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Water sorption isotherms and phase transitions in kiwifruit

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Abstract

Adsorption and desorption isotherms were determined in entire and homogenized kiwifruit tissue. Fresh samples (desorption process) and freeze-dried samples (adsorption process), were conditioned at various water activities (0–0.675) at 30 °C and, at equilibrium, had attained different water contents. In each sample, glass transition was analysed by differential scanning calorimetry (DSC). BET and GAB models were fitted to sorption data and the Gordon and Taylor equation was used to model the water plasticization effect. Results showed that the different pretreatments applied did not imply differences in those relationships. The mean values for the parameters of the fitted models were: $w_0 = 0.057$ g water/g dry product and $C = 7.9$ (BET model); $w_0 = 0.046$ g water/g dry product, $C = 10.6$ and $K = 1.20$ (GAB model); $k = 4.88$ and $T_{g(as)} = 40.3$ °C (Gordon and Taylor model). The state diagram of the kiwifruit liquid phase was obtained including the characteristic glass transition temperature of the maximally cryoconcentrated matrix (m.c.m.) $T'_g = -52.0 \pm 0.4$ °C, the melting temperature of ice crystals surrounding the m.c.m. $T'_m = -40.4 \pm 0.4$ °C, and the amount of non-freezable water content $W'_g = 0.186$ g water/g m.c.m.

Keywords: State diagram; Adsorption; Desorption; Pretreatments; Glass transition

1. Introduction

Kiwifruits have a very short shelf-life because of softening and vitamin loss during storage, even when refrigerated (Agar, Massantini, Hess-Pierce, & Kader, 1999; O'Connor-Shaw, Roberts, Ford, & Nottingham, 1994). The use of preservation processes such as freezing or drying is common to extend the product shelf-life. Freezing combines the effects of low temperature, which slows the rate of the deteriorative reactions and microbial growth, and the cryoconcentration effect of the fruit liquid phase, associated to ice crystals formation, and the subsequent water activity (a_w) reduction. However, due to the high freezable water content of kiwifruit, freezing implies important losses in product quality (Cano, Fuster, & Marín, 1993a; Cano, Marín, & De Ancos, 1993b). Dehydration treatments applied before freezing have been reported as a tool in kiwifruit cryopreservation, mainly due to the reduction of freezable water content (Chiralt et al., 2001; Robbers, Singh, & Cunha, 1997).

Partial or total dehydration of the fruit has also been widely used. Air dehydrated kiwifruit products have an extended shelf-life due to the water content removal, but the use of elevated drying temperatures implies a substantial degradation in quality attributes (Maskan, 2001). Drying of plant tissues implies great structural changes and shrinkage. The active points for water binding after these changes are modified and some of these become inaccessible to water molecules during the dampening process, thus affecting sorption behaviour (Maskan & Gögüs, 1998; Palipane & Driscoll, 1992). An advantage of freeze-drying is that is carried out at low temperatures and the quality of freeze dried products is very high in comparison with that of the products

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dehydrated using other techniques (Ratti, 2001). Moreover, due to the direct removal of water vapour from ice crystals, the freeze dried product show an interconnected porous structure which can be rehydrated very effectively (Ratti, 2001).

To optimise freezing or drying preservation processes and the quality of the final product, it is very useful to analyse the water sorption isotherms and phase transitions which occur in the product. The water sorption isotherm (relationship between water content and water activity) is an important tool, especially in low moisture foods. It can be applied in order to optimise the drying or rehydration conditions and determine the stability of the product during storage. Changes in the relative humidity of the atmosphere in contact with the dried food imply the evolution of its a_w value and changes in water content, according to sorption isotherms, that, in turn can induce phase transitions in some phases of the food. Sample pretreatments (dehydration conditions or sample homogenisation) cause changes in the tissue structure and composition and some authors not only found different water sorption behaviour between whole and homogenised plant tissue, but also differences between water adsorption and desorption processes (Moraga, Martínez-Navarrete, & Chiralt, 2004).

Water and soluble solids such as sugars are the main fruit components. During fruit processing or storage, phase transitions such as liquid–gas or liquid–solid changes can occur in the water of the aqueous phase. In processes such as freezing, concentration, air-drying, freeze-drying, spray-drying, backing, extrusion, etc., with a time short enough for the removal of water or cooling, the formation of an amorphous state which is a non-equilibrium state is usual (Roos, 1995). When the glass transition temperature (T_g) is reached by increasing temperature, amorphous materials may change from a solid glassy state to a liquid-like rubbery one increasing the molecular mobility. The importance of the T_g of amorphous food materials for processing and storage stability has been recognized and emphasized by Levine and Slade (Slade & Levine, 1991). Above the glass transition temperature, various time-dependent structural transformations may occur in amorphous foods. Structural collapse of dehydrated structures, similar to stickiness and caking of food powders are related to a drastic decrease in the viscosity above the T_g (Levine & Slade, 1988; Roos & Karel, 1991a; Slade & Levine, 1991). The increase in the molecular mobility above the T_g may allow for the crystallization of amorphous compounds, especially in food products that contain low molecular weight sugars such as fruits. On the other hand, crispy foods such as breakfast cereals, extruded snacks, and other crispy cereal foods are often amorphous and lose the crispy texture due to thermal or water plasticization (Martínez-Navarrete, Moraga, Talens, & Chiralt, 2004; Ross, Roininen, Jouppila, & Tuorila, 1998). In this sense, the determination of the critical water activity or critical water content at storage temperature for the glass transition is important to optimize storage stability and quality of foods. In the case of frozen foods, the characteristic glass transition temperature of the maximally cryoconcentrated matrix (T'_g), is extremely important in cryopreservation, and governs ice recrystallization rates and stability during food storage (Levine & Slade, 1988; Roos, 1995).

State diagrams where transition temperatures are plotted against water content of the product, at constant pressure, are important tools for establishing proper processing and storage conditions of frozen and dehydrated foods. State diagrams have been reported for grape (Roos, 1987; Sá & Sereno, 1994), strawberry (Moraga et al., 2004; Roos, 1987; Sá & Sereno, 1994), apple (Bai, Rahman, Perera, Smith, & Melton, 2001; Sá, Figueiredo, & Sereno, 1999; Sereno, Sá, & Figueiredo, 1998) pineapple (Telis & Sobral, 2001) mango (Ayala, Walter, Martínez-Monzó, Fito, & Chiralt, 2002) and persimmon (Sobral, Telis, Habitante, & Sereno, 2001), but no data were found for kiwifruit.

The aim of this work was to obtain the state diagram of the kiwifruit liquid phase and the water sorption isotherms (adsorption and desorption) in order to optimise freezing, drying or rehydration processes and the stability of the final product during storage. To study the effect of different sample pretreatments, experiments were carried out on fresh and freeze dried samples, for both entire and homogenized kiwifruit tissue.

2. Materials and methods

2.1. Material, pretreatments and analysis

Kiwifruit (var. Hayward) was used in this study. Fresh fruit was washed, peeled and conditioned to obtain the different kinds of samples.

For sorption experiments, kiwifruit was submitted to different treatments before moisture conditioning. Sliced quarters (1 cm thick) were used as entire tissue (ET) and homogenized tissue (HT) (Ultraturrax T25 at 8000 rpm for 3 min) of kiwifruit. These samples were submitted to adsorption (A) and desorption (D) experiments, thus giving four different kinds of samples: ET-A, ET-D, HT-A, HT-D. Samples were freeze dried (frozen at −40 °C and freeze dried in a Telstar Lioalfa-6 Lyophyliser at 10^{-2} Pa) for the adsorption processes, and fresh samples were used for the desorption process. In that case, sample moisture conditioning was carried out by applying vacuum to accelerate the process and avoid microbial growth. For moisture conditioning in the samples (~2 g), these were placed at 30 °C in hermetic chambers containing saturated salt solutions with different a_w