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Moisture Sorption Isotherm of Cassava Starch Film Incorporated with Kaffir Lime Oil

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The use of bioplastic film has been gaining a lot of interest especially in food packaging, however knowledge on its stability during handling is limited. Moisture sorption isotherm is a study that determines the stability of the film when exposed to certain environmental conditions. The gravimetric method was used to determine the moisture sorption isotherm of cassava starch film incorporated with kaffir lime essential oil (EO) at 30°C and 40°C. The moisture content increases with increasing water activity for both 30°C and 40°C. The sorption data were fitted into 3 models and Oswin was found to be the best model to fit the data with R^2 of 0.93 to 0.97. The sorption data were used to determine the net isosteric heat of sorption (q_{st}) through the application of Clausius – Clapeyron equation which provides an approximation of the minimum energy required to remove water from a solid. Generally, the q_{st} decreases exponentially with an increase in moisture content regardless of whether the film contains EO. The incorporation of EO within these temperatures does not affect the moisture content and heat of sorption of the starch-based bioplastic film, which shows its stability and potential as an additive in food packaging film.

Keywords: Sorption isotherm model; Isosteric heat; Biopolymer plastic; Moisture content; Kaffir lime essential oil

I. INTRODUCTION

Polysaccharides, lipids, proteins or a combination of these materials are natural polymers commonly used in the fabrication of edible film. Due to the growing concern with regard to the use of synthetic plastic used in food packaging, the edible film is seen as a suitable alternative. Among the benefits of the edible film is being environmentally friendly as it can be consumed with the food. Other than that, it could also reduce pollution since it is made of renewable resources, it can degrade easily. The most important function of an edible film as food packaging is to reduce the loss of water between the food and the surrounding environment. The film will act as a barrier in order to preserve the quality of the food.

Polysaccharides are one of the most preferred materials used in the food industry as they have favourable barrier properties toward O_2 and CO_2 (Parra *et al.,* 2004). However, they offer a poor barrier against water and weak mechanical properties. Among examples of polysaccharides are starch, cellulose, pectin, chitosan and others. Low cost, naturally abundant and its film-forming capability; are among the benefits of using starch as the material for edible film or coatings. Starch is made up of amylose and amylopectin whereby the attribute of a good film-forming property is due to the high amylose amount. Cassava starch contains 17% amylose content, however the film is brittle with weak mechanical properties. To overcome film brittleness, a plasticiser is added. Commonly used plasticisers are polyols, lipids, and others (Sothornvit & Krochta, 2005). For starch, a high amount of plasticiser with hydrophilic properties is needed. Recent studies have added antimicrobial agents to enhance the functional properties of food packaging by inhibiting the growth of microorganisms. The use of plant essential oil is seen as a natural and safer alternative compared to synthetic antimicrobial (Atarés & Chiralt, 2016).

Among factors which contribute to microbial growth includes temperature and moisture content, where moisture content is the amount of water contained in a substance. The

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*Corresponding author's e-mail: junejai@uitm.edu.my most important component in food is water. Water directly affects the stability and quality of food, therefore the transfer of water between food and the surrounding environment should be kept at a minimum. Water activity is defined as the relationship between water molecules and the food network (Fadilah *et al.,* 2019). Moisture sorption isotherm is defined as the connection between moisture content and water activity at a given temperature. The experimental data of moisture sorption studies are fitted into mathematical models available to better represent the data. The moisture sorption study is important in order to design the packaging and storage system as well as to predict the quality, stability and shelf life. Another useful thermodynamic tool is the net isosteric heat of sorption (q_{st}). It is defined as the total heat of sorption of water on a material minus heat of vapourisation of water at the system temperature (Saha *et al.,* 2018). One of the ways to determine q_{st} is through the application of the Clausius – Clapeyron equation. A positive value of q_{st} is an indication of heat evolved during adsorption while a negative value is an indication of heat adsorbed during desorption (Al-Muhtaseb *et al.,* 2002). In general, q_{st} demonstrates the binding energy between sorption sites and water vapor. In terms of film, q_{st} is used to evaluate the water activity of the film material with a variety of temperatures in order to determine the shelf life and efficiency of the film as food packaging (Saha *et al.,* 2018).

This study focuses on the stability of cassava starch-kaffir lime oil film, whereby the moisture sorption isotherm of cassava starch film with and without the incorporation EO was studied at 30°C and 40°C. Then, a suitable mathematical model was selected to best describe the sorption data. The net isosteric heat of sorption of the film was then determined by the application of the Clausius- Clapeyron equation.

II. MATERIALS AND METHOD

A. Material

Cassava starch flour (Cap Kapal ABC, Thailand) was bought from a local supermarket in Shah Alam, Selangor. Glycerol of analytical grade (Merck, Germany) was bought from a local supplier as a plasticiser for the film. Kaffir lime was acquired from the local supermarket which the peel was then extracted for Kaffir lime essential oil (EO) The hydrodistillation method was used to extract the EO using Clavenger apparatus. Saturated salt solutions were prepared using reagent grade salts (R&M Chemicals). These salts solutions were used for relative humidity environments.

B. Methods

1. Film Preparation

The preparation of the film was adapted from Manshor *et al.* (2019). The casting technique method was used to prepare the film. For film solution, cassava starch was dissolved in distilled water at 75°C using a hotplate stirrer. Next, glycerol was added to the solution and the solution was continuously stirred. EO at 1.0% v/v was added to the solution once the solution had cooled down to room temperature. Then, the solution was stirred to ensure it was thoroughly mixed. The film solution was poured onto an acrylic frame scraper to ensure that the thickness of the film was consistent and uniform. An oven (AP120, Froilabo) was used to dry the film solution at 40°C for 24 hours. Finally, the dried film was peeled off and stored in a desiccator. A similar method was used to prepare the control film but without the addition of EO.

2. Evaluation of Moisture Sorption Isotherm

The method of evaluation on moisture sorption isotherm was adapted from Manshor *et al.* (2021). The gravimetric method was used to determine the moisture sorption isotherm at 30°C and 40°C. These temperatures were selected since they are the common temperatures studied in tropical conditions (Ikhu-Omoregbe, 2006), (Enyinnaya Chinma *et al.,* 2013). Before conditioning to these temperatures, the earlier prepared film samples were cut into 25 mm × 25 mm and the initial weight of the film was recorded. These films were then placed inside airtight jars separately with each containing saturated salt solution for water activity ranging from 0.2 to 0.8. this range is a representation of the relative humidity inside the jars from 20% to 80% which represents the environment condition for the application of the film. Potassium acetate, magnesium chloride, potassium carbonate, magnesium nitrate, sodium chloride and potassium chloride were used to prepare the salt solutions. Distilled water was added to the salt until saturation. The salt solution was poured into the jar until the height of the solution was 2 cm deep from the bottom of the jar. Inside the jar, a smaller jar was placed facing downward in the middle of the container. The films were placed on top of the smaller jar. An analytical balance (AND, Japan) with an accuracy of ±0.0001g was used to determine the mass of the film every 24 hours. When two consecutive weight measurements were equal or have a difference less than 0.0001g, equilibrium was reached. Finally, an oven was used to dry the film at 105°C until the weight was constant to determine the dry mass. Then, the equilibrium moisture content (EMC) was calculated by the following equation:

$$M = \frac{M_e - M_d}{M_d} \quad (1)$$

Where M is equilibrium moisture content of the film (g water/ g dry matter). M_e is the mass of the film when reached equilibrium (g) while M_d is the film dry mass (g).

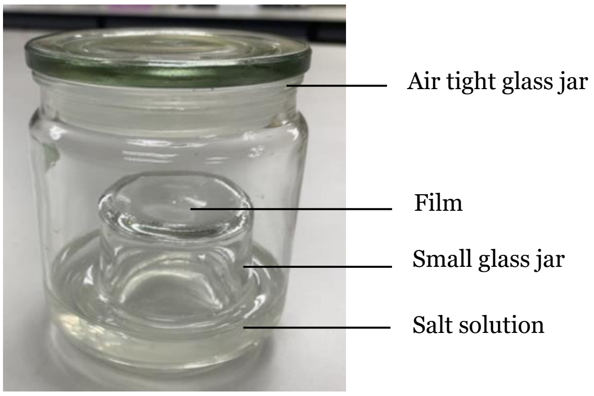

Figure 1. Experimental setup for moisture sorption

3. Fitting of Moisture Sorption Model

The experimental data were fitted into three moisture sorption isotherm models which were Brunauer – Emmett – Teller (BET), Guggenheim – Anderson – de Boer (GAB) and Oswin model.

The BET model is given as (Al-Muhtaseb *et al.,* 2002):

$$M_w = \frac{M_0 C a_w}{(1-a_w)(1+(C-1)a_w)} \quad (2)$$

Where; M_w is equilibrium moisture content (g/g dry matter), *Mo* is Monolayer moisture content (g/g dry matter), *C* is energy constant related to the net heat of sorption and a_w is water activity.

The GAB model is given as (Al-Muhtaseb *et al.,* 2002):

$$M_W = \frac{M_0 C K a_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \quad (3)$$

Where; M_w is equilibrium moisture content (g/g dry solid), M_o is monolayer moisture content (g/g dry matter), *C* and *K* are constants where the energies of interaction between first and further molecules at individual sorption sites, as shown in Equation 3 and Equation 4, respectively.

$$C = C_0 \, exp\,(\frac{H_0 - H_n}{RT}) \quad (4)$$

$$K = k_0 \, exp\,(\frac{H_n - H_l}{RT}) \quad (5)$$

Where; C_o and k_o are entropic accommodation factors, H_o, H_n and H_l are molar sorption enthalpies for monolayer, multilayers on top of monolayer and bulk liquid, respectively (kJ mol^{-1}), *R* is the universal gas constant and *T* is the absolute temperature.

The Oswin model is given as (Al-Muhtaseb *et al.,* 2002):

$$M_w = A[\frac{a_w}{1-a_w}]^B \quad (6)$$

Where, M_w is equilibrium moisture content (g/g dry matter), *A* and *B* are constants.

The least squares method was used to estimate the parameters of the models. The best fit model for the experimental data was determined using the coefficient of determination (R^2), the mean relative percentage deviation modulus (MRE %) and the root mean square error (RMSE) of each model was compared at each temperature. Microsoft Excel software was used for the estimation of parameters as well as the calculation of R^2, MRE (%) and RMSE values. The MRE (%) and RMSE were calculated using the following equations below:

$$MRE\ (\%) = \frac{100}{N} \sum_{i-1}^{N} \frac{|M_i - M_{pi}|}{M_i} \quad (7)$$

$$RMSE = \left\lfloor \frac{1}{N} \sum_{i=1}^{N} (M_i - M_{pi})^2 \right\rfloor^{\frac{1}{2}} \quad (8)$$

Where; M_i is ith experimental equilibrium moisture content value, M_{pi} is ith predicted equilibrium moisture content value, N is the number of experimental data.

A good fit for the models would mean that R^2 is near to 1, RMSE is near 0 and MRE is lower than 10% (Chowdhury & Das, 2010).

4. Determination of Net Isosteric Heat of Sorption

The moisture sorption data were used to determine the net isosteric heat of sorption using the Clausius – Clapeyron equation. The equation is given as Equation (8):

$$ln\, a_w = -(\frac{q_{st}}{R})(\frac{1}{T}) + z \qquad (9)$$

Where; a_w is water activity (dimensionless), q_{st} is net isosteric heat of sorption (kJ mol^{-1}), R is the universal gas constant, T is the absolute temperature (K) and Z and constant related to the entropy of sorption

A graph of $ln\ a_w$ against $1/T$ was plotted. The net isosteric heat of sorption was obtained through the slope of the graph which equals to q_{st}/R. A graph of q_{st} against equilibrium moisture was plotted.

III. RESULT AND DISCUSSION

A. Moisture Sorption Isotherm

Moisture sorption isotherm of cassava starch film incorporated with EO was determined through the saturated salt slurry method. The study was carried out at two temperatures which were 30°C and 40°C. Table 1 shows the result of moisture content for the control and EO film at 30°C and 40°C for each respective water activity:

Table 1. Moisture content of film at respective water activity for control and EO film

Film	**Temperature (°C)**	**Water activity, a_w**	**Equilibrium Moisture Content, EMC (g/g)**
Cassava starch without kaffir lime oil (Control film)	30	0.2	0.1178
		0.3	0.1111
		0.5	0.1585
		0.7	0.2727
		0.8	0.4013
	40	0.2	0.1247
		0.3	0.1427
		0.5	0.1762
		0.7	0.2827
		0.8	0.4102
Cassava starch with kaffir lime oil (EO film)	30	0.2	0.1109
		0.3	0.1331
		0.5	0.1719
		0.7	0.2865
		0.8	0.4175

	40	0.2	0.1101
		0.3	0.1392
		0.5	0.1722
		0.7	0.2702
		0.8	0.3987

The data from Table 1 were plotted in terms of water activity against equilibrium moisture content for each type of film at both temperatures.

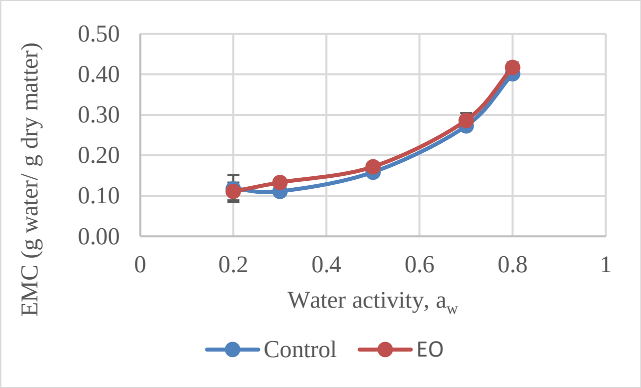

Figure 2. Moisture sorption isotherm for control and EO film at 30°C

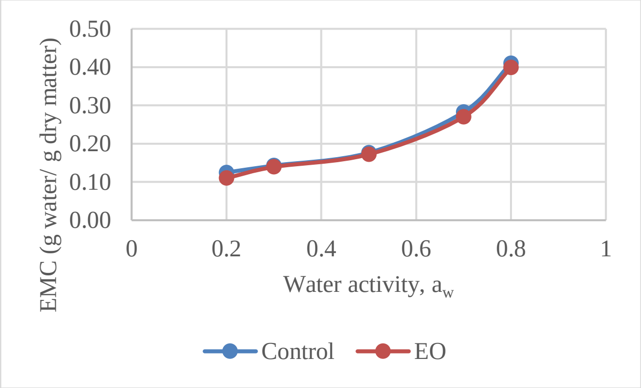

Figure 3. Moisture sorption isotherm for control and EO film at 40°C

Figure 2 and Figure 3 show the graphical relationship between the moisture content and water activity. The moisture sorption isotherm of the control film and EO film followed type III sorption behaviour. This type of isotherm was evident based on the absence of knee point at low water activity which suggests weak interaction between adsorbate and adsorbent (Otoni *et al.,* 2016). In the case of this study, water represents the adsorbate while the film represents the adsorbent. This type of isotherm is commonly found in the material that contains a high number of soluble constituents (Enyinnaya Chinma *et al.,* 2013). Normally, films that are plasticised with glycerol will observe this type of isotherm since glycerol is soluble. At a particular temperature, the moisture content increases with increasing water activity. The moisture content increased slowly until water activity of 0.65. Above this level, there was a high increase in moisture content at a small increase in humidity. The increase in moisture content at low water activity is due to the water being absorbed to the available surface sorption sites (Zhang *et al.,* 2020). Meanwhile, at higher water activity, there is an increase in moisture content due to dissolution of soluble components (Enyinnaya Chinma *et al.,* 2013).

The addition of EO acts as antimicrobial agent as well as hydrophobic agent to improve the water barrier efficiency of the film. Figure 2 shows the comparison between control film and EO film at 30°C. It was observed that the moisture content for both films was relatively similar up to a_w 0.6, an increase in a_w after that shows that EO film gains more moisture. In general, at 30°C, EO film gains slightly more moisture than the control film. The explanation for these observations is due to the incomplete dissolution of starch with the presence of EO during the film-making process. The crystallinity of a starch film depends on the dissolution of amylose content. When the gelatinisation of the film is incomplete, the structure of the film is affected thus affecting the barrier of the film. An incomplete dissolution could cause the film to become more porous thus allowing more water to permeate the film. Mainly, incomplete gelatinisation is caused by insufficient gelatinisation time during the film-making process. Therefore, the film formed has higher permeability and less elasticity (Paes *et al.,* 2008).

At water activity 0.2, the control film had more moisture compared to the EO film where there was 4.4% of moisture difference between the control and the EO film. Meanwhile, at water activity 0.3 up to 0.8, the EO film gained more moisture that varied between 0.3% to 3%. A few studies regarding the addition of EO reveal that the addition of EO should improve the water barrier efficacy of the film (Basiak *et. al.,* 2016, Galus & Kadzinska, 2016). Although it was observed that the control film had higher moisture content at a_w 0.2, it was not consistent with other a_w in this study. This was due to the irregular distribution of the EO in the film. The permeability of a film depends on its hydrophilic and hydrophobic constituents. The interactions of the oil with the starch granules as well as glycerol in the film network promote the decrease in hydrophobicity of the film thus allowing higher water permeability (Atarés & Chiralt, 2016).

Meanwhile, at 40°C, the films behaved differently. This was attributed to the addition of oil in the film which lowers the water content. The hydrophobicity of the film increases with the addition of the oil. The number of active sides for interaction with water molecules available decreases due to the addition of lipid. The starch network can resist the water uptake into the film due to the addition of the oil. Similar results were observed when lipid was incorporated in the starch films. The oil incorporated in the film reduces the water content in the film (Basiak *et. al.,* 2016, Slavutsky & Bertuzzi, 2016). The increase in temperature increases the kinetic energy of water molecules, opening more sites for lipid intake to the structure of the film thus the barrier of the film at 40°C is better compared to 30°C (Saberi *et al.,* 2015).

From Figure 3, it was observed that the moisture content for a_w 0.3 for the control and EO film were comparable. This shows that at this point, the addition of oil does not have any effect on the EO film. Since the behaviour of the films at this point was similar, it is related to irregularities found in the EO film whereby the oil was not properly distributed across the film thus does not have significant effect to the barrier of the film.

Figure 4 and Figure 5 show the comparison of the moisture sorption isotherm between the temperatures for control and EO film, respectively.

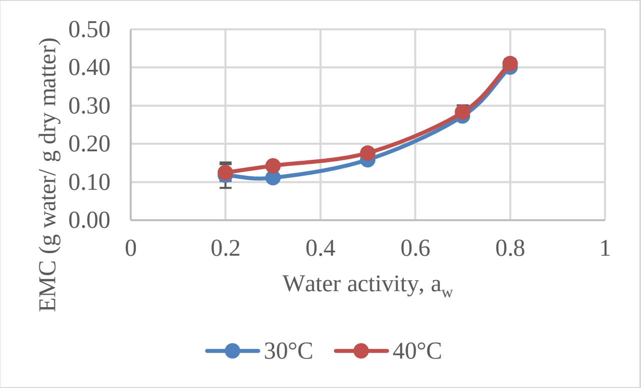

Figure 4. Moisture sorption isotherm for control film at 30°C and 40°C

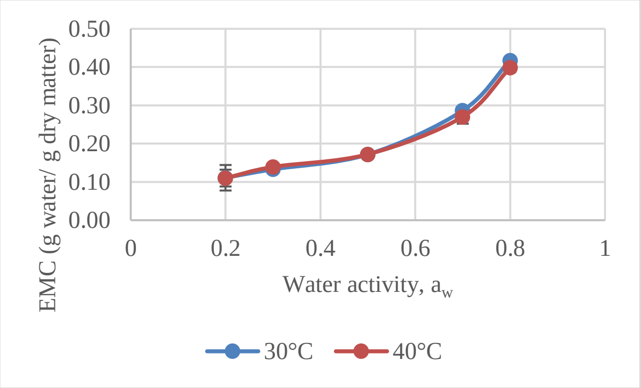

Figure 5. Moisture sorption isotherm for EO film at 30°C and 40°C

Figure 4 and Figure 5 show the effect of temperature for the control film and EO film. For the control film at a given water activity, it can be observed that as the temperature increases from 30°C to 40°C, the moisture content also increases. A similar trend was observed in a study of starch film containing antimicrobial preservatives (Chowdhury & Das, 2010). When the temperature increases, more binding sites are available at the starch backbone which reduces the energy of bound water.

For the control film, it was observed that starting at a_w 0.2, the films at both temperatures gain moisture slowly up to 0.5. Experimental data show that the moisture content for the film at 30°C and 40°C was similar within the same water activity. This shows that the barrier of film at 30°C and 40°C have similar permeability. This was related to the structure of the film whereby the film was not completely gelatinised causing the barrier to be weaker thus allowing more water to permeate. However, the difference in moisture content between these two temperatures were insignificant. Going up the a_w, the film for 40°C had slightly higher moisture content compared to the film at 30°C. It was observed that at a_w 0.3 to 0.7, the moisture content difference between these temperatures was between 1% to 3.2%. This was related to the plasticisation effect of water and glycerol. Other studies observed that the addition of glycerol normally increases the hygroscopic nature of the film (Tong *et. al.,* 2013, Sanyang *et al.,* 2015).

For the case of film containing essential oil, the increase in temperature shows a decrease in moisture content. This trend is more common among edible films (Enyinnaya Chinma *et. al.,* 2013, Fadilah *et. al.,* 2019, Zhang *et al.,* 2020). An explanation for this behaviour is that at a higher temperature, the water molecules become unstable due to the increase in kinetic energy. The intermolecular attractive forces decrease thus water molecules could easily break away from binding sites (Chowdhury & Das, 2010, Galus & Kadzinska, 2016, Zhang *et al.,* 2020). The moisture content for both of the films was found to be much lower compared to other studies of films such as cassava starch incorporated with soy protein(Enyinnaya Chinma *et al.,* 2013), corn starch incorporated with sunflower and lemon oil (Slavutsky & Bertuzzi, 2016), pea starch film (Saberi *et al.,* 2015), and carragean and carboxy methyl glucomannan (Fadilah *et al.,* 2019).

However, based in Figure 5, it can be seen that the gain in moisture between these films at 30°C and 40°C were very little (between 0.03% to 1.88%) thus seemed insignificant. This shows that the change in temperature does not cause any significant effect to the film that contains oil which suggests that the interactions between the oil and the starch granules in the film were relatively similar at 30°C and 40°C. The barrier properties of the films at both these temperatures were almost the same.

Overall, the addition of oil does not have a significant effect on the barrier of the film. The main purpose of EO was as antimicrobial additives which inhibits the microbial growth and prolongs the shelf life of the food. A study on sorption isotherm of starch film nonlaminated with sunflower oil and lemon essential oil (Starch/ELO/SO) at 25°C by Slavutsky and Bertuzzi (2016) showed that with increasing a_w, the water adsorption decreased. Below a_w of 0.8, there was low water uptake while after this value there was an exponential increase. Comparing to the EO film in this study, the Starch/ELO/SO film have improved water barrier due to the amphiphilic and hydrophobicity characteristics of the oils. This shows that the starch/ELO/SO film is a better film with regards to the moisture adsorption.

Another study of sorption isotherm for cassava bagasse incorporated with oregano essential oil (OEO) at 25°C by Debiagi *et al.* (2014), showed that the moisture content increased with increasing a_w. However, the OEO film had lesser moisture content than the control film in that study. Similar findings were obtained by Basiak *et al.* (2016) and Galus and Kadzinska (2016), whereby the addition of oil does not have significant changes to the sorption behaviour up to a_w 0.8. The findings in this study observed similar trends whereby the addition of EO does not have significant effect to the barrier of the film. With the increase in a_w, the number of sites for adsorption increases due to swelling of the material. This suggests that the EO and control film behaved similarly in terms of barrier properties. Therefore, both films are applicable for food packaging since the addition of EO did not affect the sorption behaviour of the film, hence the film produced contains antimicrobial agent with good barrier property.

The binding strength between sorbate and the adsorptive sites could be determined through net isosteric heat of sorption. This thermodynamic parameter is an indication of the mechanisms for the moisture adsorption process.

B. *Modelling of Moisture Sorption Isotherm*

The moisture sorption isotherm for cassava starch film with and without the addition of EO were studied at two temperatures namely 30°C and 40°C. It is important to study the sorption behaviour at different temperatures as the water activity changes with temperature (Slavutsky & Bertuzzi, 2016). The moisture sorption data was inserted into 3 models which are GAB, BET and Oswin model. The RMSE and MRE (%) were calculated while the R^2 value was obtained from the graph. Table 2 shows the parameters for all 3 models. It was observed that the values for parameter *C* in BET and GAB models in most sets had negative values. The *C* parameter should be a positive value which is a representation of the first layer's total heat of sorption. Therefore, a negative value is impossible (Alamri *et al.,* 2018). A study on water sorption of Libyan date paste showed similar findings whereby the Halsey, Smith, Iglesias and Chirife, Henderson and Oswin model showed good fit to sorption data meanwhile the BET and GAB model were found to be unsuitable due to the negative value of the *C* parameter (Houssein, 2007).

Other than that, the *K* parameter in the GAB model was found to be more than 1 which indicates the model invalidity. Similar findings was observed in a study of air-dried papaya whereby it was concluded that the temperature for the study is unsuitable to be used with the GAB model since the *C* and *K* parameter are temperature dependent (Thalerngnawachart & Duangmal, 2015). Therefore, the BET and GAB model are not suitable to represent the moisture sorption data for both films. It is concluded that the Oswin model is the best fit model to represent the moisture sorption data. Other than the R^2 value that is near 1, the RMSE and MRE (%) value for the model is near 0 and below 10%, respectively (Saha *et al.,* 2018).

For the Oswin model, it was observed that the R^2 value at 30°C for the Control and EO film was similar. When the temperature rose to 40°C, the value of R^2 increased for the control film and decreased for the EO film. This suggests that the change in temperature affected the R^2 value. The addition of EO did cause slight changes to the moisture content of the film. At 30°C, the addition of EO caused changes to the moisture content of the film between 4% to 18% while at 40°C the changes on the moisture content of the film were between 1.8% to 12.5%. It was concluded that the addition of EO does not bring significant effect to the barrier of the film and the Oswin model is written as in Table 3.

Table 2. Estimated parameters and comparison for BET, GAB and Oswin model of sorption isotherm at 30°C and 40°C

Model	**Parameter**	**Temperature (°C)**			
		30		40	
		Control	EO	Control	EO
BET	*Mo*	0.08	0.0839	0.08179	0.0795
	C	-72.657	-37.6608	-16.282	-19.3476
	R^2	0.986	0.9688	0.9866	0.9864
	RMSE	0.0067	0.0046	0.0062	0.0086
	MRE (%)	0.0045	0.0021	0.00388	0.0074
GAB	*Mo*	0.0724	0.0882	0.0885	0.09081
	C	-22.7086	-106.166	-26.2428	-116.186
	K	0.973	1.015	1.024	1.044
	R^2	0.9898	0.9836	0.9821	0.9779
	RMSE	0.0371	0.0257	0.0411	0.0754
	MRE (%)	0.1374	0.0659	0.1691	0.569
Oswin	*A*	0.1867	0.1979	0.2052	0.1953
	B	0.4659	0.4712	0.4224	0.4444
	R^2	0.9965	0.9964	0.9969	0.9967
	RMSE	0.0263	0.0210	0.0237	0.0208
	MRE (%)	0.0692	0.0440	0.0561	0.0432

Table 3. Equation for Oswin model for control and EO film at respective temperatures

Temperature (C)	Control film	EO film
30	$M_w = 0.1867[\frac{a_w}{1-a_w}]^{0.4659}$	$M_w = 0.1979[\frac{a_w}{1-a_w}]^{0.4712}$
40	$M_w = 0.2052[\frac{a_w}{1-a_w}]^{0.4224}$	$M_w = 0.1953[\frac{a_w}{1-a_w}]^{0.4444}$

The values of *A* and *B* obtained are correction factors for the system accordingly. It was found that the R^2 value for Oswin Model is between 0.9964 to 0.9967 while the RMSE values are all near 0. Other than that, the MRE (%) values are all less than 1% thus showing that the model is suitable to describe the moisture sorption isotherm for the control and EO film.

C. *Net Isosteric Heat of Sorption*

The net isosteric heat of sorption for cassava starch film with and without the incorporation of EO was determined through the application of the Clausius – Clapeyron equation at 30°C and 40°C. The moisture sorption data used was applied to the Clausius – Clapeyron equation to determine the energy required for sorption as it is highly dependent on moisture content (Saberi *et al.,* 2015). In general, the heat of sorption provides an approximation of the minimum energy required to remove water from a solid. Therefore, the value of isosteric heat of sorption is directly proportional to how closely the water binds. Based on Figure 6, the film generally decreases exponentially with the increase in moisture content regardless of whether the film contains EO. At low moisture content, the value of heat of sorption was high due to sorption occurring at the most active sites. This shows the intermolecular attraction forces between the sorption site and water vapour (Enyinnaya Chinma *et al.,* 2013). As the moisture content increases, the number of sites available for sorption decreases thus lowering the energy. However, it was observed that there was a sharp increase of heat of sorption at low moisture content which was explained by highly active polar site available at the surface of both films. Water molecules covered these sites causing the formation of monomolecular layer (Sahu *et al.,* 2018). Plotting heat of sorption against moisture content shows exponential relationship. According to (Chowdhury & Das, 2010), the exponential relationship indicates that the sites are heterogenous. Other studies have also observed exponential relationship (Chowdhury & Das, 2010, Bajpai *et. al.,* 2011, Xiao & Tong, 2013, Saberi *et. al.,* 2015, Saha *et. al.,* 2018, Zhang *et al.,* 2020). Figure 6 shows that the net isosteric heat of sorption of the control film and EO film is relatively similar. Therefore, the addition of EO does not have a significant effect to the net isosteric heat of sorption of the films.

In conclusion, the value of q_{st} determined in this section validates the findings of the previous section whereby the addition of oil does not have a significant effect on the film in terms of moisture adsorption. Since both films does not have significant difference at high and low moisture content, both films are applicable at any moisture content.

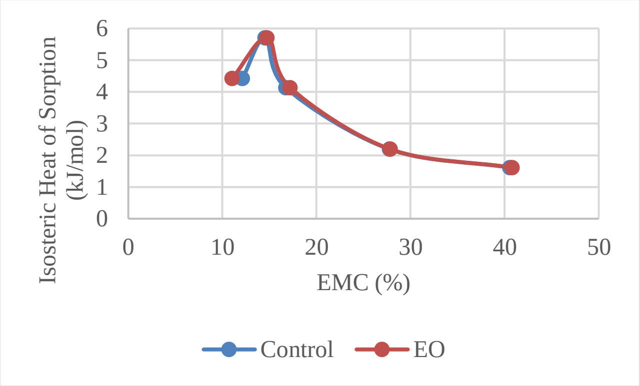

Figure 6. Net Isosteric Heat of Sorption of both films at different moisture content

IV. CONCLUSION

In conclusion, there was an increase in equilibrium moisture content with increasing water activity. Both films showed a slow increase in moisture for a_w below 0.65. At a_w more than 0.65, there was high uptake of moisture content for both films. The addition of EO to the film does not show any significant effect on the moisture properties of the film. Oswin model was the best model to represent the moisture sorption data for both films at both temperatures. It had the highest R^2 values and the lowest RMSE and MRE (%) values compared to the GAB and BET models. The value of net isosteric heat of sorption for both films were relatively similar which supports the insignificant effect of EO addition. The incorporation of EO within these temperatures does not affect the moisture content and heat of sorption of the starch-based bioplastic film, which shows its potential as an additive in food packaging film.

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