small amount of toluene in a special support. Three replications of the same experiment were carried out. Equilibrium was established between the environment and the sample when the sample weight difference between two consecutive measurements was less than 0.001 g. The time required for equilibrium between the environment and samples was about 5 weeks or more depending on RH and temperature of the samples. Moisture content of the samples was measured by Karl Fischer titration method before and after equilibration.

2.2. Crystal separation

Crystals were separated physically from sugared raisins. Residual flesh removed to some extent by means of washings with cooled (−20 °C) absolute ethanol (Venir et al., 2010). The washing process was repeated until white crystals were obtained. Ethanol was removed from crystal mass by evaporation with dry nitrogen flow.

2.3. Determination of thermal transitions

To determine the glass transition temperature, the thermal transition experiments in equilibrated raisins were conducted with a differential scanning calorimeter (DSC823^e Mettler Toledo Stare System, USA) provided with a system for temperature control using liquid nitrogen. Heat flow and temperature calibration was performed with indium and distilled water. Following equilibration, 15–50 mg of equilibrated raisins at 25 °C ($0.1 < a_w < 0.8$) were placed in pierced lid pans (volume 40 μL) and cooled from room temperature to −80 °C. Then samples were scanned from −80 °C to 100 °C at a rate of 10 °C/min. Triplicate samples were used for thermal transition experiments. Initially selected sample with a_w of 0.44 was scanned at 5, 10, 20, 30, 60, 90, 120, 150, and 180 °C/min. Separated raisin crystals and α-D-glucose monohydrate were placed in 100 μL pierced lid pans, then scanned from −80 °C to 200 °C at a rate of 5 °C/min. An empty pan was used as a reference in each test.

2.4. Water sorption modeling

Various equations can be fitted to the experimental sorption data for grapes and dried grapes (Esmaiili et al., 2007). In this research the BET (Brunauer, Emmett and Teller) (Eq. (1)) and the GAB (Eq. (2)) models were used to predict the water sorption behavior of the samples.

$$M_e = M_b B a_w/(1 - a_w)[1 + (B - 1)a_w] \quad (1)$$

where M_e is the equilibrium moisture content (g water/g dry product), a_w is water activity, M_b is the BET monolayer moisture content and B is sorption energy constant:

$$M_e = M_g K C a_w/(1 - C a_w)[1 + (K - 1)C a_w] \quad (2)$$

where M_g is the GAB monolayer water content (g water/g dry product), C is a constant related to monolayer heat of sorption and K is a constant related to multilayer sorption heat.

2.5. Glass transition modeling

Gordon–Taylor and linear Gordon–Taylor models (Gordon and Taylor, 1952) were applied to predict T_g as a function of the solid fraction. Furthermore Khalloufi model (Khalloufi et al., 2000) and a new empirical equation were tested to predict T_g as a function of a_w (Table 1).where T_{gs} is glass transition temperature of anhydrous solids, T_{gw} is glass transition temperature of amorphous water (−135 °C), X_s is mass fraction of total solids (g solids/g product), X_w is mass fraction of water (g water/g product) and k_1, k_2, A, B, C, α and β are the constant of models. C_{kh} and A_{em} parameters in Eqs. (5) and (6), respectively, are equal to T_{gs} of the samples. All parameters were estimated by non-linear regression.

Table 1
Models used for fitting the glass transition temperature of sultana raisins.

Expression		Model
$T_g = \frac{T_{gs}X_s + k_1 T_{gw} X_w}{X_s + k_1 X_w}$	(3)	Gordon–Taylor
$T_g = T_{gs} + k_2 \frac{X_w (T_{gw} - T_g)}{(1 - X_w)}$	(4)	Linear Gordon–Taylor
$T_g = \frac{A_{kh} a_w^2 + B_{kh} a_w + C_{kh}}{\alpha a_w^2 + \beta a_w + 1}$	(5)	Khalloufi
$T_g = \frac{A_{em} + B_{em} a_w}{1 + C_{em} a_w + D_{em} a_w^2}$	(6)	Empirical model