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State diagram for freeze-dried mango: Freezing curve, glass transition line and maximal-freeze-concentration condition

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ABSTRACT

Freeze-dried mango powders containing unfreezable and freezable water were measured to explore the state diagram of mango. The state diagram was composed of the freezing curve, glass transition line, and ultimate maximal-freeze-concentration condition. Freezing points and glass transition temperatures were determined using differential scanning calorimetry (DSC) as a function of water contents. The freezing curve was fitted according to Clausius–Clapeyron model and adjusted with unfreezable water, and glass transition line was fitted to the Gordon–Taylor model. The ultimate maximal-freeze-concentration conditions were calculated as X'_w (characteristic water content, i.e. unfreezable water content) = 0.16 g water/g sample (w.b.) with the characteristic temperature as T'_g (characteristic glass transition) = −54.6 °C and $(T'_m)_u$ (characteristic end point of freezing) = −33.0 °C. The state diagram of freeze-dried mango is useful for determining the stability during storage and selecting the optimum processing conditions.

1. Introduction

Mango (*Mangifera indica* L.) is one of the most important fruits worldwide (Liu et al., 2013). The worldwide mango production was approximately 42.1 million tons, and China produced approximately 4.6 million tons according to FAO data for 2012 (FAO, 2013). Mango is a good source of health-promoting compounds, such as carotenoids, vitamin C and phenolic compounds, which show preventive effects against cardiovascular disease and cancer (Pott et al., 2003; Berardini et al., 2005). However, as a result of its perishability, the post-harvest shelf life of mangoes is relatively short. At present, drying and freezing are the most common forms of mango preservation because they can prevent the growth of microorganisms and retard many moisture-mediated deteriorative reactions. However, during these processes, the formation of glassy or rubbery non-equilibrium amorphous states frequently occurs, which is very harmful for quality preservation because it relates to collapse, stickiness, caking and re-crystallization phenomena (Roos, 1995a; Ohkuma et al., 2008; Fabra et al., 2009; Shi et al., 2012). The formation of solute crystals implies an increase in the free water and, thus, water activity, with a consequent increase in the rate of the deteriorative reactions (Fabra et al., 2009; Shi et al., 2012). In addition, foods in a rubbery state (above the glass transition temperature) become more liquid, corresponding to a more unstable state. In contrast, foods can be considered very stable in the glassy state because the molecular mobility is significantly reduced below the glass temperature (Guizani et al., 2010). Therefore, it is very important to know the storage temperatures and relative humidities (RH) that ensure the stability of freeze-dried or frozen products and help avoid changes from the stable glassy state to the rubbery one.

The state diagram of a food is the correct tool to use to identify a food's stability during storage and select suitable conditions of temperature and water content for processing (i.e., freezing and drying) (Slade and Levine, 1991; Rahman, 2004, 2010, 2012; Vásquez et al., 2013). A state diagram is the stability map of the different states of a food as a function of water or solid content and temperature. It usually consists of a freezing curve, glass transition line and maximal-freeze-concentration condition. Recently, several macro–micro regions and new terminologies have been developed for state diagrams (Rahman, 2009, 2010, 2012; Ruiz-Cabrera and Schmidt, 2015). The glass transition concept was investigated extensively in polymers, materials, pharmaceuticals and food

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sciences to relate to physical, chemical and structural changes in the physical state of a material (Rahman, 2009; Syamaladevi et al., 2009; Kasapis, 2006). For low water content products, the glass transition temperatures (T_g) at their different water contents can be obtained from experimental values. However, for high water content products, glass transition and ice formation is a more complicated process, and annealing is necessary to achieve the maximal-freeze-concentration condition. In the literature, it has been demonstrated that proper annealing protocols within a narrow temperature range between the glass transition temperature and the onset of melting (T'_m) are necessary to allow for delayed crystallization (Roos and Karel, 1991; Sahagian and Goff, 1994). However, in fact, it is very difficult to form ice at concentrations above 70% solute without extensive annealing (long times) and/or temperature cycling. Therefore, it is impossible to achieve real maximally freeze-concentrate within realistic time-frames (Le Meste and Huang, 1991; Guizani et al., 2010). The determination of the characteristic glass transition temperatures (T'_g or T''_g) of products containing freezable water by the maximal-freeze-concentration condition in the state diagram should be a more accurate method. There is a real point (T'_m) in the state diagram when all possible freezable water formed ice (Rahman, 2004; Rahman et al., 2005, 2010; Wang et al., 2008; Syamaladevi et al., 2009; Guizani et al., 2010; Shi et al., 2012).

State diagrams for aqueous solutions of pure components and model systems are more commonly reported than those of the real food because real foods are complex multi-component mixtures. A complete state diagram using glass lines and freezing curves has been reported for fruits, including apples, strawberries, grapes, dates, Chinese gooseberry, raspberry and grapefruit (Bai et al., 2001; Kasapis et al., 2000; Rahman, 2004; Guizani et al., 2010; Sá and Sereno, 1994; Sá et al., 1999; Wang et al., 2008; Syamaladevi et al., 2009; Fabra et al., 2009). However, to the best of our knowledge, the complete state diagram of mango has not been reported. Moreover, few studies in the literature include three characteristic temperatures (T'_m, T'_g or T''_m) in the state diagram (Rahman et al., 2005; Rahman, 2009, 2010, 2012; Wang et al., 2008; Guizani et al., 2010).

The objective of the current work was to determine the state diagram of freeze-dried mango by measuring the glass line (glass transition temperature versus water content), freezing curve (freezing point versus water content), ultimate maximal-freeze-concentration conditions [$(T'_m)_u$, T'_g and X'_w] and other related characteristics using DSC. In addition, the adsorption and desorption isotherms of mango were also established.

2. Materials and methods

2.1. Sample preparation and modeling of water activity

Fresh Keitt variety mangoes (*M. indica* L.) were obtained directly from a local market in Beijing, China. The water content was determined gravimetrically by placing small pieces in an oven at 110 °C for 24 h (Zhao et al., 2014). The fresh mangoes were cut into cubes (5 mm × 5 mm × 5 mm) and then completely frozen at −60 °C. The frozen mangoes were placed into a freeze-dryer (Model LGJ-12, Beijing Songyuan Experimental Instrument Co., Ltd, Beijing, China) with a vacuum of 10 Pa, while the shelf temperature was set at −45 °C and dried for 48 h. All of the samples were removed and ground immediately to fine powder by a laboratory scale grinder (Joyoung, Beijing, China). The freeze drying and powdering may affect the cellular tissue of mango, and lead to some losses of the bioactive compounds, such as carotenoids, vitamin C and phenolic compounds. But, the freeze drying is one of the most efficient methods to maintain its original physicochemical properties of mango (Sogi et al., 2014). The powdered freeze-dried mangoes were further dried in a desiccator over P_2O_5 for 1–3 weeks to completely dry the materials (Roos and Karel, 1991).

The fruits and vegetables can usually be considered the binary mixtures of solids and water. To obtain samples with water activity ranging from 0.12 to 0.94, powdered freeze-dried mangoes (1.000 g) were placed in open weighing bottles (25 mm × 40 mm) and stored in airtight containers and equilibrated for three to four weeks using saturated salt solutions with constant water activities at 25 °C (Roos and Karel, 1991; Wang et al., 2008; Ruiz-Cabrera and Schmidt, 2015). The salts used were as follows: LiCl, CH_3COOK, $MgCl_2{\cdot}6H_2O$, K_2CO_3, $Mg(NO_3)_2{\cdot}6H_2O$, $NaNO_2$, NaCl, KCl and KNO_3 with equilibrium relative humidities of 12%, 23%, 33%, 44%, 52%, 61%, 75%, 85% and 94%, respectively (Sá et al., 1999). A small amount of thymol was placed inside the airtight containers for higher a_w ($a_w \geqslant 0.75$) to prevent microbial growth during storage.

After equilibrium was reached, samples of about 4–5 mg were taken for DSC analysis. In addition, the main soluble solids of mango are sugars that are in an amorphous state, and samples were also analyzed as to the total sugar content as soluble solids using the anthrone–sulfuric acid method. The water content (dry basis) values of equilibrated samples were calculated from the weight differences of the samples before and after equilibration. At the same time, the adsorption isotherm of freeze-dried mango powders can be developed. To obtain samples with water activities higher than 0.94, pre-calculated amounts of distilled water were added directly into the freeze-dried powders in weighing bottles, and then, the bottles were sealed and placed in a dry desiccator at 4 °C for 24 h (Telis and Sobral, 2001; Shi et al., 2012).

In order to evaluate the differences between the desorption and adsorption isotherms of mango, the desorption isotherm of fresh mango slices (1.000 g) were also carried out by the above conditions of adsorption isotherm of freeze-dried mango powders. When equilibrium was reached (three to four weeks), the equilibrium water contents (dry basis) of samples were calculated from the values of initial water content and from final weights of the samples (Djendoubi Mrad et al., 2012).

The relationship between the water activity and water content (dry basis) was modeled using the Guggenheim–Anderson–de Boer (GAB) equation (Rahman, 1995; Wang et al., 2008). The GAB equation is shown in Eq. (1):

$$X_w = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where X_w is the water content in dry basis; X_m is the water content at fully occupied active sorption sites with one molecule of water, which is secure water content for high quality preservation of freeze-dried food; C and K are the GAB parameters associated with the enthalpies of monolayer and multilayer, respectively. The model parameters in GAB were estimated using non-linear regression analysis in Origin software (version 8.6).

2.2. Determination and modeling of the thermal transitions using DSC

The glass transition and initial freezing point of the mango samples at different moisture contents were measured using differential scanning calorimetry (DSC-60, Shimadzu Co. Ltd., Japan), following the method described by Xiao et al. (2012) with slight modifications. Liquid nitrogen was used to cool the samples. The DSC was calibrated for heat flow and temperature using distilled water (melting point 0.0 °C, $\triangle H_m$ = 334 kJ/kg) and indium (melting point 156.5 °C, $\triangle H_m$ = 28.5 kJ/kg). The samples (4–5 mg) were enclosed in hermetically sealed aluminum pans and loaded onto the equipment at room temperature. An empty aluminum pan