
Sorption Isotherm of Corn Chips Made from Blends of Corn Flour and Bambara Groundnut Nut Flour

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Abstract: The adsorption equilibrium moisture contents of corn chips (kokoro) made from blends of maize flour and Bambara nut flour was investigated by measuring water activities at 27°C, 37°C and 40°C using the static gravimetric method. Sorption isotherms followed a type II shape in water activities range from 0.10 - 0.80 showing characteristics of most biological tissues. Five isotherm model equations were used which are BET, GAB, Oswin, Halsey and Henderson. The experiments were performed using polythene packaging and exposed petri dishes. The samples were weighed at two days interval until equilibrium was attained when three identical measurements were obtained. The equilibrium moisture content (EMC) decreased with increase in temperature at constant water activity and polythene packaging had lower EMC compared to petri-dishes. Oswin and Henderson model were best fit at 27°C with $RSS = 1.929 \times 10^{-5}$, $SEE = 0.00011$, $R^2 = 0.99531$ and $RSS = 0.001192$, $SEE = 0.00011$, $R^2 = 0.9807$ for polythene and petri-dish respectively. Oswin model was best fit for both storage conditions at 37°C and 40°C. The monolayer moisture content at the three temperatures ranged from 0.0193 - 0.0752 and the general model observed for this study that could predict the sorption behavior of Bambara-corn chips was Oswin model.

Keywords: Bambara Nut, Corn Chips, Equilibrium Moisture Content, Sorption Isotherm, Temperature, Model

1. Introduction

A fundamental property of biological materials which influences dehydration, shelf-life prediction and storage stability is the water sorption characteristics [1]. The sorption characteristics are often represented by moisture sorption isotherms which are plots of moisture content against water activity (a_w) at certain temperatures [2]. The relationship between water activity and water content at a given temperature is known as the moisture sorption isotherm [3]. The knowledge of the sorption equilibrium is very important for predicting the stability and quality changes during packaging and storage of dehydrated foods and formulations that deteriorate mainly by gaining moisture such as flours, cookies and snacks.

Since current predictive methods are not able to simulate system as complex as foods, experimental determination of moisture sorption isotherm of foods is required [4]. The sorption isotherm can be measured by means of three different techniques namely gravimetric, manometric or hygrometric [5]. Gravimetric technique which is based on weight change of the food at various relative humidity or water activity is commonly used. A precise method of presenting food sorption isotherms is through the use of isotherm models, where the constants of the equations can be tabulated for each isotherm. These constant (parameters) are used to construct moisture isotherms and thus helpful in describing moisture changes during drying, packaging and storage of foods [4]. Diverse models have been developed such as, non-linear, linear regression models, constituted in their parameters by two, three, four and partial regression coefficients aiming to

mathematically express the relation between the water activity of food and its moisture content. Isotherm equation varies in terms of origin (empirical, semi-empirical, or theoretical) and applicability (water activity limit and type of food). The usefulness of a particular model depends on the objective of the user. Important factors in selecting sorption models include closeness of fit to the experimental data, the range of applicability, the theoretical basis of the parameters, simplicity of the model and the desired objectives [3]. Certain isotherm equations mathematically describe data better for some foods than for others. Several mathematical models have been proposed to describe sorption isotherms. The most common equations that are used for describing sorption in food products are the Langmuir equation, the BET equation, the Oswin model, the Smith model, the Halsey model, the Henderson model, the Iglesias-Chirife equation, the GAB model, and the Peleg model [6].

Maize (*Zea mays* L.) is a major staple food crop throughout the world, and a major feedstuff in developed and developing countries. It is an economically important vegetable crop grown in many parts of the world including Middle East, Africa, India, Pakistan, Malaysia, Brazil, Turkey, southern states of USA etc. [7]-[8]. In the world, it is cultivated on more than 142 million hectare of land with an estimated production of 913 million tons approximately [9]. Maize is the fourth most important cereal crop in Nigeria ranking behind sorghum, millet and rice in the number of preferred food for people [10]. It is reported that maize seeds have moisture (11.6 - 20.0%), ash (1.10 - 2.95%), protein (4.50 - 9.87%), fat (2.17 - 4.43%), fiber (2.10 - 26.70%) and carbohydrates contents (44.60 - 69.60%) [11]. Maize also provides many of the B vitamins along with fiber, but lack some other nutrients, such as vitamin B12 and vitamin C [12]. In addition to nutrients (high level of vitamins, minerals and dietary fibers), maize grain also contain a number of elements (Cu, Fe, Ni, Mn and Zn) [13]. Based on its abundance and great nutritional value, it can be used as raw material for manufacturing many industrial products [14]. As industrial product, maize, being popular as a food item, is enjoyed by people in various forms, like whole corn, corn flour, corn starch, corn syrup, corn meal, popcorn, cornflakes. Other areas of its uses reported are in corn gluten, tortillas, tortilla chips, polenta cornmeal, corn oil e.t.c.

Due to the reported low protein content in maize coupled with its large scale consumption by people in the tropics, there is need to enrich maize based food in order to enhance its nutritional value. Many researches have been done on supplementing maize flour with various legumes [15] to improve its nutritional values. Among the outcome of this development is the production of corn chips. Corn chips is a rod-like shaped crunchy Nigerian snack, popular in the western parts of Nigeria. The nutritional evaluation done on several corn chips produced in Nigeria has been reported to contain low amount protein, deficient in essential amino acids [16] and therefore, there is a need to search for cheaper but good quality protein sources that are readily available for

the supplement of corn chips.

Bambara groundnut (*Vigna subterranean* (L)) is an underutilized legume grown in the sub-Saharan Africa. It is cultivated for subterranean pods, and extremely hard. It is regarded as the third most important legume after groundnuts (*Arachis hypogea*) and cowpeas (*Vigna unguiculata*) in Africa but due to its low status, it is seen as a snack or food supplement but not a lucrative cash crop [17]. Bambara groundnut is composed of high carbohydrate (65%) and relatively high protein (18%) as well as sufficient quantities of fibre (6.5%) [18]. Bambara seeds have been found to be richer than peanuts in essential amino acids such as isoleucine, lysine, methionine, phenylalanine, threonine and valine [19] validated by [17]. Bambara groundnut can be consumed in several ways. The seeds may be prepared into Bambara milk, which is often preferred to milk prepared from other pulses because of its characteristic flavor and colour. The seeds may also be eaten fresh or grilled [20]. Due to the nutritional composition of Bambara nut, it is seen as a very good supplement for corn. There is a possibility of producing acceptable snacks (kokoro) with better nutritional content and sensory quality from maize flour by fortifying with Bambara groundnut.

Kokoro is a popular local rod-like shaped crunchy snack made from corn meal or corn flour which contains mainly carbohydrates and is usually deep fried. Kokoro is widely known in the Western part of Nigeria [21]. It is mostly sold in motor parks and junctions by street hawkers. It is known for its distinct fermented taste. As a product that is widely consumed, it will be important to enhance its nutritional quality. It is therefore necessary to produce a highly nutritious snack that will be useful in nutritional programs to combat malnutrition and nutrient deficiencies. They are deficient in some essential amino acids like lysine. These amino acids can be supplemented in the food by complementing with legume such as groundnuts, soybeans, cowpea which are better sources of sulphur containing amino acids [22]. These usually improve balance of amino acid in the product made from such combination. Recent researches have been done to improve the nutritional content of kokoro using groundnuts, soybean [23].

Due to product's sensitivity to gain or lose moisture, the stability of the product can be distorted and based on this reason, there's need for determination of the best model for corn-bambara chips to determine the best storage condition. In order to adequately preserve the food potential of corn-bambara chips, knowledge from this study would be used to develop a portable and hygienic storage condition.

2. Materials and Methods

2.1. Source of Sample

Dried maize and Bambara groundnut samples used in the production of Bambara-corn chips for the sorption isotherm experiment were purchased from International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria.

2.2. Preparation of Samples

The purchased white maize specie after sorting and cleaning was soaked in hot water for 24 h and then wet milled with a milling machine to a coarse paste. The Bambara nut was cleaned and sorted and dry milled to a fine powder. In a mixing bowl, the cornmeal and the Bambara nut flour was mixed together in a ratio of 70: 30. Salt, chilli pepper, grated ginger and finely chopped onions were added to the mixture. The corn-bambara meal was then kneaded until it resulted in very soft dough. The vegetable oil used for deep frying was heated until very hot (300 °C). Pinch lime sized corn Bambara-corn meal was rolled into long fingers and then slid into the hot oil until evenly fried. The fried chips were removed into paper towels to remove excess oil.

The required relative humidity was prepared relying on the static gravimetric method with concentrated sulphuric acid (H₂SO₄) according to [3] showed in Table 1. Different amount of H₂SO₄ with deionized water was used to make up 250 ml of dessicant prepared at 27, 37 and 40°C and a different range of relative humidity being selected to give different water activity values in the Bambara-enriched corn chips.

Table 1. Control of humidity using concentrated H₂SO₄ at different temperatures.

Relative humidity (%)	Quantities of H ₂ SO ₄ at 27°C (ml)	Quantities of H ₂ SO ₄ at 37°C (ml)	Quantities of H ₂ SO ₄ at 40°C (ml)
10	164.43	165.71	165.50
20	146.17	147.43	147.07
40	120.89	122.13	121.28
60	97.74	98.77	97.03
80	69.89	69.91	66.19

Source: Oyelade (2008)

2.3. Determination of Sorption Isotherm

The adsorption equilibrium moisture contents of Bambara nut flour enriched corn chips was determined at temperatures 27°C, 37°C and 40°C over a water activity range of 10-80% using the static gravimetric method as described by [24]. 10g of the Bambara enriched corn chips was placed in nylon and another 10 g was placed in petri dishes. The samples were placed in dessiccators at each a_w point and temperature level. The dessiccators containing hydrogen tetraoxosulphate (vi) acid and samples were placed inside temperature controlled Gallenkamp DV 400 incubators which was set at 40°C, 37°C and room temperature (27°C). The samples were weighed at 3 days interval. Equilibrium was observed when three identical consecutive measurements were obtained. The dry matter content was obtained by oven drying at 105°C for 3 h [25]. The equilibrium moisture contents were calculated on dry basis from which the moisture sorption isotherm was determined.

2.4. Isotherm Equations and Modelling

Five widely recommended isotherm equations were

investigated in accordance with the experimental data and are shown in Table 2. The modeling of the equilibrium moisture content data was done using excel solver. Five widely recommended isotherm equations which were used include Guggenheim-Anderson-de Boer (GAB), Brunauer-Emmett-Teller (BET), Oswin, Henderson (HDE), and Halsey.

Table 2. Isotherm Models for Fitting Experimental Data.

Models	Equations	Reference
GAB	$X_{eq} = \frac{M_o a_w c k}{(1 - k a_w)(1 - k a_w + c k a_w)}$	[25]
BET	$X_{eq} = \frac{c M_o a_w}{(1 - a_w)(1 + (c - 1) a_w)}$	[25]
OSWIN	$X_{eq} = c \left[\frac{a_w}{1 - a_w} \right]^n$	[26]
HALSEY	$X_{eq} = \left(-\frac{c}{\ln a_w} \right)^{1/n}$	[25]
HENDERSON	$X_{eq} = \left(-\frac{1 - a_w}{c} \right)^{1/n}$	[25]

Where X_{eq} is the Equilibrium moisture content, a_w is water activity, a, b, c, n are constants, k is the GAB constant and M_o is the monolayer moisture content.

$$RSS = \sum_{i=1}^n (M_{cal} - M_{pred})^2 \quad (1)$$

$$R^2 = \frac{\sum_{i=1}^n (M_{cal} - M_{pred})^2}{\sum_{i=1}^n (M_{pred} - M_{cal})^2} \quad (2)$$

$$SEE = \sqrt{\frac{\sum_{i=1}^n (M_{cal} - M_{pred})^2}{df}} \quad (3)$$

Where, M_{cal} is the experimental equilibrium moisture content,

M_{pred} is the predicted equilibrium moisture content, n represent number of experimental unit, df (degree of freedom) = n – 1, RSS represent residual sum of squares and SEE is standard error of estimate.

The analysis was carried out using a Personal computer. The experimental data was manually inserted into excel and graphs were prepared from the data. Excel solver was used in analyzing and determination of the parameters of the models. The formulated algorithm was carried out and the predicted curve was overlaid on the experimental data points. The best fit was determined based on closeness of R² to unity, the least values of RSS and SEE or closer to zero, the models were evaluated in terms of reliability of fit [27-28].

3. Results and Discussions

3.1. Moisture Isotherm of Kokoro

The adsorption isotherm curve of Bambara-corn chips is as shown in Figures 1 and 2 at the three different temperatures 27, 37 and 40 °C using different storage conditions, which was determined by plotting the equilibrium moisture content calculated against different water activities. The shapes of the curves were sigmoidal which conforms to the sorption curve for agricultural products by [29] reported by [3] for lafun, [30] for cassava and [31] for pupuru. This is typical of isotherms of products which starch contents are very high as observed by [3]. The kokoro produced from maize and Bambara

groundnut showed that the food also contained some amount of starch. The adsorption curve also showed that as temperature increased, there was decrease in the equilibrium moisture content. As temperature varies, the excitation of molecules, as well as the distance, and thus attraction between molecules, varies. This causes the amount of sorbed water to change as temperature varies, at a given relative humidity [32].

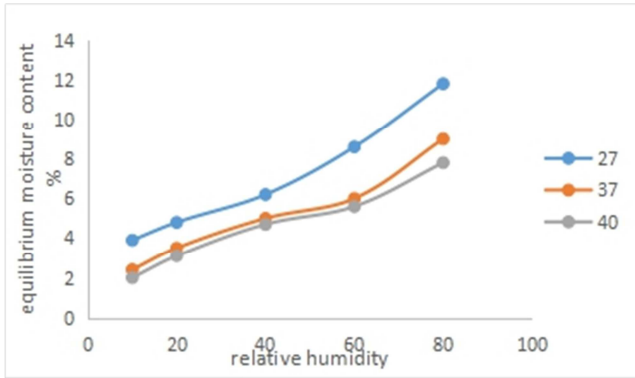


Figure 1. Sorption isotherm graph of corn chips at 20°C, 37°C and 40°C using petri dishes.

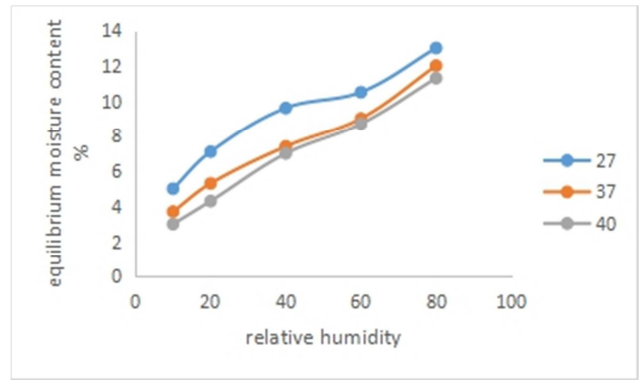


Figure 2. Sorption isotherm graph of corn chips at 20°C, 37°C and 40°C using low density polyethylene.

3.2. Effect of Packaging Material

The effect of petri-dish and polyethylene at different temperatures is shown in Figure 3. It was observed that nylon (polythene) had lower equilibrium moisture compared to petri-dish. The absorption of moisture by different packaging material is a reflection of the porous structure of the material. The importance of moisture content help in determining the keeping quality of food during storage.

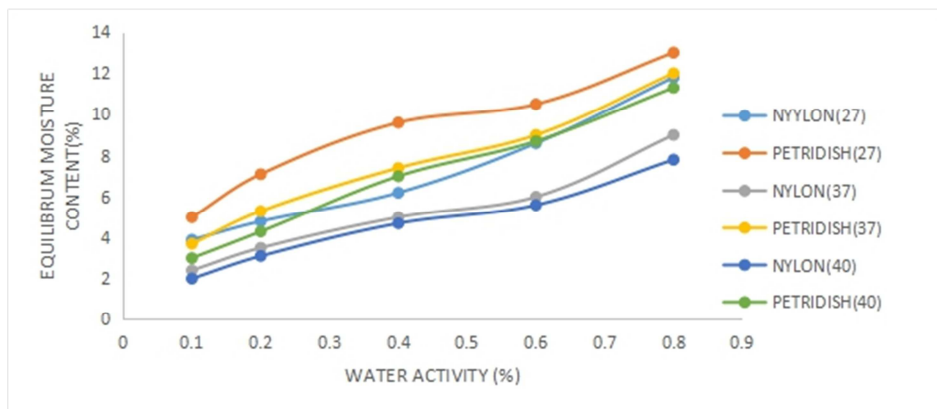


Figure 3. Effects of packaging materials on the sorption behavior of kokoro.

3.3. Fitting of Experimental Data to Sorption Isotherm Models

Table 3 showed the constants generated for six model that were validated with the experimental data. The models fitted for kokoro using different packaging materials at 20°C, 37°C

and 40°C, the values of the parameters (estimated unknown values) for the models which includes R^2 , RSS, SEE and the constants. Based on the closeness of R^2 to unity, the least values of RSS and SEE or closer to zero, the models were evaluated in terms of reliability of fit.

Table 3. Estimated values for fitting models and model evaluation indicators of corn chips at 27°C, 37°C and 40°C.

Models	Polythene packaging	open Packaging	Polythene Packaging	open Packaging	Polythene Packaging	Open Packaging
	27°C		37°C		40°C	
GAB	k = 0.1112	k = 0.1243	k = 0.0916	k = 0.1162	k = 0.1243	k = 0.110212
	c = 10.8026	c = 10.8027	c = 10.8026	c = 10.2662	c = 10.802	c = 10.8027
	M_0 = 0.0652	M_0 = 0.0752	M_0 = 0.0552	M_0 = 0.0723	M_0 = 0.046	M_0 = 0.0656
	RSS = 0.0020	RSS = 0.00626	RSS = 0.00089	RSS = 0.00271	RSS = 0.00626	RSS = 0.001784
	SEE = 0.0162	SEE = 0.0281	SEE = 0.0102	SEE = 0.0144	SEE = 0.0281	SEE = 0.0142
	R^2 = 0.9973	R^2 = 0.9214	R^2 = 0.9784	R^2 = 0.9795	R^2 = 0.9214	R^2 = 0.9736
BET	c = 15.625	c = 13.209	c = 6.675	c = 13.964	c = 5.715	c = 6.602
	M_0 = 0.0316	M_0 = 0.0283	M_0 = 0.0206	M_0 = 0.0274	M_0 = 0.021	M_0 = 0.0193
	RSS = 0.000685	RSS = 0.0012	RSS = 0.000192	RSS = 0.000585	RSS = 0.000103	RSS = 0.00045
	SEE = 0.01077	SEE = 0.0165	SEE = 0.0058	SEE = 0.0122	SEE = 0.0040	SEE = 0.0147
	R^2 = 0.9957	R^2 = 0.9723	R^2 = 0.9890	R^2 = 0.98244	R^2 = 0.9924	R^2 = 0.9736

Models	Polythene packaging	open Packaging	Polythene Packaging	open Packaging	Polythene Packaging	Open Packaging
	27°C		37°C		40°C	
OSWIN HASLEY	c = 0.074	c = 0.0960	c = 0.05483	c = 0.103	c = 0.0493	c = 0.0730
	n= 0.3252	n= 0.2329	n= 0.3503	n= 0.548	n= 0.3382	n= 0.3351
	RSS= 1.929 ×10 ⁻⁵	RSS= 0.000141	RSS= 2.046×10 ⁻⁵	RSS= 0.0116	RSS=2.9×10 ⁻⁵	RSS= 9.36×10 ⁻⁵
	SEE= 0.00011	SEE=0.0002	SEE= 2.55×10 ⁻⁶	SEE=-0.0341	SEE= 0.000168	SEE=0.000363
	R ² = 0.9953	R ² = 0.9635	R ² = 0.9921	R ² = 0.9631	R ² = 0.9859	R ² = 0.9796
HENDERSON	c= 0.0046112	c= 0.0371	c=0.0532	c=0.0472	c=0.0334	c=0.0454
	n= 1.459	n= 1.568	n=1.4261	n=1.4386	n=1.595	n=1.4712
	R ² = 0.9485	R ² = 0.9371	R ² =0.7974	R ² =0.8882	RSS=0.00025	RSS=0.0051
	SEE= 0.0204	SEE=0.0137	See=0.032	See=0.0229	SEE=0.0129	SEE=0.0194
	RSS= 0.00334	Rss=0.00162	Rss=0.00889	Rss=0.00443	R ² =0.8852	R ² =0.8524
	c= 0.748	c= 0.866	c= 0.917	c= 0.6861	c= 0.726	c= 0.7551
	n= 15.891	n= 18.377	n= 0.1947	n= 14.558	n= 15.559	n= 16.022
	RSS= 0.0025	RSS= 0.001192	RSS= 0.000104	RSS= 0.0071	RSS= 0.00328	RSS= 0.0025
	SEE= 0.017	SEE= 0.0118	SEE= 0.0109	SEE= 0.0287	SEE= 0.0196	SEE= 0.0162
	R ² = 0.9965	R ² = 0.9807	R ² = 0.9591	R ² = 0.8968	R ² = 0.9645	R ² = 0.9477

a, b, c, n and k are the model constants, RSS represent residual sum of squares, SEE represent the standard error of estimate, and R² the co-efficient of fit.

From Table 3, the polythene and petri-dish showed that Oswin model and Henderson model respectively was best fit at 27°C based on the closeness of R² to unity, the least values of RSS and SEE are closer to zero (Famurewa *et al.*, 2012). It has RSS= 1.929×10⁻⁵, SEE= 0.00011, R²= 0.9953 and petri-dish RSS= 0.001192, SEE= 0.0118 and R²= 0.9807. At 37°C, Oswin model was also the best fit for the model with RSS= 2.046×10⁻⁵, SEE= 2.55×10⁻⁶ and R²= 0.9921 and BET was best for petri-dish which has value of RSS= 0.000585, SEE= 0.0122 and R²= 0.98244. At 40°C it was revealed Oswin model was best fit for polythene and petri-dish with values of RSS=2.9×10⁻⁵, SEE= 0.000168 and R²= 0.9859 for polythene and RSS= 9.36×10⁻⁵, SEE=0.000363 and R²= 0.9796 for petri-dish.

3.4. Monolayer Moisture Content

Monolayer moisture content of GAB was higher than BET which agreed with Onayemi and Oluwamukomi (1987) and Oyelade (2008). The monolayer moisture content ranged from 0.0283 to 0.0752 for 27°C, 0.0206 to 0.0723 for 37°C and 0.0193 to 0.0656 for 40°C.

4. Conclusion

The study of sorption isotherm of kokoro was stored at different temperatures (27, 37 and 40°C) in polyethylene showed sigmoid shape type II typical for most food products. The equilibrium moisture contents for kokoro snacks increased with increase in water activity. The fitting of experimental data to model revealed that comparison between experimental results and predicted equilibrium moisture contents showed that Oswin model appears to be the most suitable in describing the experimental results of polyethylene packaged kokoro at 27°C, 37°C and 40°C while Henderson model was suitable for exposed package at 27°C, BET at 37°C and Oswin at 40°C. The general model observed for this study that could predict the sorption behavior of kokoro was Oswin model.

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