Influence of Chemical Composition and Environmental Conditions on the Textural Properties of Dried Fruit Bars

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Abstract

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The influences of the composition, environmental humidity, and temperature on the stability of dried fruit bars during storage were investigated. Sultana bars were chosen to represent similar types of fruit bars. The moisture sorption isotherms and textural stability of sultana bars with and without glucose and maltodextrin additives were determined at 20°C and 40°C using the standard static gravimetric method. The shape of all of the isotherms was found to be typical of high sugar foods and could be explained by four different models. Additives and storage temperatures affected the monolayer moisture content, equilibrium moisture content, and the textural stability of the sultana bars during storage at the same water activity. The relationship between the loss of stiffness and water activity had a sigmoid shape and was explained by Fermi's equation. This paper fills an important gap with that which does not exist in a large number of sorption behaviour publications available in the literature. It presents real data explaining the true mechanism of textural change during storage with both water activity and glass transition theories for high sugar fruit pastes. The information obtained from this study may help the food producers, who make high sugar containing dried fruit products, to create better textural and sensory properties, and may also help to predict the storage stability and packaging requirements.

Keywords: sorption isotherms; glass transition; textural change; fermi equation; sultana; maltodextrin; sugar

Dried fruits are used for direct consumption and as ingredients in many products including baked goods, dairy foods, cereals, and cereal based products, confectionery goods, and fruit bars. Water activity is an important quality factor affecting the chemical, microbial, and textural stability of the dried fruit systems (Kaya *et al.* 2002). Moisture sorption isotherms are extremely important in the food process design, formulating new food products, selecting the appropriate packaging material, predicting the optimum storage conditions, and determining the product stability (Arevalo-Pinedo *et al.* 2004). The chemical composition of foods, processing temperature, and storage temperature have a substantial influence on the sorption characteristics of dried fruit products (Kaya *et al.* 2002; Gabas *et al.* 2007). Earlier studies have shown that the moisture sorption behaviour of prunes and raisins is affected by the sugar content, maturity, processing, and storage conditions (Bolin 1980). Studies with raisins, currants, figs, prunes, apricots, freeze-dried blueberries, and dates have also confirmed the effects of the food composition and storage conditions on the characteristic behaviour of moisture sorption isotherms (Ayranci *et al.* 1990; Tsami *et al.* 1990; Lim *et al.* 1995; Myhara *et al.* 1998). The hygroscopic nature of fruit juices with a high sugar content creates difficulties in the drying process. The difficulties associated with the moisture sorption and thermoplastic properties of these products can be overcome by the addition of maltodextrin, gums, pectin, and carboxy-methylcellucose (Gabas *et al.* 2007).

Several mathematical equations for a better understanding of the different factors in the relationship between the water activity and equilibrium moisture content of foods are presented in the literature (Brunauer *et al.* 1938; Halsey 1948; Henderson 1952; Peleg 1993; Janjai *et al.* 2007; Samapio *et al.* 2009). The agreement of these models with the experimental data shows variations depending on the water activity range and the type of food (Ayranci *et al.* 1990; Boki & Ohno 1991; Palou *et al.*1997).

The hardening of the added dried fruit pieces in breakfast cereal mixes caused consumers' complaints and drew the attention to research. It is possible for some dried fruits to maintain their optimum textural quality, while others in the same batch become very hard during storage. The changes in the physical state of dried fruit products may reflect the moisture uptake from a relatively high humidity environment or moisture loss by adsorption to other food components in the same package (e.g. cereals). Some additives are used to control the rates of the moisture transfer between the ingredients in breakfast cereals to keep the textural quality (Labuza *et al.* 2004). Maltodextrin is one of the basic additives used for improving the dried product stability during storage (Gabas *et al.* 2007).

The data published to date do not yet allow us to identify fully the cause of the variation in the physical (textural) properties of dried fruit products. The true mechanism of the textural changes during processing and storage may be explained by both water activity and glass transition theories (Sonthipermpoon *et al.* 2006). The mechanical behaviour of many solid foods and biomaterials at and around their glass transition is characterised by a sigmoid relationship between the stiffness parameters (e.g. the modulus, storage modulus, or the force at the given deformation) and the temperature, moisture, or water activity. The stiffness-water activity relationship at a constant temperature is described empirically by Fermi's model (Harris & Peleg 1996) as:

$$Y(a_w) = Y_0/\{1 + \exp[(a_w - a_{wc})/b]\} \quad (5)$$

where:

$Y(a_w)$ – stiffness parameter

Y_0 – magnitude in the glassy or dry state (assumed to be practically constant)

a_{wc} – critical water activity representing the inflection point of the corresponding $Y(a_W)$

b – constant (Harris & Peleg 1996)

The steepness of the region depicting the mechanical integrity loss is characterised by the magnitude of the constant b. Thus, when parameter b approaches zero, the shape of the curve approaches that of a steep function, and when parameter b has a relatively large value, the relationship is rather flat. The main advantage of the proposed model is that it accounts for the right concavity in the transition region. Therefore, it is especially attractive for describing the rheological behaviour of materials just before, during, and/or soon after the transition (Peleg 1994a). Peleg (1994b), Harris *et al.* (1996), and Suwonsichon and Peleg (1998) described the sigmoid relationship between the perceived degree of cereal crunchiness/crispness and the water activity by the proposed model for different types of cereal foods. Peleg (1994a,c) also tested the model using the data published on various biomaterials and obtained a consistent description of the mechanical changes at and around the transition, founding a very satisfactory fit.

This study aims at showing the effects of the composition, storage temperature, and relative humidity of the environment on the sorption characteristics and textural behaviours of dried fruit products. This paper fills an important gap with that which does not exist in a large number of sorption behaviour publications available in the literature. It presents real data explaining the true mechanism of textural changes during storage with both water activity and glass transition theories for high sugar fruit pastes. The information obtained from this study may help the food producers, who make high sugar containing dried fruit products, to create better textural and sensory properties, and may also help to predict the storage stability and packaging requirements.

MATERIALS AND METHODS

Preparation of sultana bars and composition analysis. The sultanas were products of Iran and were purchased in a local supermarket.

Table 1. The composition of the different sultana bar samples (g/100 g dry solid)

	Control	Glucose		Maltodextrin	
		experimental	theoretical	experimental	theoretical
Protein[1]	2.6	2.5	2.0	2.9	2.1
Glucose[2]	36.9	51.3	51.5	33.2	29.5
Fructose[2]	39.4	34.8	30.3	36.1	31.5
Sucrose[2]	1.0	1.0	0.8	0.9	0.8
Fat[3]	1.8	1.3	1.4	1.7	1.4
Ash[4]	2.0	2.7	1.5	2.2	1.6
Rest[5]	16.3	6.4	12.5	23.0	33.0

[1]Kjeldahl nitrogen × 6.25; [2]HPLC analysis; [3]Soxhlet analysis;[4]dry ashing at 550°C; [5]100 minus sum of all measured components

All sultanas used for bar making came from the same batch. Three different model fruit pastes, a control, glucose-added, and maltodextrin-added, were prepared. The control system was prepared by blending sultanas to a paste. The other model fruit pastes were prepared by mixing the sultanas either with 30% (dry basis) glucose or 25% (dry basis) maltodextrin (DE 5) followed by blending them to a homogeneous paste. The samples were analysed for the fat content, protein content, and ash following the standard procedures of determination (AOAC 1990). The sugar contents were measured by HPLC analysis. The chemicals that were not directly measured are listed as "rest", which may include other simple sugars, fibers, maltodextrin, etc. (Table 1). Each paste was spread on a tray and dried in an air oven at 30 ± 1°C for two days. The oven temperature was then lowered to 25 ± 1°C for 24 h, and the tray was covered with a stretch film to allow the establishment of an uniform moisture content within the paste.

Storage conditions and sorption procedures. The sorption isotherms for the model fruit systems were determined at two different temperatures. Standard saturated salt solutions with water activities ranging from 0.11–0.76 were prepared by using reagent grade salts, LiCl, $C_2H_3O_2K$, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $SrCl_2$, and NaCl. The salt solutions were prepared with distilled water and placed in desiccators. The desiccators were sealed and left at rest at 20 ± 1°C or 40 ± 1°C for 24 h for equilibration. The dried pastes were cut into 1 cm × 1 cm × 1 cm cubes, placed in Petri-dishes, and weighed. The samples were transferred into different desiccators over saturated salt solutions. Three sets from each desiccator were stored at 20 ± 1°C or 40 ± 1°C to study the moisture-humidity-temperature effects. The samples were weighed at regular intervals and considered to be at equilibrium when the differences between three consecutive readings were smaller than 0.5% of the sample weight. This typically took 4–5 weeks.

Moisture content determination. The equilibrium moisture content of the samples was measured by using the vacuum oven method (AOAC 1990) and the Karl Fischer method. The samples from the vacuum oven were dried over P_2O_5 for about three weeks for better accuracy. The results of three replicates were used to determine the equilibrium moisture content of each sample. The equilibrium moisture content of the samples was given as g/100 g dry solids.

Texture analysis. The changes in the texture of the model fruit systems were analysed using a Model 4502 Instron Universal Testing machine moving at a crosshead speed of 10 mm/min for a distance of 3 mm. Each sample was penetrated using a probe with the diameter of 0.5 cm.

Mathematical models. Four different models, GAB, Peleg, Henderson, and Iglesia and Chrifife, were used in modelling the water sorption (Table 2, Eqs 1–4). Fermi's equation (Eq. 5) was used to explain the changes in the physical state and the subsequent mechanical behaviour of the model dried food systems due to the equilibration with the environmental relative humidity and/or the alteration of the system composition at a constant temperature. The model parameter estimations were carried out using the nonlinear regression module of Data Fit Vers. 9 (Oakdale Engineering, Oakdale, USA).

Table 2. Selected equations describing the sorption equilibrium isotherms

Model	Equation		Model parameters
Peleg (Peleg 1993)	$M = k_1 a_{w1}^{n} + k_2 a_{w2}^{n}$	(1)	M – equilibrium moisture content (g water/100 g dry matter) a_w – water activity k_1, k_2, n_1, n_2 – empirical constants $n_1 < 1$ and $n_2 > 1$
GAB (Guggenheim-Andersen-de Boer) (Van den Berg 1985)	$M = m_0 CKa_w/((1 - Ka_w) \times (1 - Ka_w + CKa_w))$	(2)	M – equilibrium moisture content (g water/100 g dry matter) a_w – water activity C – dimensionless parameter, related to heat of sorption of monolayer region K – dimensionless parameter, related to heat of sorption of multilayer region m_o – monolayer moisture content (g water/100 g dry matter)
Chirife & Iglesias (Iglesias & Chirife 1982)	$M = b_1(a_w/(1 - a_w)) + b_2$	(3)	M – equilibrium moisture content (g water/100 g dry matter) a_w – water activity b_1, b_2 – constants
Henderson (Henderson 1952; Janjai *et al.* 2007)	$1 - a_w = \exp(-kM^c)$	(4)	M – equilibrium moisture content (g water/g dry matter) a_w – water activity k, c – constants

RESULTS AND DISCUSSION

The sultana bars were prepared in order to reduce the experimental variations caused by the natural physical structure and chemical composition of individual fruits, i.e., the post-harvest age of the sample, and to modify the physical and chemical characteristics through changing the system composition. The compositions of all sultana bars are presented in Table 1. There was about 12% difference between the experimental and theoretical amounts of glucose in the maltodextrin added samples and in the amount of fructose in both glucose and fructose added samples. Maltodextrin is a polymer of glucose units (DE = the degree of polymerisation minus the number of monosaccharide units in the molecules). The higher the DE, the higher is the level of monosaccharide and short chain polymers. In this study DE was 5 and there is a possibility that there were glucose monomers in the maltodextrin and these were measured in the HPLC analysis together with glucose of the formulation, therefore the experimentally measured amounts of glucose were higher than those given by the theoretical values in the maltodextrin added samples.

The total sugar concentration was high in all samples. Although the HPLC method recovers high percentages of all sugars, there might be some variations (coefficient of variation is 1.39–13.31%) from the actual values when the sugar concentration is high (Wilson *et al.* 1981). The difference between the experimental and theoretical amounts of fructose might arise from this fact.

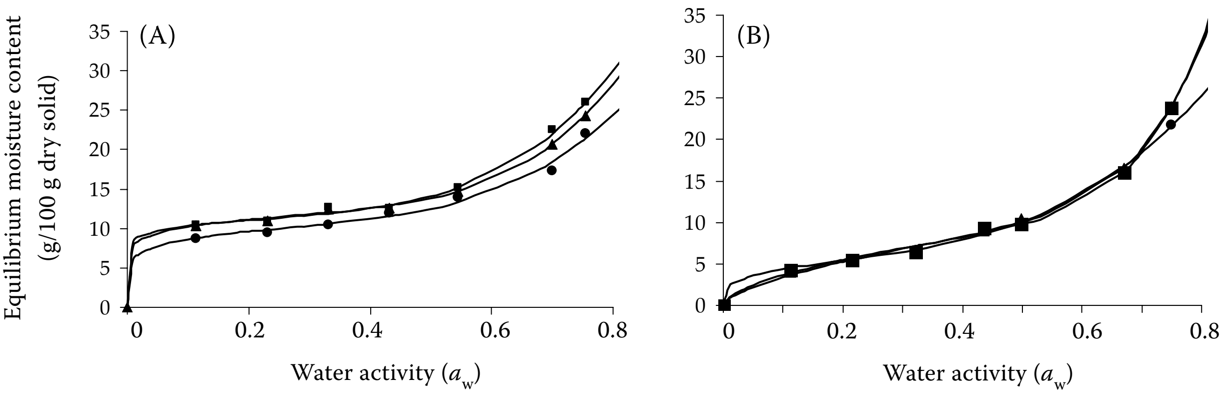

Figure 1. Peleg sorption isotherms for the control (■), maltodextrin-added (▲), and glucose-added (•) sultana bar samples at (A) 20°C, (B) 40°C

The moisture sorption isotherms for the different sultana bar formulations at 20°C and 40°C are shown in Figure 1. The shape of the isotherms at both temperatures is characteristic of high sugar containing foods, which sorb relatively small amounts of water at lower water activities and large amounts at higher water activities. Since the dissolved and supersaturated sugar systems show different behaviours, the solubility of sugars was assumed to be the primary factor in the sorption characteristics of our model foods. The equilibrium moisture content was low at low water activities since the sugar was mostly in a crystalline state, fewer sites being thus available for water adsorption. An increase in the moisture content was observed with an increase in the water activity. This was probably the result of the dissolution of sugar and an increase in the water sorption sites as a result of the transition from the crystalline sugar structure to the amorphous state. At water activities higher than 0.6, the increase was sharper for all of the samples, especially at 40°C, which is also typical of high sugar foods.

Glucose and fructose were the main constituents of all of the samples (Table 1). Glucose is less soluble in water compared to fructose. As seen in Figure 1, the equilibrium moisture content of the glucose-added sultana bar was lower than of the other two formulations at the given water activities. A decrease in the moisture sorption isotherm might be the indication of a higher proportion of glucose in the crystalline form in the medium. As explained before, crystalline sugar has fewer sites for water adsorption. Similar results were observed in one of the recent studies with different date varieties (Myhara *et al.* 2005). These results clearly show the effect of the chemical composition, which changes with the variety and stage of maturity among other things, on the sorption behaviour of foods with high sugar contents.

The control and maltodextrin samples behaved similarly at lower water activities, but the difference became clear when with an increasing water activity (a_w > 0.4) when a lower isotherm was observed for the maltodextrin-added sultana bars. This might be an indication of crystallisation in the maltodextrin-added samples, whereby the molecules rearrange themselves to be more tightly packed, due to which they cannot hold water as much as before (Samuhasaneetoo *et al.* 2004). A lower fructose concentration or the interaction between maltodextrin and sugars might also be the reason for the lower isotherms in the maltodextrin-added samples.

The decrease in the equilibrium moisture content was observed with an increasing temperature for all sultana bar formulations up to certain water activities. The equilibrium moisture content was lower at 40°C than at 20°C, at water activities below 0.7 for the glucose-added sultana bars. However, above this region, the intersection of the isotherms was observed and the moisture content increased with increasing temperature (Figure 2). A similar behaviour was also observed with the control and maltodextrin-added sultana bars at higher water activities (around 0.8). The isotherm crossing

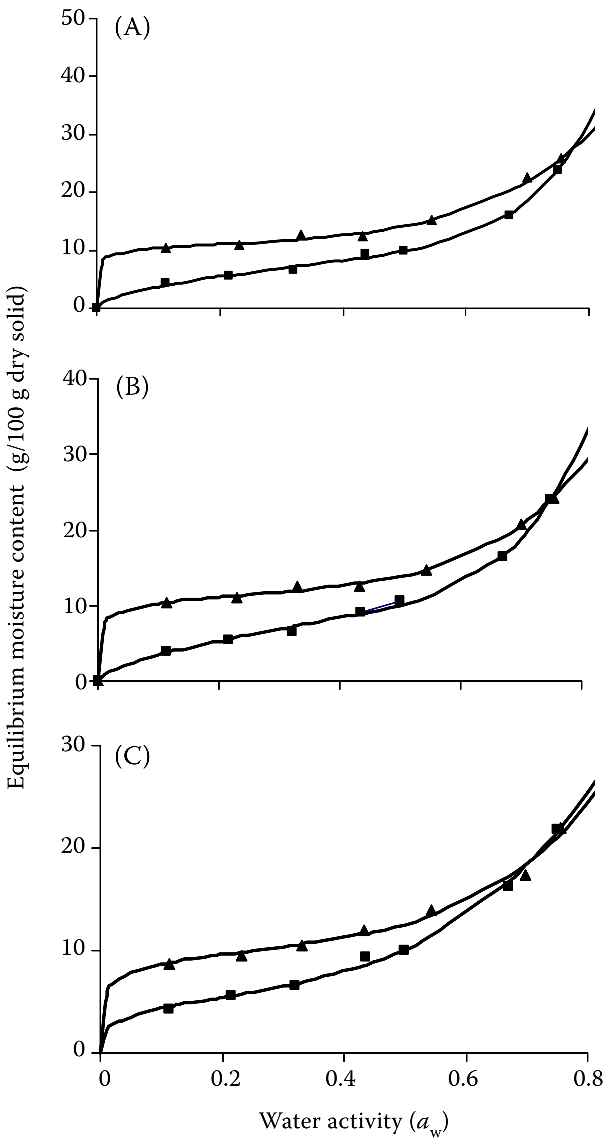

Figure 2. Peleg sorption isotherms for (A) the control, (B) the maltodextrin-added, and (C) the glucose-added sultana bar samples at 20°C (▲) and 40°C (■)

behaviour might be the result of dissolution of more sugar in water at higher temperatures, since the process is known to be endothermic. Two different temperatures were employed in this study. Similar results were obtained in the studies carried out at different temperature values. According to Arevalo-Pinedo *et al.* (2004), as the temperature increases, some water molecules are activated to an energy level that is high enough for them to break away from the sorption sites. In agreement with this study, the isotherm crossing behaviour was also observed by other researchers (Labuza *et al.* 1985; Ayranci *et al.* 1990; Lim *et al.* 1995; Gogus *et al.* 1998; Liendo-Cardenas 2000; Cervenka *et al.* 2008) but at different water activity levels depending on the type and amount of the sugar present, sugar size distribution, and food composition.

The moisture sorption behaviour of all of the sultana bar formulations was mathematically described using four different models. The constants for the models were estimated by fitting the mathematical model to the experimental data and are depicted in Table 3. All of the models fitted perfectly well to all of the data sets. Among the models used, the constants of the GAB model have physical meanings and depend on the product properties and temperature. The monolayer moisture content (m_o) is the amount of water that is strongly adsorbed to the available hydrophilic sites on the food surface and is considered as the optimum value for the product stability. A decrease in the monolayer moisture content was observed with an increasing temperature for all of the samples, which might be the result of structural changes. Similar results for the dried fruits with high sugar contents were observed by many researchers (Ayranci *et al.* 1990; Tsami *et al.* 1990; Kaymak-Ertekin *et al.* 2004; Gabas *et al.* 2007). In the present study, the monolayer moisture content was calculated to be 10.34% (dry basis) for pure sultana samples at 20°C. Ayranci *et al.* (1990), Tsami *et al.* (1990), and Kaya *et al.* (2002) have obtained similar results in the studies performed with grapes and raisins in similar temperature ranges. Maltodextrin addi-

Table 3. The estimated parameters for selected models of sorption equations for different sultana bar samples at different temperatures (°C)

Model	Parameters (constants)	Control		Glucose added		Maltodextrin added	
		20°C	40°C	20°C	40°C	20°C	40°C
Peleg	k_1	12.75	13.67	12.26	8.27	13.45	14.50
	n_1	0.09	0.57	0.15	0.28	0.12	0.63
	k_2	47.08	103.90	34.33	38.88	45.95	98.80
	n_2	4.44	7.42	4.52	3.56	4.97	7.02
	R^2	0.99	0.99	0.99	0.99	0.99	0.99
	SE	0.52	0.49	0.68	0.44	0.37	0.43
GAB	m_o	10.34	6.01	9.50	5.64	10.54	6.33
	C	19.30	7.36	18.13	12.44	18.98	6.35
	K	0.798	0.990	0.734	0.995	0.749	0.992
	R^2	0.96	0.99	0.97	0.99	0.95	0.99
	SE	1.57	0.80	1.20	0.36	1.55	0.65
Chirife & Iglesia	b	5.44	6.62	4.27	6.06	4.74	6.79
	c	9.34	3.51	8.36	3.88	9.56	3.43
	R^2	0.99	0.99	0.99	0.99	0.99	0.99
	SE	0.67	0.57	0.58	0.39	0.44	0.43
Henderson	c	2.12	1.22	2.18	1.33	2.14	1.19
	k	0.00178	0.036	0.0022	0.028	0.0018	0.038
	R^2	0.90	0.97	0.94	0.97	0.91	0.97
	SE	0.08	0.044	0.06	0.043	0.076	0.040

m_0 (g/100 g dry solids)

tion resulted in a small increase in the monolayer moisture content of the product compared to the control sample since there might be more hydroxyl end groups as adsorbents. The monolayer moisture content for the glucose-added sultana bars was lower than for the other two samples, probably because of crystallisation, which results in fewer hydrophilic sites to bind water. The constant *c* of the GAB equation is related to the first layer interaction between the molecules and it decreased with an increased temperature for all sultana bar formulations.

All sultana bar formulations exhibited varying degrees of textural changes during storage depending on the relative humidity, temperature, and the product composition. A sigmoidal relationship between stiffness and water activity was observed at and around the transition for all the systems and was well described by Fermi's equation (Eq. 5). The fit of the model to the experimental data is shown in Figure 3, and the parameters are given in Table 4.

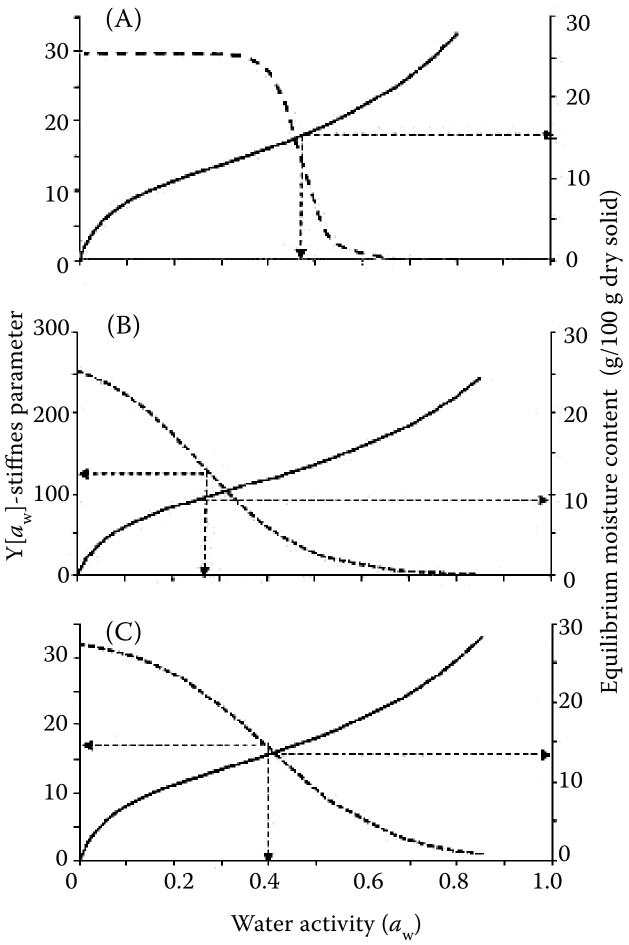

Figure 3. The effect of the water activity on the stiffness loss (.....) of (A) the control samples, (B) the glucose-added samples, and (C) the maltodextrin added-samples

Table 4. Description of the textural change in the different sultana bar formulates using the Fermi Equation (Harris & Peleg 1996)

Sample	Equation
Control	$Y(a_w) = 29.6/\{1 + \exp(a_w - 0.47)/0.03\}$
Glucose added	$Y(a_w) = 278.1/\{1 + \exp(a_w - 0.26)/0.11\}$
Maltodextrin added	$Y(a_w) = 33.4/\{1 + \exp(a_w - 0.4)/0.13\}$

The values of $Y(a_w)$ were referred to as indicators of stiffness in this study and mentioned as stiffness parameters in the text for simplicity (Peleg 1994a). The magnitude of the stiffness parameter in the glassy or dry state, expressed by Y_0, was similar for the control and maltodextrin samples (29.6 and 33.4, respectively), but an obvious difference was observed for the glucose sample (278.1). As seen in Figure 3, the glucose added samples were very hard compared to the other two samples. One can conclude from these results that the maltodextrin-added samples were plasticised at a lower moisture level than the control samples (m_c = 13.4% vs 15.2% and a_{wc} = 0.4 vs 0.47, respectively). However, the transition was steep for the control samples, which occurred in wider ranges for maltodextrin samples (b = 0.03 and 0.13, respectively). The rate of stiffness loss lowered with the addition of maltodextrin, since it is difficult for water molecules to diffuse through the macromolecules. With both samples, the critical moisture content was higher than the monolayer moisture value obtained from the GAB equation. The textural change occurred at lower moisture levels and water activities (m_c = 9.5%, and a_{wc} = 0.26) in the glucose-added samples compared to the other two samples. The transition was wider compared to the control samples (b = 0.03, and 0.11, respectively), but the samples were very stiff, even after the transition. All of the samples were very soft to test at 40°C, even at very low water activities.

CONCLUSION

In this paper, the importance was studied of the chemical composition, environmental humidity, and temperature on textural stability of sultana bars during storage. The adsorption isotherms of the samples followed the characteristic shape of high sugar foods. The equilibrium moisture content was the lowest in the glucose-added samples compared to the other two samples at the given water activities. The moisture sorption behaviour of the control and the maltodextrin-added samples was similar below a water activity of 0.4, but a decrease in the equilibrium moisture content was observed with the maltodextrin-added samples above that level. At the same water activity, the samples showed lower equilibrium moisture contents with increasing temperature. The GAB model was used to predict the monolayer moisture contents of the sultana bar samples. Monolayer moisture content increased with the maltodextrin addition and decreased with the glucose addition. The temperature increase caused a decrease in the monolayer moisture contents. The experiments were done at two temperatures only in this work. Although similar findings are reported in previous studies as explained in the discussion part, the results of the temperature effect might be taken with limited validity. This study showed that the loss of textural structure of sultana bars is related to the product composition, environmental humidity, and temperature. The addition of maltodextrin lowered the rate of the structure loss during storage. The sultana bars with higher glucose concentrations were extremely hard. The samples got softer as the temperature increased. The textural loss was sigmoidal for all of the samples and was explained by Fermi's equation at the given temperatures.

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List of abberation

a_w	water activity
a_{wc}	critical water activity
b, c, k, n	empirical parameters
C, K	GAB parameters
M	equilibrium moisture content (g/100g dry solids)
m_0	monolayer moisture content (g/100g dry solids)
Y	stiffness parameter (KPa)
Y_0	stiffness parameter in glassy or dry state (KPa)

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