Moisture sorption curves of fruit and nut cereal bar prepared with sugar and sugar substitutes

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Abstract Low sugar, low fat, dry fruit and nut cereal bars without sugar were prepared using cereals, nuts, and sugar substitutes. The sorption characteristics of the bars prepared with sugar substitutes in comparison with that of sugar were studied by keeping the bars at water activity (a_w) from 0.1 to 0.9. The sorption isotherms of low sugar bars were practically identical below a_w of 0.5 but above a_w of 0.5, a clear differentiation in the isotherms could be observed compared to that of sugar counterpart. A sharp increase in moisture content was observed in the bars prepared with alternative sweeteners, above a_w 0.6, whereas a gradual increase in a_w was observed in the case of bar prepared with sugar. The ERH (Equilibrium relative humidity) value for bar with sugar was 50 %, and for bars prepared with alternative sweeteners, it was about 60 %. Low sugar cereal bar prepared with sorbitol + maltitol (SM) syrup scored higher sensory quality compared to other product prepared with sorbitol + nutritose (SN) as the former retained softness and chewiness on storage. Thus, it was observed that bars with alternative sweeteners will be more stable as their ERH is closer to normal ambient conditions compared to that prepared with sugar.

Keywords Moisture sorption · Low sugar cereal bar · Dry fruit and nuts · Sugar substitutes · ERH

Introduction

Cereal bars are ready to eat sweet products, providing nutritional value without sacrificing the taste or flavour, as well as possess a reasonable shelf life during which the texture remains chewy without being sticky, hard or crumbly. They can be fortified with vitamins, minerals and dietary fibre to make them into a wholesome food. Also, other ingredients like dry fruits, fruit concentrates, oat products, wheat flakes etc. could be incorporated to prepare a variety of cereal bars. Cereal bars are popular as portable foods and can be consumed in between meals or along with lunch or dinner or even as meal substitutes. These cereal bars normally contain sugars as main ingredient, which act as binder and sweetener. Due to increased health consciousness of the consumer and negative effects of sugar on glycemic index and its associated ailments, the demand for sugar free products is increasing. To meet these requirements, a low fat nutri cereal bar with no added sugar was prepared. In the present paper, appropriate sugar alternatives were used to obtain low-sugar, low fat nutri cereal bar similar to that of sugar counterpart and hence can be consumed by health conscious consumers as well. For this purpose, sugar alternatives having physical properties closer to those of sugar, such as sorbitol in combination with maltitol and nutritose, were used. These alternatives in addition to having lower glycemic index, impart lower calories compared to that of sugar. In cereal bars, texture has a significant effect on its acceptance by consumers because texture perception influences overall sensory appreciation (Wilkinson et al. 2000). This is especially true in food/cereal/cereal bar industry, where the surface hardening occurs during storage, which results in lowering consumer acceptance (Stefan 2003).

Padmashree et al. 2012 have developed a shelf stable protein rich composite cereal bar, using soya concentrate and soya isolate with a shelf life of 6 months. They observed

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that development of hard texture during storage was the limiting factor for shelf life though the product remained chemically and microbiologically safe and stable during the entire storage period studied. The protein level, texture and taste were improved by incorporation of whey protein concentrate and whey protein isolate in date bars without affecting the sensory characteristics during storage (Nadeem et al. 2012). The influence of chemical composition and environmental conditions on the texture of dried fruit bars were studied by Ozlügen (2011) with special emphasis on the relationship between the loss of stiffness and water activity of fruit bars with high sugar content.

Sorption isotherms of food stuffs are essential for design, modeling and optimization of processes such as drying, aeration and storage (Labuza 1968 and Bala 1991). Knowledge of sorption isotherms is important for predicting stability and quality changes during packaging and storage of dried foods. To select suitable packaging material and to protect the product against quality deterioration, sorption isotherm data is essential. In recent years, an increasing amount of attention has been given to sorption properties of foods. These are being examined especially in light of their effect on the storage stability of dehydrated products, as well as the effects on diffusion of water vapor, under conditions such as removing the final traces of water from foods. The information from moisture sorption data reveals deteriorative reactions in foods. It also provides an easy way to evaluate physical, chemical and microbiological parameters for the determination of stability of dehydrated foods (Labuza et al. 1970 and Mizrahi and Karel 1977). Sorption isotherms of food stuffs are essential for design, modeling and optimization of many processes such as drying, aeration and storage (Labuza 1968 and Bala 1991).

The main objective of the present work was to study the effect of sugar substitutes on moisture sorption characteristics of low-sugar, low-fat, dry fruit and nut cereal bar in comparison with that of sugar counterpart.

Materials and methods

Sucrose (cane sugar) was procured from the local super market. Sorbitol syrup (70 % solids) was obtained from Loba Chemie, Mumbai, India. Maltitol, nutritose and sucralose were procured from Roquette India pvt Ltd., Mumbai, India. Skimmed milk powder, defatted soya flour, cocoa powder, oats, rice flakes, raisins, almonds, dates, peanuts, wheat bran and refined sunflower oil were procured from the local market of Mysore, Karnataka, India. Guar gum used was procured from S.D. Fine chem. Ltd, Mumbai, India and maltodextrin was procured from Sukhjit Starch and chemicals Ltd, Phagwara, Punjab, India.

Preparation of dry fruit and nut cereal bar Binding syrup (40 g) consisting of sugar, glucose syrup (78°B) and glycerol

(66°B) is heated to 115 ± 1 °C. All the dry solid ingredients (39 g) such as maltodextrin, gum, skimmed milk powder, defatted soya flour, cocoa powder, oats, wheat bran, fried rice flakes were mixed into hot syrup. Dry fruit and nuts (20 g), including raisins, almonds, dry dates, peanuts were weighed into a container and were added to the hot syrup and mixed thoroughly. 1 g of oil was added to the hot mass to reduce stickiness and improve sheeting and cutting. The mass was sheeted and cut into $6.5 \times 3 \times 1$ cm cubes. Sugar and glucose syrups were replaced in case of sugar free bars. Two types of sugar free binder syrups were prepared. One with sorbitol syrup (70°B)+maltitol syrup (55°B) in the ratio 70:40 (w/w) (SM) and another with sorbitol syrup (70°B)+nutritose powder in the ratio 75:45 (w/w) (SN). Sucralose was added to both syrups at equi-sweetness levels (0.06 g/100 g of syrup) compared to sugar. The processes remain same for the preparation of both sugar and low sugar cereal bars. The finished bars were placed in metalized polyester pouches, sealed, labeled and kept for storage at room temperature of 27 ± 1 °C 65 % RH.

Sorption studies Saturated salt solutions of lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, magnesium nitrate, sodium nitrate, sodium chloride, potassium chromate and ammonium phosphate were used to obtain different RH combinations having a_w values of 0.11, 0.22, 0.33, 0.44, 0.54, 0.64, 0.72, 0.86 and 0.92 respectively (Wolf et al. 1984). These saturated solutions were taken in different desiccators and were used for sorption studies. Prior to keeping the bars in these desiccators, the samples were conditioned to Indian standard conditions of 65 % RH at 27 °C. The initial moisture contents (IMC) of these cereal bars were measured in triplicate on dry weight basis (db) by toluene distillation method (AOCS 2001). The sorption experiments were carried out by keeping approximately 10 g of each sample ($n=3$) in desiccators and recording their weights at frequent intervals until they reached constant weight (with ± 5 %). All the chemicals used were of analytical grade.

Sorption models Moisture sorption isotherms describe the mathematical relationship between a_w and moisture content. The parameters of the equations could be used to construct the moisture isotherm for a particular food. Many investigators have reviewed sorption isotherm equations in literature [Eqs. (1) and (3) in Table 1]. These parameters are useful for prediction of moisture content of food during ingredient mixing, preparation, packaging and storage. The parameters of all the equations are presented in Table 2. A number of sorption isotherm models have been reported. In the present study, Caurie (Caurie 1970), Khun (Chirife and Iglesias 1978) and Guggenheim Anderson de Boer (GAB) models (Table 1) were used for fitting the sorption data. The equations were rearranged to linear

Table 1 Selected isotherm equations for experimental data fitting

Model	Equation	Linearized equation	Constants	Reference
GAB	$\frac{M}{M} = \frac{Gka_w}{(1-Ka_w)[1-Ka_w+GKa_w]}$	$M = \frac{a_w}{(A * -a_w^2)[B-a_w + C]}$ $A = \frac{k}{M_0(1/G)^{-1}}$ Where $B = \frac{1}{M_0[1-(1/G)]}$	Mo, G, K	Bizot (1984)
Caurie	$M = a + b * a_w$	$M = a + b * a_w$	a, b	Caurie (1970)
Kuhn	$M = a + b a_w$	$M = a + b \left(\frac{1}{\ln a_w} \right)$	a, b	Chirife and Iglesias (1978)

form to determine the appropriate constants (Table 2) by regression analysis using MS Excel software. The sorption data were analyzed according to the models and the corresponding constants were determined. The goodness of fit of each model was computed in terms of coefficient of determination (R^2) from the plot of experimental (M_{pre}) sorption moisture and root mean square error (RMSE) values calculated as follows:

$$RMSE = \left\{ \left[\frac{(M_{exp} - M_{pre})}{M_{exp}} \right]^2 / N \right\}^{0.5} \times 100$$

M_{exp} Moisture content experimental (% db)

M_{pre} Moisture content predicted (% db)

N Number of observations

Linear models with high R^2 and low RMSE values are considered to be statistically acceptable.

Texture measurement The hardness of cereal bars ($6.5 \times 3 \times 1$ cm) was measured by compression using a Universal testing machine (Model: LR—5 K, Lloyds, England, UK) with cylindrical plunger for 50 % of deformation using a load cell of 1 KN with 8 replicates with a cross head speed of 50 mm/min. The maximum force during deformation was recorded as hardness (N).

Sensory evaluation The desirable characteristics of cereal bars were evaluated sensorily by a trained panel of 12 judges by following the method of Quantitative Descriptive Analysis (QDA). The definitions of the attributes were discussed and descriptors developed by asking the panelists to describe the product with the suitable descriptive terms for development of a score card, which consisted of each attribute on a 15 cm line scale. Quantitative descriptive analysis methods were adopted and the panelists were asked to mark the intensity of each attribute (Stone and Sidel 2004). Freshly prepared as well as stored (90 days) cereal bars were evaluated for sensory quality. The judges were asked to perceive the attributes such as color, surface stickiness, hardness, crunchiness, sweetness,

Table 2 Estimated coefficient of determination (R^2) and RMSE values of different models for sorption isotherms for cereal bars prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutrose (Low sugar SN)

Model Isotherm	Range of water activity (a_w)	Type of cereal bar	Constants of Linear fitting			R^2	RMSE
			M_0	G	K		
GAB	0.1–0.9	Sugar	4.94	125.21	0.87	0.97	7.84
		Low Sugar SM	3.02	−122.76	0.90	0.93	10.32
		Low Sugar SN	3.15	−120.45	−0.86	0.92	11.64
Caurie	0.1–0.9	Sugar		1.435	−0.168	0.93	15.41
		Low Sugar SM		4.47	−0.0411	0.95	10.32
		Low Sugar SN		4.76	−0.0541	0.93	12.11
Khun	0.4–0.9	Sugar		0.15	−2.54	0.94	15.17
		Low Sugar SM		3.76	−3.11	0.92	20.21
		Low Sugar SN		3.14	−2.76	0.90	25.46

chewiness and the overall quality score were evaluated by drawing a vertical line on the scale for coded products.

Statistical analysis The results of the proximate composition of the cereal bars were statistically analysed by comparing the means using Duncan's Multiple Range Test (DMRT, Duncan 1955).

Results and discussion

Sorption models The time to reach equilibrium for different samples of cereal bars at 92 % RH was about 20–25 days and mold growth was detected by visual inspection at the end of 28 days. The sorption curves for equilibrium moisture content (dry basis) obtained for different bar samples are shown in Fig. 1. The isotherm showed three regions: region A, corresponding to $a_w < 0.2$, which relates to adsorption of monomolecular film of water; region B corresponds to adsorption of additional layers over this monolayer at a_w 0.2–0.7 and region C, for $a_w > 0.7$, corresponding to condensation of water in the pores of the material followed by dissolution of soluble material (Labuza 1968). At lower a_w , the slope of the curve was less and the slope increased rapidly with increase in a_w . Cereal bars prepared with sugar showed low moisture pick up in the region a_w 0.1 to 0.6, whereas bars prepared with no added sugar showed moisture pick up above a_w 0.7. The sorption isotherms of low-sugar bars were practically identical below a_w of 0.5 but above a_w of 0.5, a clear differentiation in the isotherms could be observed compared to that of sugar counterpart. A sharp increase in the moisture content was observed in the bars prepared with alternative sweeteners above a_w 0.6, compared to a gradual increase in the case of bar with sugar.

In general, the equilibrium moisture content (EMC) increased slowly at lower a_w between 0.1 and 0.6, followed by

Fig. 1 Sorption isotherms of cereal bars prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutritive (Low sugar SN)

Fig. 2 Sorption isotherms of cereal bar prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutritive (Low sugar SN) by various models; EMC=equilibrium moisture content, dry basis (db)

a steep rise at a_w 0.7. Similar curves have been reported by Agarwal and Clary (1971) for rice and also *dudh churpi* and by Hossain et al. (2002) in dairy products like casein and khoa. Pistachio nuts also showed similar curves even at different temperatures (Tavakolipour and Ashtari 2008). At lower water activities, the physical state of the sugars may

Fig. 3 Compression (n) values of cereal bars prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutritive (Low sugar SN) on storage (27 °C, 65 %RH)

Fig. 4 Sensory quality of cereal bars prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutritive (Low sugar SN). Initial (a) and stored (b) at 27 °C, 65 % RH for 90 days

have an effect on the sorption properties. Amorphous sugars are known to absorb more water than the crystalline materials (Chinachoti and Steinberg 1986). At higher water activities >0.7, an exudation (leaching of sugars) is observed.

The experimental and predicted sorption curves of bars prepared with and with no added sugar by various models are shown in Fig. 2. Various equations for fitting the three mathematical equations on experimental moisture sorption data are shown in Table 1.

Sorption model analysis The fitness of three moisture isotherm mathematical models to the moisture sorption data for both cereal bars over entire range of a_w was evaluated and judged by R^2 and RMSE values. The value of root mean square error (RMSE) represents the fitting ability of a model in relation to the number of data points. The smaller the RMSE value, the better the fit of a model (Hossain et al. 2001). Sorption analysis of different models showed different fitness levels. The degree and range of fitness depends on the model and type of product. The constants for respective models and RMSE are shown in Table 2.

The GAB model is the most popular in the area of food technology. Sorption fits extremely well for most food material over a wide range of a_w (Bizot 1984). The most successful three parameter model is the GAB model (Guggenheim-Anderson De Boer). The GAB constants M_0 , G and K were computed from linear regression of I/M versus a_w . The lowest RMSE values (7.8–11.64) were observed for GAB models. The M_0 values ranged from 3.02 to 4.94. The best fit and lowest RMSE values were obtained from the GAB equation (Table 2) for all the three types of bars studied.

Caurie model is valid from a_w 0.1–0.9. The R^2 values for bar prepared with sugar substitutes were 0.93 to 0.95 and showed high RMSE values indicating a moderate fit (Table 2) for the bar prepared with sugar and a good fit for the bars prepared using sugar alternatives.

The Khun model holds good for a_w ranging from 0.4 to 0.9 and the constant 'a' ranged from 0.4 to 0.9 and the constant 'b' from 0.15 to 3.76. The RMSE values ranged from 12.84 to 16.8 for all the samples studied indicating a poor fit.

The constants derived from different sorption models are useful in the evaluation of stability of low sugar cereal bars. The GAB model, which had the lowest RMSE and highest R^2 values indicates it to be the best suitable model, compared

Table 3 Proximate composition cereal bar prepared with sugar, mixture of sorbitol and maltitol (Low sugar SM) and sorbitol and nutritive (Low sugar SN)

	(%)	Sugar	Low sugar SM	Low sugar SN
Moisture		8.78±0.30 ^b	7.75±0.10 ^a	8.12±0.40 ^b
Protein		11.00±1.51 ^a	12.81±1.62 ^b	11.7±1.58 ^a
Fat		8.41±0.67 ^b	7.61±0.72 ^a	7.60±0.77 ^a
Minerals		2.94±0.13 ^a	2.74±0.18 ^a	2.86±0.16 ^a
Crude fiber		1.80±0.25 ^a	2.17±0.18 ^a	1.94±0.28 ^a
Calcium (mg)		324.75±9.01 ^a	340.28±8.51 ^b	336.40±9.78 ^{ab}
Iron (mg)		6.67±1.32 ^a	7.13±1.87 ^a	6.85±1.93 ^a
Energy (kcal)		374±5.67 ^c	331±6.01 ^b	295±5.50 ^a

Mean values bearing different superscripts in a row are significantly different ($p \leq 0.05$) ($n=3$)

to the other models. These equations can be used to predict storage stability or conditions needed to prevent microbial growth and also to predict water activity of similar foods (Table 2).

Texture analysis of cereal bar Hardness of freshly prepared cereal bars ranged from 183 to 301 N. The highest value of 301 N obtained for bar prepared with sugar (Fig. 3). All the products on storage showed a gradual increase in hardness. It was reported that hardening is influenced by the polyol used in the bar formulation as well as the combination of protein and polyol (Liu et al. 2009). Cereal bar prepared with sugar showed crystallization on storage and low sugar SM bar had the lowest value for hardness after 90 days of storage. McMahon et al. (2009) observed hardening of bars with increase in a_w . Li et al. (2008) found that hardness of the bars made with polyol syrup increased from initial a_w of 0.52 to 0.56 after 42 days of storage at 32 °C. Liu et al. (2009) also compared influence of different polyols on hardening of the bars and reported that glycerol was better in preventing hardness than sorbitol or maltitol. Glycerol acts as a better plasticizer because it is smaller and less excluded from the hydrophobic regions on the protein surface protein surface (Chanasattru et al. 2008).

Sensory analysis Sensory analysis showed that the color of both sugar and low sugar cereal bars were slightly dark brown in color. Surface stickiness was higher in sugar and low sugar SM cereal bars. Low sugar SN cereal bar showed lower surface stickiness, chewiness and crunchiness compared to the other two products (Fig. 4A). Sweetness of all the 3 cereal bars was the same. The overall acceptability scores of sugar and low sugar SM were similar whereas low sugar SN cereal bar showed slightly lower overall quality score mainly due to harder texture and reduced chewiness.

On storage, the cereal bars showed decreased intensity in the intensity of brown color and in surface stickiness. Hardness of all the three products increased slightly on storage (Fig. 4B). Similar results were observed by Padmashree et al. 2012, where the bar became harder during storage and influenced the overall acceptability scores and hence the shelf life. Chewiness of the cereal bars also decreased on storage and the overall quality of the stored cereal bars was lower than that obtained for freshly prepared cereal bars. Low sugar SM bar scored the highest among the stored products indicating that it was better than low sugar SN as it maintained the chewiness and crispness on storage. Cereal bar prepared with sugar showed crystallization and was less chewy. Low sugar SN cereal bar was harder and less chewy thus scored the least (4.0) for overall quality.

Proximate composition The proximate nutritional composition of all the 3 cereal bars is given in Table 3. The moisture

content of the bars varied from 7.7 to 8.7 %±1. The protein content ranged from 11 to 12 %±0.4. The fat content of cereal bar with sugar was marginally higher compared to those of the other 2 bars. Crude fiber of all the bars ranged from 1.8 to 2.1 %. Mineral content i.e., calcium was between 324 and 340 mg, iron content ranged from 6.6 to 7.1 mg. No substantial changes in nutritional values were observed among all the bars and hence the differences in ERH between the bars observed were mainly due to the type of syrups.

Conclusion

Low sugar, low fat, dry fruit and nut cereal bar is soft and chewy, ready-to-eat sweet snack. The sugar and low sugar cereal bars prepared were evaluated for physico-chemical characteristics such as moisture, texture and nutritional facts. The moisture content of the bars was very critical as it determined the quality of the product. The sorption isotherms of low sugar bars were practically identical below a_w of 0.5, but above a_w of 0.5, a clear differentiation in the isotherms were observed compared to that of sugar counterpart. A sharp increase in moisture content was observed in the bars prepared with no added sugar (SM and SN) above a_w 0.6. But in the case of the bar with sugar, a gradual increase in a_w was observed. The ERH value for bar with sugar was 50 %, whereas for bars prepared with no added sugar, was about 60 %. Thus, it was observed that bars with no added sugar was more stable as their ERH are close to normal ambient conditions compared to that prepared with sugar.

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