Investigation and modeling of moisture sorption behaviour of rice starch/carboxymethyl chitosan blend films

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Abstract. The biopolymer films from rice starch (RS) and carboxymethyl chitosan (CMCh) were developed by solution casting. The effect of the ratios of rice starch to CMCh (100:0, 88:12, 67:33, 50:50, 33:67, 12:88 and 0:100) on water barrier properties and moisture sorption isotherm of blend films was studied. Water vapor permeability of rice starch film and CMCh film were 4.8 and 9.1 g.mm/m².mHg.day, respectively, while those of the RS/CMCh blend films ranged between 5.0 and 9.1 g.mm/m².mHg.day. The sorption isotherm of RS/CMCh blend films was determined at 25°C. The sorption behaviour of RS/CMCh blend films could be categorized as type II and type III isotherms. The highest equilibrium moisture content (63.5 g water/100 g dry solid) was obtained in the CMCh film at a_w of 0.87. For further application of sorption isotherm data, the moisture sorption characteristic of the films can be predicted using empirical models. Lewicki, Peleg, Guggenhe im-Anderson-deBoer (GAB), Brunauer–Emmett–Teller (BET), and Oswin models were tested to fit the experimental data. The Peleg equation showed the best fit to the experimental data of the RS/CMCh blend films with r² ≈ 0.997 and the lowest %RMS of 6.2-44.3.

1. Introduction

Natural biopolymers are the main materials used to prepare edible films. These edible films can improve handling properties, extend shelf life of food products, and help reduce the environmental pollution caused by synthetic polymer packaging waste [1]. Edible films can be prepared from polysaccharides, proteins, and lipids. Among these biopolymers, starch is one of the most attractive materials because of its good film forming capability, biocompatibility, relative inexpensiveness, renewability and abundance. Rice starch is made from a rice by-product after rice processing. The major components of rice starch—amylose and amylopectin—are attractive raw materials to be utilized as barriers in packaging materials [2]. Although films of polysaccharides have overall suitable mechanical and optical properties [3], their application is limited by their efficient barrier against low polarity [2]. Therefore, there is a current trend to combine different biomaterials for food packaging.
and coatings in order to overcome the shortcomings [3]. Starch film is often blended with another biopolymer to create a new biocomposite with the more overall benefits than when used individually [2, 3].

Chitosan is a linear polysaccharide containing β-(1-4)-linked N-acetyl-D-glucosamine and D-glucosamine units [4]. It is nontoxic and biodegradable. Chitosan is extracted from chitin, which is abundantly available in nature. Chitosan exhibits excellent biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. [4]. Thus, it has a wide range of applications, including utilization in food processing, agriculture, biomaterials, biotechnology, biomedicine, and pharmaceuticals [4]. However, its limitation of only dissolving in acidic water affects the finished product by causing a bad odor [5]. Carboxymethyl chitosan (CMCh) is an etherified chitosan, which can be used in various industries including food and non-food. It is an interesting choice for use in polymer blending because of its dissolvability in cold water. There are a few studies that have been carried out to investigate the preparation and properties of blends between starch and CMCh [6].

To date, no research has presented the moisture sorption characteristics of rice starch/carboxymethyl chitosan (RS/CMCh) blend film. The objectives of this study were (1) to determine the moisture sorption isotherm including their relation to water vapour permeability and (2) to investigate the sorption model and determine the best fitted model.

2. Methodology

2.1. Materials

Rice starch was purchased from Thai Flour Industry Company Ltd. (Bangkok, Thailand). Shrimp chitosan flakes (molecular weight ranging between 900,000-1,300,000 Dalton, degree of deacetylation=98%) were purchased from Taming Enterprises (Thailand). Monochloroacetic acid was purchased from Sigma-Aldrich (Steinheim, Germany). Sodium hydroxide, glacial acetic acid, isopropanol, ethanol and methanol were purchased from Lab-scan Co., Ltd. (Bangkok, Thailand). Glycerol was purchased from Union Science Co., Ltd. (Chiang Mai, Thailand). All chemicals used in the experiment were AR grade or the equivalent.

2.2. Synthesis of carboxymethyl chitosan (CMCh)

Chitosan was synthesized into CMCh according to the method propounded by Chen and Park [7] and Rachтанапун and Suriyatem [8] with slight modifications. Chitosan flakes were grounded into powder using a hammer mill to obtain particle size smaller than 60 mesh. Chitosan powder (25 g) was suspended in solution of NaOH:isopropanol:distilled-water (50 g:400 mL:100 mL) with continuous stirring at 50°C for 1 h using a hotplate stirrer (IKA C-MAG HS 7, USA). The solution of monochloroacetic acid (etherifying agent) and isopropanol (50 g: 50 mL) was added into the mixture and continuously stirred at 50°C for 4 h. Next, the mixture was separated into two phases—liquid phase and solid phase—and the liquid phase was removed. The solid phase was suspended in methanol, neutralized with glacial acetic acid, and filtered. The residue was washed with 500 mL of 70% (v/v) ethanol five times; followed by washing with 500 mL of 95% (v/v) ethanol to remove undesirable products. The last product, CMCh, was dried in an oven at 55°C for 18 h and stored in a sealed container.

2.3. Film preparation

Film forming solutions (5% w/v) with different rice starch (RS) to CMCh ratios were prepared to yield different RS/CMCh blended films (table 1). RS was dispersed in distilled water and constantly stirred at 90°C for 5 min. CMCh was dissolved in distilled water at 80°C for 10 min. The RS and CMCh solution were mixed and glycerol (25% wt of solid content) was added as a plasticizer. The mixture was degasified, cooled to 25°C, casted on a silicone plate, and then dried at 25°C for 36 h. The films were peeled and kept in an aluminium foil bag until use.
2.4. **Water vapor permeability (WVP)**

WVP was investigated using the ASTM E96-93. The cups containing dried silica gel were covered with the circular specimens and sealed with paraffin wax. Sealed cups were weighed and kept in a desiccator with saturated solution of NaNO₂ to provide 65% RH at 25°C. The cups were re-weighed daily for seven days. WVP was calculated by equation (1) [9]:

\[
WVP = \frac{\text{WVTR}}{\Delta P} \times L
\]  

where \( L \) is the thickness of the film specimen and \( \Delta P \) is the partial pressure difference of water vapor across the film. The WVTR (water vapor transmission rate) was acquired from the calculation of the slope of the linear relationship between time (independent variable) and weight gain (dependent variable) divided by the area of the mouth of the test cup. All measurements were performed in triplicate.

2.5. **Moisture sorption isotherm**

The film specimen, approximately 1.0 g in weight and 20 mm x 20 mm in size, was dried in an oven at 55°C for 24 h and preconditioned in a desiccator containing dried silica gel for seven days. The film specimen was placed in the desiccators containing various saturated salt solutions. The specimen was weighed every 24 h until equilibrium was achieved; this occurred when the change in weight did not exceed 0.1% for three consecutive weight measurements. Equilibrium moisture content was calculated by equation (2) [10]:

\[
EMC = \left\{ \frac{W_e}{W_i} (M_i + 1) - 1 \right\} \times 100
\]

where EMC is the equilibrium moisture content (g water/100 g dry solid); \( W_e \) is the equilibrium weight of the film specimen (g); \( W_i \) is the initial weight of the film specimen (g); and \( M_i \) is the initial moisture content of the film specimen (g/g).

2.6. **Moisture sorption isotherm model**

Five isotherm models from the literature were selected to fit the experimental data of adsorption isotherms of RS/CMCh blend films. The models are characterized as given in table 1 [11-16].

| Nomenclature | Model | Mathematical expression |
|--------------|-------|-------------------------|
| \( a_w \)    | water activity in desiccator | Lewicki |
| RH           | relative humidity in desiccator | Peleg |
| A, B, C, D   | Peleg model constants of the | GAB (Guggenheim–Anderson–deBoer) |
| C, k         | GAB model constants of the | BET (Brunauer–Emmett–Teller) |
| C₁           | constant of the BET model | Oswin |
| F, G, H      | constants of the Lewicki model | |
|              | M, Equilibrium moisture content; \( M_0 \), monolayer moisture content; A, B, C, C₁, C₂, D, F, G, H, and k constants specific to individual mathematical expression. |
2.7. Statistical analysis
All data was analyzed by an analysis of variance (ANOVA) and Duncan’s multiple range test (DMRT; \( P \leq 0.05 \)) using the SPSS version 11.

3. Results and discussion

3.1. Water vapor permeability
The various RS/CMCh film-forming solutions were prepared and casted into seven different blend films using the ratios between the two main solids—rice starch and carboxymethyl chitosan—as shown in table 2. The WVPs of the blend films were measured at a vapor pressure difference of 0/65% across the film and are listed in table 2. The results presented that CMCh film (RS/CMCh-07) and the film containing 88% CMCh (RS/CMCh-06) provided around two times higher WVP than rice starch film (RS/CMCh-01). This result could be explained by the higher hydrophilicity of CMCh material (NH\(_3^+\) and COO\(^-\) groups) than rice starch (OH\(^-\) groups) [2]. The other RS/CMCh blend films, which composed 12–67% CMCh, showed no significantly different WVPs, but all were lower than that of CMCh film. These results are similar to previous researches by Wu et al. [17] for pullulan-CMCh blend film and Bourtoom and Chinnan [2] for rice starch-chitosan blend film. They presented that WVPs of the films increased with an increase of chitosan [2] or CMCh content [17]. This tendency is due to the higher hydrophillicity of NH\(_3^+\) groups by chitosan in the films [2] or the bulkier side groups of chitosan and CMCh that caused the increased free-volume of the blend matrix [17]. Likewise, Zhong et al. [1] studied the physicochemical properties of chitosan and kudzu starch composite film, and they found that the WVP declined when starch content increased.

| Film code | Composition (g/100g solid) glycerol | WVP (g.mm/m².mHg. day) |
|-----------|-----------------------------------|-------------------------|
| RS/CMCh-01| 100 0 25                           | 4.800 ± 0.342 a         |
| RS/CMCh-02| 88 12 25                           | 5.459 ± 0.492 a         |
| RS/CMCh-03| 67 33 25                           | 5.059 ± 0.426 a         |
| RS/CMCh-04| 50 50 25                           | 5.368 ± 0.628 a         |
| RS/CMCh-05| 33 67 25                           | 5.985 ± 0.767 a         |
| RS/CMCh-06| 12 88 25                           | 9.078 ± 1.909 b         |
| RS/CMCh-07| 0 100 25                           | 9.068 ± 0.669 b         |

3.2. Sorption Isotherm
Moisture sorption isotherm curve (\( a_w \) versus EMC) of RS/CMCh blend films are presented in figure 1a. The isotherm curve of rice starch film is classified as a sigmoid-shaped curve type II (figure 1a), which is a behaviour of a glassy polymer-organic on a water vapour system [18]. This curve type is typically obtained for the soluble material and displays an asymptotic trend as \( a_w \) tends toward 1 [16, 19]. The isotherm is more rapid in the initial stages (\( a_w \) 0.00–0.20), and a lesser amount of moisture is adsorbed while \( a_w \) increased toward 0.56. The EMC of film was dramatically raised above \( a_w \) 0.85. However, it can be verified that the isotherm curve of CMCh film shown as type III displays the crystalline components (figure 1a) [10]. The more RH surrounding, the more pronounced the effect. The EMC of the film soared after \( a_w \) 0.77. By analysing the curve of other blend films, it (except the RS/CMCh-02) can be classified as the type III isotherm (figure 1a), which is similar to that of CMCh film. This is possibly due to the effect of increasing the proportion of CMCh in the blend films. However, the isotherm curve of RS/CMCh-02 can be categorized as type II (figure 1a) because it contains a small amount of CMCh. The results indicate that the sorption isotherm characteristic is dependent on the composition of the main material. In this study, CMCh has more influence on the moisture sorption characteristic of the blend than rice starch. This is possibly because of its bulkiness and polar side chain. Similar results were found in a previous study for the moisture isotherm of rice starch/carboxymethyl cellulose from durian rind blend films [16]. Furthermore, these observations are
in agreement with those of carboxymethyl cellulose from papaya peel/corn flour blend films [10], cassava flour film [19] and cassava starch/carboxymethyl cellulose blend films [9].

![Graph](image)

**Figure 1.** (a) Moisture sorption isotherm curves of RS/CMCh blend films and (b) equilibrium moisture content versus proportion of CMCh in RS/CMCh blend film at various $a_w$. (mean values ± standard error; in triplicate).

Figure 1b exhibits the moisture sorption isotherm curve of RS/CMCh blend films in terms of proportion of CMCh versus EMC. The difference between the sorption capacities of each film can be more obviously seen at higher $a_w$. The CMCh film provided a significant higher EMC than the rice starch. This result is in agreement with the previous works for the blend films between starch and derivatives from carboxymethylation [9, 16]. In this case, the EMC of the blend film decreased with a decrease of the CMCh composition (12–100 g/100 g solid). Interestingly, when small amounts of CMCh were employed in the films (12–33 g/100 g solid), the EMC of the blend film dropped and it was lower than that of the films of both main materials.

3.3. **Fitting of sorption isotherm models to experimental data**

Experimental sorption isotherm data of the RS/CMCh blend films were fitted to Lewicki, Peleg, GAB, BET and Oswin’s equations. Table 3 lists sorption isotherm model constants including coefficient of determination ($r^2$) and percentage root mean square error (%RMS), which are the criteria used to estimate the fit of each model. All models showed a good fit to the experimental data ($r^2 > 0.99)$.

The Lewicki model was followed to predict the moisture sorption data at a high range of $a_w$ and it fitted well with the data at high humidity [11]. This model predicted that the amount of water tented toward infinity as $a_w$ reached 1.0 [11]. Therefore, the Lewicki model is considered to be a suitable choice to predict the moisture adsorption of materials at different environmental humidities. The %RMS value was in the range between 12.5 and 184.7%.

The Peleg model was applied to predict both sigmoid and non-sigmoid isotherms, and it can fit comparably to or better than the GAB model [12]. However, its constants have no physical meaning. In this case, the range of %RMS was the lowest (6.2–44.3%) among all test models.

The GAB and BET models are the most accepted model for foods and edible materials [15]. The GAB equation gave the best fit for many kinds of the fruits, meats and vegetables examined [20]. The BET model is the most significant isotherm model for the explanation of multilayer sorption isotherms, especially for sigmoidal type II isotherm characteristics [21]. Both models allow for the evaluation of monolayer moisture content ($M_0$) values. The $M_0$ is utilized to measure the number of sorption sites, and indicates the maximum moisture content which can be adsorbed in a single layer of 1 g of dry film [9]. The $M_0$ calculated from the GAB and BET equations for the RS/CMCh blend films ranged between 8.6–220.6 g/100 g (dry basis) and 4.6–9.4 g/100 g (dry basis), respectively. Results
Table 3. Sorption isotherm model constant, coefficient of determination ($r^2$) and percentage of root mean square error (%RMS) for RS/CMCh blend films.

| Sample | Parameters | BET | Oswin | Peleg |
|--------|------------|-----|-------|-------|
|        | Lewicki    |     |       |       |
| Parameter | F | G | H | $r^2$ | RMS(%) | m0 | C1 | $r^2$ | RMS(%) |
| RS/CMCh-01 | 5.091 | 1.197 | 0.620 | 0.996 | 13.66 | 8.19 | 1.01 | 0.996 | 19.705 |
| RS/CMCh-02 | 8.640 | 0.729 | 6.006 | 0.999 | 14.45 | 4.58 | 1.99 | 0.997 | 10.320 |
| RS/CMCh-03 | 8.403 | 0.840 | 4.560 | 0.995 | 184.75 | 6.12 | 1.22 | 0.992 | 191.315 |
| RS/CMCh-04 | 10.424 | 0.801 | 4.221 | 0.997 | 79.56 | 6.82 | 1.50 | 0.994 | 95.344 |
| RS/CMCh-05 | 11.628 | 0.804 | 4.697 | 0.998 | 35.87 | 7.64 | 1.44 | 0.995 | 43.471 |
| RS/CMCh-06 | 92.331 | 0.089 | 4.642 | 0.998 | 12.54 | 7.17 | 3.61 | 0.981 | 37.995 |
| RS/CMCh-07 | 15.249 | 0.776 | 4.427 | 0.996 | 95.78 | 9.42 | 1.48 | 0.992 | 108.248 |

The Oswin model allows good descriptions of the moisture isotherms all over the entire range of water activity [14]. This model is used for predicting sigmoid shape curve and is able to provide a better fit for protein and starchy foods [14]. Unfortunately, in this case, the maximum %RMS (14.6-242.4%) was found for the Oswin model.
Therefore, the Peleg model is the best estimator for predicting the EMC of RS/CMCh blend films, followed by the GAB, Lewicki, BET and Oswin models, respectively. This is in agreement with the previous study for rice starch/carboxymethyl cellulose from durian rind [16]. However, Suppakul et al. [19] found that the GAB model was the most optimal (among the Peleg, Lewicki and Oswin models) to fit the sorption isotherm for cassava flour film. Furthermore, other researches revealed that the GAB model was found to be the best fit for cassava starch based films blended with gelatin and carboxymethyl cellulose [9] and carboxymethyl rice starch films [22].

Figure 2 reveals the experimental versus predicted moisture sorption contents by the Lewicki, Peleg, GAB, BET and Oswin models for the RS/CMCh blend films. The achieved points are placed on the diagonal for low and intermediate $a_w$ levels (0.20–0.77). This observation indicated low interaction occurring between the film compositions, according to their separation in the independent phases as appeared during film drying [19]. The point increased rapidly on the diagonal, as an effect of the interaction between the water molecules and the polar groups of the film, at a high level of $a_w$ (0.85) [19]. These results pointed out that these four types of predicting models can be used to predict the moisture content of the RS/CMCh blend films at $a_w$ 0.20–0.87.

Figure 2. Comparison between experimental and predicted data of moisture content by (a) model, (b) BET model, (c) Peleg model for RS/CMCh blend films.

4. Conclusion
Hydrophilicity of carboxymethyl chitosan and its proportion in the blend films were the interrelated factors in an investigation of water resistance and moisture sorption characteristics for the blend film composed of rice starch and carboxymethyl chitosan. The Peleg, GAB, Lewicki, BET and Oswin models were beneficial to fit moisture sorption isotherm data. The Peleg model was found to give the best prediction of sorption isotherm of RS/CMCh blend films at 25°C. These blend films possess a
potential use as an edible coating and food packaging using moisture-resistant and/or antioxidative modification.

Acknowledgments
The authors gratefully acknowledge the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program as well as Chiang Mai University for the financial support.

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