Moisture sorption isotherm modelling of cassava starch edible film incorporated with kaffir lime and glycerol

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Abstract

The moisture sorption isotherm (MSI) of the cassava starch edible film with added of glycerol as a plasticizer and kaffir lime oil as essential oil was studied. The MSI were determined gravimetrically over a relative humidity of 6.1 – 97% at room temperature 25°C. The film then was weighed and calculated to obtain the equilibrium moisture content (EMC) value. The graph between EMC and water activity (a_w) was plotted. The models of moisture sorption isotherm GAB, BET, Olswin, Helsey, Peleg and Langmuir were applied to describe the moisture sorption behaviour by varying the composition of kaffir lime oil from 0 mL, 0.20 mL, 0.4 mL, 0.6 mL, 0.8 mL and 1.0 mL. The MSI modelling shows that Peleg model is the best fitted model to describe the moisture sorption behaviour for this starch film with the regression coefficient (R^2) values are 0.9811, 0.9895, 0.9885, 0.9927, 0.9983 and 0.9969 respectively. This research also proves that the addition of kaffir lime essential oil could reduce the equilibrium moisture content toward the film.

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1.0 Introduction

Plastics are man-made polymer molecules. They are widely used, economical materials characterized by superior features, easy printing and manufacturing. Traditional plastic is very stable and not easily damaged in the surrounding environment. As a result, environmental pollution from synthetic plastics has been recognized as a major problem. Most of this plastic waste has accumulated on the ground [1]. Most of this plastic is based on crude oil, and any increase in production has led to increased use of oil and this has caused serious environmental pollution, because polymers are polished and stationary.

Edible and biodegradable polymers should be considered as a substitute for more traditional recycling procedures and this has encouraged researchers to synthesize new polymers that can be returned to the biological cycle after exercise. Therefore, the use of biodegradable agricultural polymers will not only solve this problem, but also provide potential new uses for excess agricultural products [2]. Biodegradable polymers can be achieved through a variety of agricultural and food waste products. Various botanical sources containing starch such as cassava, wheat, rice, corn, peas, potatoes, etc. are the most promising natural polymers for packaging use because of their availability and biodegradable ability [3].

This work will study on the moisture sorption isotherm as the parameter. Moisture sorption isotherm is a significant thermodynamic aid for determining interaction between water and food components as well as estimation of heat requirements for certain processes (drying and packaging). Moisture sorption isotherm can be developed using several equations such as based on monolayer model Brunauer–Emmett–Teller (BET), multilayer and condensed film models Guggenheim–Anderson–de Boer model

(GAB), semi-empirical models (Halsey model) and empirical models (Smith and Oswin models) [4].

This research project will provide an investigation on cassava starch edible film incorporated with glycerol as a plasticizers and kaffir lime oil as an essential oil by focusing on the parameter of moisture sorption isotherm modelling. The methods chosen are GAB, BET, Olswin, Helsey, Peleg and Langmuir.

2.0 Methodology

2.1 Film Preparation

Five sheets of film had been prepared in the laboratory. All the sheets of film has different ratio of glycerol:cassava:kaffir lime oil. All the sheets of film produced are varied with different composition of kaffir lime essential oil at which 5:30:0, 5:30:0.2, 5:30:0.4, 5:30:0.6, 5:30:0.8 and 5:30:1 and all the films are labelled as 0 mL, 0.2 mL, 0.4 mL, 0.6mL, 0.8 mL and 1.0 mL respectively.

2.2 Methods

These salts were prepared and introduced in six glasses of 1L each with an insulated lid. About 1 cm x 3 cm of the film were weighed and placed in each glass containing the saturated salt solution. The samples were weighted after 5 days. The final moisture content of each sample was determined by using drying oven at 105 °C for 24 h, until we get a constant sample mass over time. The difference of mass before drying (M_h) and after drying (M_s) at 105 °C which gives the product moisture content X_{eq} at hygroscopic equilibrium Eq.

$$\frac{\quad}{\quad} \qquad (1)$$

2.3 Computer Modelling

For the purpose of this work, several equations as indicated in Table 1 were chosen to fit the experimental sorption data. Non-linear regression analysis by using Statistica 12.5 was used to estimate the model coefficient simultaneously including the monolayer moisture content from the experimental sorption data. Meanwhile, coefficient of regression (R^2) that varies between 0 to 1, expressed as Eq(2), whereby is an average of..............................R^2 values are calculated using Excel by inserting the estimated constant that obtained from Statistica.

$$\frac{\sum}{\sum \quad \sum} \qquad (2)$$

The following 6 mathematical models describing the relationship between EMC of wet material and a_w were statistically investigated and reviewed.

Table 1: Models for Fitting the Sorption Isotherms Isotherm models used for experimental data fitting [5] [6]. x is water content; $x_m$is monolayer water content; C is energy difference between the upper layers and the monolayer; K is degree of freedom of water molecules; a, b, $n_1$and n_2 are empirical parameter

Name of Model	Model
GAB:	$x= CKx_mA,/[(1-KA,)(1-KA, + CKA,)]$ (3)
BET:	$x=(x_mCA_w)/((1-a_w)(1+(C-1)a_w)$ (4)
Oswin:	$x= A(A_w/(1 - A_w)^B$ (5)
Helsey:	$Aw=e^{(-a/xb)}$ (6)
Langmuir:	$x=(x_mCA_w)/(1+CA_w)$ (7)
Peleg:	$x=K_1(A_w^{n1})+K_2(A_w)^{n2}$ (8)

3.0 Results and discussion

3.1 Equilibrium Moisture Content

The experimental curves for the equilibrium moisture contents of cassava starch with addition of glycerol and kaffir lime oil for each water activity at composition of the oil at 0 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL and 1.0 mL film are presented in Figure 1. All the film shows the moisture content of the film increased with increased humidity.

The form of the isotherms for 0 mL film shows different pattern compared to the rest of the film. The moisture content of the film at 0 mL presents to be the highest than all the incorporated films with kaffir lime oils. This is due to the fact that essential oil acts as the barrier properties toward the water content as the essential oil is naturally hydrophobic [7].

The addition of glycerol as plasticizer is also the reason why the moisture content is high. It is assured that the nature of glycerol that is hydrophilic has tendency to bind water rapidly [8]. The shape of the curve is also almost to be sigmoidal. It is affirmed that the addition of glycerol could change the shape of isotherm to be more sigmoidal [9].

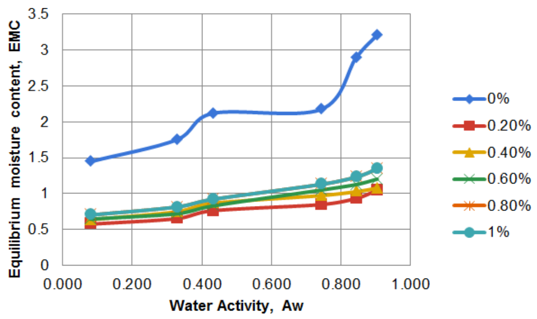

Fig. 1: Moisture sorption isotherms at different composition of kaffir lime

Meanwhile the curve of film that incorporated with kaffir lime oil is almost to be straight line but after the water activity, $a_{w=}$0.8, there is a bit increasing of moisture especially except for 0.4%. The equilibrium moisture content does show significant changes regarding with all composition of kaffir lime oil content at all humidities. It is shown that the increasing of essential oil increasing the moisture content of the film. But there are several research paper found that the additional of essential oil may decreasing the moisture content of the film because of the nature of essential oil is hydrophobic. However, the composition of citric fruit such as kaffir lime fruit is generally composed by 90% of terpens, 5% of oxygenated compounds and less than 1% non-volatile compounds, such as pigments and waxes. Different amount of monoterpenes could influence the hyphobicity. In short, the governing factor of hydrophobicity is on the citrus' monoterpens [10].

3.2 Mathematical modelling and fitting of sorption isotherms

The value of constants at the 6 investigated kaffir lime oil composition of 0 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL and 1.0 mL for all models are shown in Table 2. The Peleg equation is the best fitted model to describe 0 mL kaffir lime oil film which is R=0.9811 followed by Halsey, Bet, Oswin, GAB and Langmuir. For the film incorporated with kaffir lime oil, GAB and Peleg is the most suitable model to describe the experimental data for all composition studied as its coefficient regression averaging about 0.99. However Peleg achieve the highest value of R^2 which at 0.4 mL, 0.8 mL compared to GAB only at 1 mL. In a bigger picture, Peleg's model is the best model to describe moisture sorption isotherm over all the composition of kaffir lime oil. To be added, the Oswin model fit the best to describe 0.6% film. Meanwhile the Langmuir model pulls the lowest R^2 value throughout all the composition.

Model	Constant	0 mL	0.20 mL	0.40 mL	0.60 mL	0.80 mL	1 mL
GAB	Xm	1.4010	0.4874	0.5670	0.7077	0.6200	0.6915
	C	4580.8100	251.8388	1056.8620	209.1896	2485.1070	768.6880
	k	0.6040	0.5636	0.4860	0.3822	0.5380	0.5302
	R^2	0.9541	0.9932	0.9799	0.9904	0.9964	0.9971
BET	Xm	43.0299	19.3591	21.5686	23.1891	22.4597	24.7119
	C	0.0189	0.0136	0.0127	0.0127	0.0143	0.0144
	R^2	0.9632	0.9756	0.9221	0.9812	0.9783	0.9441
Oswin	a	2.0807	0.6841	0.7598	0.8491	0.8697	0.9585
	b	0.1777	0.1703	0.1309	0.1125	0.1484	0.1484
	R^2	0.9617	0.9932	0.9849	0.9940	0.9873	0.9943
Halsey	a	10.6254	0.1372	0.1534	0.2654	0.3216	0.4965
	b	3.9404	3.9275	5.0235	5.3946	4.3610	4.5291
	R^2	0.9620	0.9928	0.9802	0.9741	0.9899	0.9943
Langmuir	Xm	3.2159	1.0645	0.9838	1.0664	1.2059	1.3264
	C	5.8865	5.5909	12.4827	14.3167	8.8618	8.9761
	R^2	0.7918	0.8980	0.8060	0.8773	0.8123	0.8240
Peleg	k_1	2.5310	0.4328	0.8218	0.0034	0.1835	0.9268
	n_1	8.8231	3.0421	0.1475	-1.5426	-0.3957	0.1119
	k_2	2.2600	0.6839	0.4903	1.0921	1.0788	0.5547
	n_2	0.1767	0.1499	7.3415	0.3383	0.7920	2.8995
	R^2	0.9811	0.9895	0.9885	0.9927	0.9983	0.9969

Table 2 Isotherm model parameters for cassava starch film at 0 mL, 0.20 mL, 0.40 mL, 0.60 mL, 0.80 mL and 1.0 mL of kaffir lime oil

Conclusions

Moisture adsorption isotherm of cassava starch film incorporated with glycerol and kaffir lime oil at different composition has been established experimentally at various water activities. The addition of kaffir lime essential oil do give significant observation as it lowering down the moisture content of the film as the properties of the essential oil is to be hydrophobic, hence it allowing less water to adsorb into the film. Meanwhile, the moisture sorption isotherm modelling shows that Peleg is the best fitted for the film over all of the oil's composition. Peleg achive the highest value of R^2 at 0 mL, 0.4 mL and 0.8 mL. Aside Peleg, GAB also achieves good result as its R^2 value obtained averaging at 0.99.

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