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Contributed Paper

Effect of NaOH Concentration on Sorption Isotherm of Carboxymethyl Rice Starch Films and Prediction Models

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ABSTRACT

Effect of NaOH concentration on the sorption isotherm of carboxymethyl rice starch (CMSr) films was investigated. Sorption isotherms are important for predicting moisture sorption properties of the films via moisture sorption empirical models. The moisture sorptions isotherm of CMSr films synthesized with different NaOH concentrations (0, 10, 20, 30, 40 and 50% w/v) were studied at various relative humidity (16, 35, 55 and 76% RH), at $25\pm 1^\circ\text{C}$. The equilibrium moisture content of the films increased dramatically above $a_w = 0.6$. Guggenheim-Anderson-de Boer (GAB), Brunauer-Emmett-Teller (BET) and Oswin sorption models were fitted to the experimental data. The results showed that the increase in NaOH concentration caused a decrease in the monolayer water content (M_m) of the films. The GAB model was found to be the best-fit model for CMSr films at a_w 0.1-0.76, $25\pm 1^\circ\text{C}$.

Keywords: biopolymers, starch, carboxymethyl rice starch, sorption isotherm, sodium hydroxide.

1. INTRODUCTION

Rice starch is well known in food and non-food industrial applications. It is used in the manufacturing of corrugated board adhesives, papers, textiles, pharmaceuticals, cosmetics [1]. Starch is regarded as an attractive starting material for such production because it is natural polymer which can be mass-produced from sustainable agricultural products [2]. However, the applications of native rice starch are still

limited because it is slightly opaque and insoluble in cold water [3].

Starch modification is one of the methods that can improve the physical and chemical properties of rice starch. Carboxymethyl starch (CMS), starch derivatives by etherified starches, has attracted a lot of attention recent years [4]. In the literatures, many starches have been used for synthesis of CMS such as cassava starch [5], corn starch

[6], sago starch [7], mungbean starch [8, 9], arrowroot starch [10], pigeon pea starch [4], water yam starch [11] and rice starch [12]. Much research has been done to investigate the effect of reaction parameters on the carboxymethylation of starch such as molar ratio or concentration of NaOH [4-7, 13], amount of etherifying agent [4, 5, 7, 13], types of solvents [4, 6, 8, 10, 13, 14], temperature [4, 7, 10, 13] and amylose content [12]. The major properties of CMS include a low gelatinized temperature, swelling ability and cold water solubility [7]). These properties of CMS can be characterized by the degree of substitution (DS), the average number of hydroxyl groups substituted by carboxymethyl groups [15].

The properties of CMS are reflected in many applications more than native starch. CMS has been applied in non-food industries, for example, being used as a sizing and printing agent in the textile industry [1, 16], a film-former for tablet coating and a gel base coating in the pharmaceutical industry [9]. Carboxymethyl rice starch (CMS_r) is widely used in many fields of food science, for example, it can be used as a stabilizing agent for ice-cream, vegetable and soft drink and a preservative for fresh meat, vegetable and fruit. CMS has also been produced as biodegradable film but it's very sensitive to moisture [2].

Most biodegradable films, excepted lipid-based, are sensitive to moisture, thus their properties change with relative humidity. The water transmission of hydrophilic films varies nonlinearly with water vapour pressure. If the films are cationic and strongly hydrophilic, water will interact with the polymer matrix, which increases its permeation for water vapour [17]. The water sorption isotherm of a material represents the relationship between their equilibrium moisture content and the water activity at constant temperature and

pressure. The sorption isotherm obtained from experimental data results in an estimation of equilibrium moisture content, which is necessary to predict the properties of films in different environments pertinent to their applications [18]. Some researchers have studied sorption isotherms of biodegradable films. Rachtanapun and Tongdeesoontorn [19, 20] studied sorption isotherm of carboxymethyl cellulose from papaya peel/cornflour blended films and carboxymethyl cellulose films from waste of mulberry paper, respectively. Tongdeesoontorn *et al.* [21] studied sorption isotherm of cassava starch based films blended with gelatin and carboxymethyl cellulose. However, there is no report of sorption isotherm of carboxymethyl starch film. Therefore, this research was aimed to prepare carboxymethyl rice starch film with various NaOH concentrations (10, 20, 30, 40, 50% w/v), determine the effect of NaOH concentration on its moisture sorption isotherm and fit the experimental data with prediction models.

2. MATERIALS AND METHODS

2.1 Materials

Native rice starch was donated from Thaiflour industry Co.,Ltd (Nakornprathom, Thailand). Sodium hydroxide, glacial acetic acid, isopropanol, hydrochloric acid (Merck, Germany), sodium chloride (Merck, Germany), chloro acetic acid (Fluka, Switzerland) are all analytical grade. Absolute methanol is commercial grade from Northern Chemical Co., Ltd. (Chiang Mai, Thailand). Carboxymethyl rice starch (CMS_r) was synthesized from previous study [22].

2.2 Film Preparation

Native rice starch or CMS_r (3% w/v) was added to 100 ml distilled water with vigorous stirring. The film solution was heated to 70°C and held for 10 minutes. Next, the sorbitol 30%

w/w of starch was added into the solution and then degassed to release all air bubbles by using Ultrasonic the elmasonic S series model S10H (JJsciencelab, Thailand). Film were casted by pouring the film-forming solution in flat 15×15cm plastic plate and dried in a hot air oven at 50°C for overnight.

2.3 Moisture Sorption Isotherms

Moisture sorption isotherm measurement was according to Suppakul [23]. Native rice starch and CMSr film specimens (25×25mm.) were conditioned for 7 days at 25±2°C in desiccators containing silica gel to eliminate the initial moisture content. Sample were placed in separate desiccators over saturated salt solutions having known relative humidities (16, 35, 55, 76.3%) at 23.8±0.9°C for 7 days. At the conditions of relative humidity higher than 60% was used ethanol as a fungistatic agent. Moisture content of the films were determined in triplicate using hot air oven at 105°C for 3 h. Percent equilibrium moisture content (%EMC) was calculated by equation 4 [24, 25]:

$$Me = \frac{We}{Wi}(Mi + 1) - 1 \quad (\text{g/g dry product}) \quad (4)$$

where; We is the equilibrium weight of carboxymethyl rice starch films (g), Wi is the initial weight of carboxymethyl rice starch films (g), and Mi is the initial moisture content of the carboxymethyl rice starch films (g/g).

2.4 Moisture Sorption Isotherm Curve Fitting

The state of water in foodstuffs is the great importance since it affects their microbiological and chemical stability. Numerous attempts to explain the state of water in foods based on sorption isotherms have been published [26]. Models available in the literature to describe moisture sorption isotherm can be divided into several categories; kinetic models based on a monolayer (BET

model), kinetic models based on a multilayer and condensed film (GAB model), semi-empirical (Ferro- Fontan, Henderson and Halsey models) and empirical models (Smith and Oswin models) [26]. Isotherm models from the literatures [23, 25, 27] were selected for fitting the experimental data of sorption isotherm of cassava flour film and instant noodles with rice flour, respectively. These models are expressed and rearranged as given below.

GAB (Guggenheim-Anderson-de Boer) model: [23]

$$M = \frac{M_0 C k a_w}{(1 - a_w)[1 + (C - 1)k a_w]} \quad (5)$$

where M = equilibrium moisture content on a dry basis, M_0 = GAB monolayer moisture content, C = Guggenheim constant, k = factor correcting properties of the multilayer molecules corresponding to the bulk liquid and a_w = water activity. The three parameters of GAB model were obtained from its second-order polynomial form ($y = \alpha x^2 + \beta x + \gamma$), as follows:

$$\alpha = \frac{k}{M_0[1 + C - 1]}, \beta = \frac{1}{M_0[1 - 2/C]}, \gamma = \frac{1}{M_0} k C \quad (6)$$

This model was solved using linear regression analysis with the least sum of squares method to obtain α , β and γ and subsequently the parameter values M_0 , C and k.

BET model: [25]

$$M = \frac{M_0 C a_w}{(1 - a_w)[(1 - a_w) + C a_w]} \quad (7)$$

where M_0 and C = constants. Both constants were obtained from the slope and intercept of the linear plots of $a_w/[(1 - a_w) \cdot M]$ vs. a_w . $M_0 = 1/(\text{intercept} + \text{slope})$ and $C = 1/(\text{intercept} \cdot M_0)$

Oswin model: [23, 27]

$$M = k[a_w/(1 - a_w)]^C \quad (8)$$

where k and C = constants. Both constants were obtained from the slope and intercept of

the linear plots of $\log M$ vs. $\log [a_w/(1-a_w)]$.

3. RESULTS AND DISCUSSION

3.1 Moisture Sorption Isotherms

Plotting between %EMC and time at difference relative humidity provides the sorption isotherm curve as shown in Figure 1. The sorption isotherms of CMSr films gave the characteristic sigmoid-shaped type II isotherm curve of normal moisture adsorption isotherm [28] similar to those observed for salted crackers [24], potato flakes [29], starches [30, 31], and CMC film from waste of mulberry paper [20]. At the same NaOH concentration, the increasing of percent relative humidity resulted in increasing the equilibrium moisture content (EMC) of CMSr films. At each % relative humidity when NaOH concentration increased, EMC of CMSr films increased as well due to the increasing of degree of substitution (DS) value [22]. The cause was the substitution of carboxymethyl groups when DS value increased, hydrophilic also increased. At 40% NaOH concentration, the film showed the

highest EMC which related to the highest DS value (DS = 0.38) from our previous study [22]. Moreover, the EMC results from this study also agreed with our previous CMSr morphology study [22]. The morphology of CMSr from scanning electron microscope showed more roughness and collapse on surface of CMSr which synthesized with increasing NaOH concentration (10-40% NaOH). Thus, the CMSr film could adsorb more water and EMC increased. Conversely, at 50% NaOH concentration, the morphology was agglomerate and DS value decreased (DS = 0.32) which make EMC decreased, so film adsorbed less water [22].

3.2 Fitting of Sorption Isotherm Models to Experimental Data

Measured sorption isotherm data were fitted to GAB, BET and Oswin's equations. The constants are shown in Table 2. For BET and GAB models, the most accepted model for foods or edible materials [23], monolayer water content (M_0) of CMSr films synthesized with NaOH (0, 10, 20, 30, 40 and 50 %) were

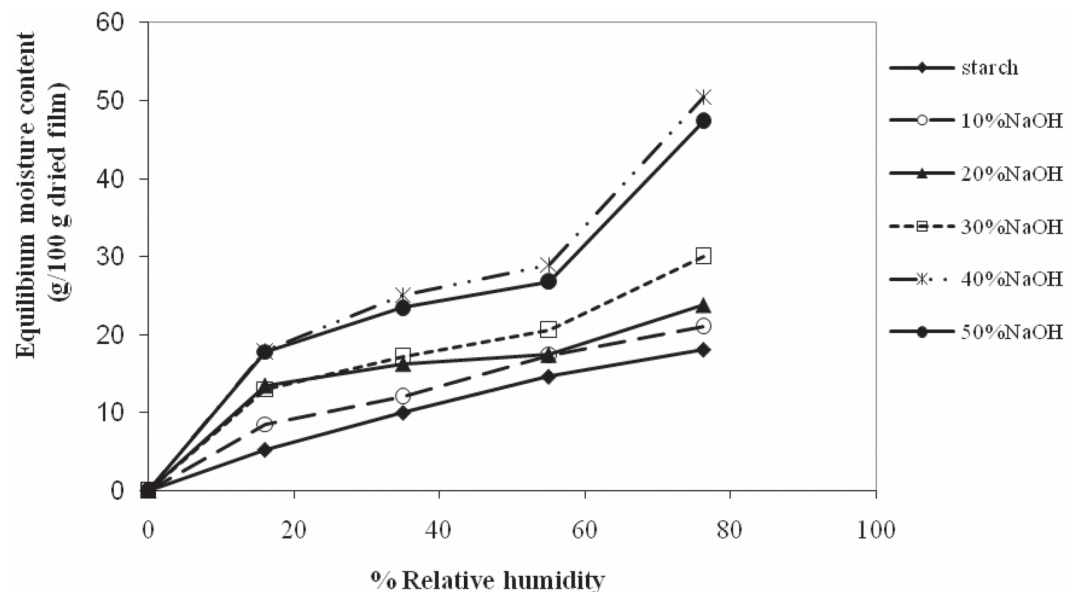


Figure 1. Effect of moisture sorption isotherm of rice starch film and CMSr films synthesized with various NaOH concentrations.

Table 1. Sorption isotherm model constants of CMSr films synthesized with 0 (rice starch film), 10, 20, 30, 40 and 50% NaOH at 25±1°C.

Film	GAB					BET			Oswin				
	C	M ₀	k	r ²	%RMS	M ₀	C	r ²	%RMS	k	C	r ²	%RMS
Rice starch 1.	0910	0.9116	0.0353	0.8542	29.96	0.1214	0.3909	0.9899	92.08	0.0481	0.6693	0.9550	18.38
CMSr with 10% NaOH	1.2670	0.7631	0.0378	0.8362	26.61	0.1264	0.3872	0.9741	94.98	0.0493	0.6797	0.9257	38.02
CMSr with 20% NaOH	111.6104	0.0294	0.5960	0.9830	9.57	0.1262	0.6414	0.8747	110.06	0.0644	0.5203	0.9775	8.66
CMSr with 30% NaOH	8.7975	0.1456	0.3904	0.9755	73.73	0.5678	0.3318	0.9823	87.79	0.2079	0.7116	0.9808	73.21
CMSr with 40% NaOH	4.7966	0.1587	0.1895	0.9869	31.47	0.4389	0.1560	0.9730	57.50	0.1054	0.8948	0.9861	29.67
CMSr with 50% NaOH	9.2393	0.1048	0.2411	0.9847	12.41	0.4187	0.1837	0.9507	69.36	0.1159	0.8124	0.9810	16.33

presented in a range of 0.3328 - 0.8403 and 0.0309 - 0.1082 g water/g dry film, respectively. This value indicated the maximum amount of water that could be adsorbed in a single layer per gram of dry film and it is a measure of number of sorbing sites [32]. The results showed that BET models reported higher M₀s than GAB models, likely because the BET model is based on the monolayer but the GAB model is based on multiple layer [33]. These results agreed with those of Arévalo-Pinedo *et al.* [34] and Tongdeesoontorn *et al.* [21] who found the similar trend of M₀ values from BET and GAB models for Inga pulp and cassava starch based films blended with gelatin and carboxymethyl cellulose sorption isotherms, respectively. For GAB model, the C parameter in GAB model is related to the difference of the magnitude in the upper layers and in the monolayer [34]. M_{0GAB} and M_{0BET} of CMSr films decreased with increasing NaOH concentration. These results may be related to higher hygroscopicity of CMSr synthesized with increasing NaOH concentration (upto 40 % w/v NaOH) [20].

Oswin model provided good descriptions of the moisture isotherms throughout the entire range of water activity [23, 26]. However, GAB model was found to be the better estimator for predicting the equilibrium moisture content of CMSr films synthesized with various NaOH concentrations than BET and Oswin models. This result is agreed with cassava flour film plasticized with sorbitol which was best fitted with GAB model [23].

Figure 2 showed experimental vs. predicted moisture content by GAB, BET and Oswin's models of the CMSr film synthesized with NaOH which obtained the diagonal lines for low and intermediate a_w levels (0.1-0.76), indicating low interaction between components in accordance with their separation in independent phases as observed during the film drying [35]. These results indicated that

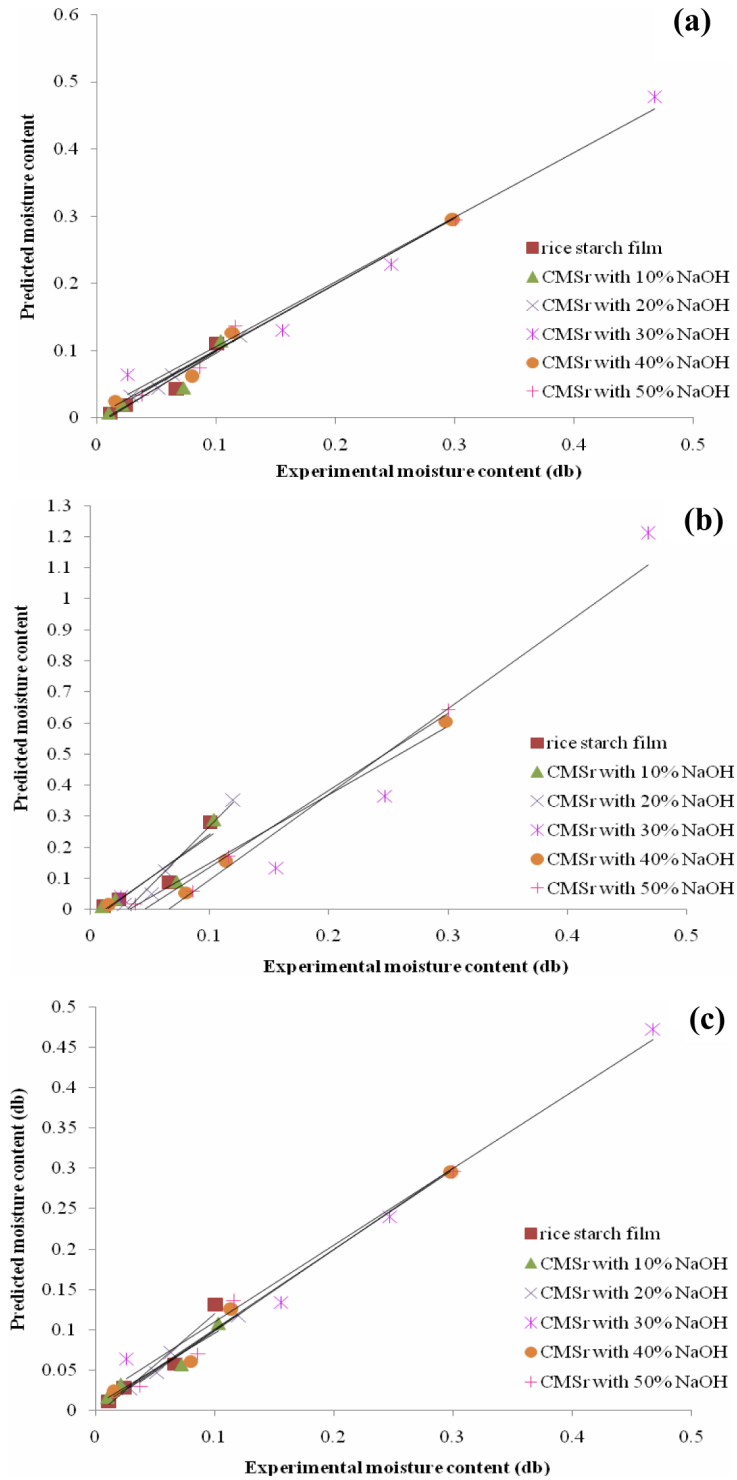


Figure 2. Comparison between experimental moisture content and those predicted by (a) GAB model, (b) BET model and (c) Oswin model of CMSr films synthesized with 0 (rice starch film), 10, 20, 30, 40 and 50 % NaOH.

all model can be used to predict moisture content of CMSr film synthesized with NaOH at a_w 0.1-0.76.

4. CONCLUSIONS

In this research, the moisture sorptions isotherm of CMSr films synthesized with NaOH (0, 10, 20, 30, 40 and 50% w/v) were studied at various relative humidities (16, 35, 55 and 76% RH), $25\pm 1^\circ\text{C}$. The equilibrium moisture content of the films increased dramatically above $a_w = 0.6$. Guggenheim-Anderson-de Boer (GAB), Brunauer-Emmett-Teller (BET) and Oswin sorption models were fitted to the experimental data. The results showed that increasing NaOH concentration caused an decrease in the monolayer water content (M_0) of films. The GAB model was found to be the best-fit model for CMSr films at a_w 0.1-0.76, $25\pm 1^\circ\text{C}$.

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