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Research Article

Moisture sorption isotherms and water vapour permeability of carboxymethyl cellulose from papaya peel/cornflour blended films

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Abstract

The moisture sorption isotherm of carboxymethyl cellulose from papaya peel (CMCp)/cornflour blended films (0:100, 25:75, 50:50, 75:25, 100:0 w/w) determined at different relative humidities (13.5, 36.5, 46.5, 66.8, 77.3 and 93.8%RH), at 25 ± 1°C, showed that water content sharply increased above $a_w = 0.6$. Knowledge of sorption isotherms is also important for predicting moisture sorption properties of films *via* moisture sorption empirical models. Increasing cornflour content gave higher equilibrium moisture contents in blended films. Guggenheim-Anderson-de Boer (GAB), Brunauer–Emmett–Teller (BET) and Oswin sorption models were fitted to the experimental data. The BET model was found to be the best-fit model for blended CMCp/cornflour films at 33-77%RH, 25 ± 1°C. The water vapour permeability of films was also examined. Permeability values of films were found to increase from 1.391×10^{-4} to 1.897×10^{-4} $g \cdot m \cdot m^{-2} \cdot mmHg^{-1} \cdot day^{-1}$ with increasing cornflour concentration.

Keywords: Carboxymethyl cellulose from papaya peel; cornflour; sorption isotherm; water vapour permeability, Thailand

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Introduction

Papaya (*Carica papaya L.*) is widely cultivated for its edible fruit or for use as a vegetable. In Thailand, raw papaya fruit is used for papaya salad or pickled papaya, in addition to be eaten ripe. Papaya peel thus becomes a significant waste from restaurants and pickled papaya manufacture and is estimated to be more than 1,000 per year. Despite this significance, there have been very few publications on the utilization of papaya peel [1, 2, 3].

Carboxymethyl cellulose (CMC) is a linear, long-chain, water-soluble, anionic polysaccharide. Purified CMC is a white to cream-coloured, tasteless, odorless, free-flowing powder [4, 5]. Some papers have reported on the synthesis of CMC from various agricultural wastes such as from banana pseudo stems [5], orange peel [6] and papaya peel [1, 2, 3].

From the literature reviews, corn starch appears to be an interesting alternative for edible films due to it is abundance, cheap price, being biodegradable as well as edible [7, 8, 9]. Through plant breeding, three types of cornstarch are commercially available; waxy (< 1% amylose), pearl (~ 25% amylose) and high amylose (50-70% amylose) [8].

Most biodegradable films, except lipid-based, are sensitive to moisture, and 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 [9]. The water sorption isotherm of a material represents the relationship between their equilibrium moisture content and the water activity (a_w) 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 [10]. Some researchers have studied the WVP and sorption isotherms of biodegradable films. Li *et al*. [11] studied WVP of rice starch/CMC blended film. Suppakul [12] reported the sorption characteristics of cassava flour film plasticized with sorbitol.

In our previous work, papaya peel was sun-dried and ground to powder. In order to produce the cellulose pulp, papaya peel powder was delignified by pulping process with NaOH. Cellulose was then modified to carboxymethyl cellulose through a substitution reaction using monochloroacetic acid or under alkaline conditions [1, 2, 3]. Applications of carboxymethyl cellulose from papaya peel (CMCp) were biodegradable film [1, 2, 11] and coating for mango (*Mangifera Indica L.*) [13]. However, mechanical properties of CMCp film were less than that of commercial carboxymethyl cellulose film. From the results of a previous study it was shown that cornflour addition can improve strength of CMCp films [3], however, there is no known research about water vapour permeability and sorption isotherms of CMCp film blends. Therefore, the objectives of this work were to study the effect of the composition of CMCp/cornflour film blends on water vapour transmission rate (WVTR), permeability coefficient (P) and moisture sorption isotherms of CMCp films.

Materials and Methods

Materials

Fresh papaya peel was collected from *Somtum* shops in Chiang Mai, Thailand. All chemicals (NaOH, isopropyl alcohol (IPA), chloroacitic acid, methanol, ethanol, acetic acid and glycerol) were purchased from Northern Chemical Company (Thailand).

Preparation and synthesis of carboxymethy cellulose from papaya peel

CMC from papaya peel preparation and synthesis were described in our previous work [3]. Dried papaya peel was ground and cooked with 0.5 molar NaOH. The black slurry obtained was filtered and washed with cold water. The residue was dried in an oven at 55°C over night. The cellulose was ground and kept in polyethylene bags for modification of CMC in the next process. Cellulose powder was added in isopropyl alcohol (IPA) and then stirred. NaOH was added into the mixture before it was added with chloroacetic acid and stirred. Mixture separated into two parts (liquid and solid phase). The liquid phase was removed and the solid phase was washed with absolute methanol, neutralized with acetic acid (90% v/v) and then filtered. The final product was washed by soaking in ethanol (70% v/v) to remove any undesirable byproducts and then it was washed again with absolute methanol. The obtained CMCp was dried at room temperature overnight [1, 3].

Film casting

The film-forming solutions of CMCp/cornflour (100:0, 75:25, 50:50, 25:75 and 0:100 w/w) were stirred at 90-95°C for 10 min. The solution was cooled down to 20-25°C [3, 5] and then casted by a tape casting machine at 10 rpm. CMCp/cornflour films were dried at room temperature.

Water vapour transmission rate (WVTR) and permeability coefficient (P)

Water vapor transmission of casted films was measured following ASTM E96-93 [14]. Aluminium cups with a diameter of 8 cm and a depth of 2 cm were used to determine WVTR. After placing 10 g of dried silica gel in each cup, they were covered with film samples prepared in our experiment, cut circularly (ϕ=7 cm) and sealed using melted paraffin. The cups including their contents were weighed and placed in desiccators kept at 25 ± 1°C. The relative humidity was maintained by saturated solutions of NaCl in the bottom of the desiccator to provide 75%RH at 25 ± 1°C. Cups were weighed every 24 hours for 2 weeks. WVTR (g·day^{-1}·m^{-2}) was calculated from slope of weight gain and time per area of film sample as follows [15, 16, 17]:

$$WVTR = \frac{weight\ gain\ (g)}{time\ (day) \times area\ of\ \ film\ sample\ (m^2)} \tag{1}$$

Permeability coefficient (P) (g.m/m^2.mmHg.day) was calculated from Equation 2 [18, 19]:

$$P = \frac{WVTR \times L}{\Delta p} \tag{2}$$

where $WVTR$ is the measured water vapor transmission rate (g·day^{-1}·m^{-2}) through the film specimen, L is the mean thickness of the film (m), and Δp is the partial water vapour pressure difference (mmHg) between two sides of the film specimen.

The partial water vapour pressure difference (Δp) across the film specimen was calculated by using the following equation [8, 14, 17]:

$$\Delta p = Ps\,\frac{(RH_{out} - RH_{in})}{100} \tag{3}$$

where *Ps* is the saturated water vapour pressure at 25 ± 1°C, RH_{out} is the relative humidity outside the aluminium cup, RH_{in} is the relative humidity inside the cup.

Moisture sorption isotherms

Film specimens were dried in a hot air oven for 3 hours and placed in a desiccator for 2 days. Then the films were placed in desiccators containing different saturated solutions that produced the desired relative humidity (13.50, 36.50, 46.50, 66.80, 77.30 and 93.80%RH). The film specimens were weighed every 24 hours. When the two consecutive weights were equal, it was assumed that an equilibrium condition was reached. Under the above conditions, an equilibrium period of 7 days was sufficient to establish moisture equilibrium [12]. Percent equilibrium moisture content (%EMC) was calculated by equation 4 [17, 20]:

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

Where; *We* is the equilibrium weight of the films (g),

Wi is the initial weight of the films (g), and

Mi is the initial moisture content of the films (g/g).

Moisture sorption isotherm curve fitting

Isotherm models of cassava flour film, pumpkin cracker and instant noodles with rice flour [11, 18, 20] were selected for fitting the data of sorption isotherms in this present study. These models are expressed and rearranged as given below.

Guggenheim-Anderson-de Boer (GAB) model:

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

Where M is the equilibrium moisture content on a dry basis, M_0 is GAB monolayer moisture content, C is Guggenheim constant, k is the factor correcting properties of the multiplayer molecules corresponding to the bulk liquid and a_w is water activity. The three parameters of GAB model were obtained from its second-order polynomial form as follows:

$$y = \alpha x^2 + \beta x + \gamma \tag{6}$$

Where $\alpha = {}^{k}\!/_{M_0[1/c - 1]}$, $\beta = {}^{1}\!/_{M_0[1 - 2/C]}$, $\gamma = {}^{1}\!/_{M_0\ kC}$

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.

Brunauer-Emmett-Teller (BET) model:

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

Where M_0 and C are constants obtained from the intercept and the slope of the linear plots of $a_w/[(1-a_w).M]$ vs. a_w, respectively. M_0 = 1/ (intercept + slope) and C = 1/ (intercept. M_0)

Oswin model:

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

Where k and C are constants obtained from the intercept and the slope of the linear plots of log M vs. log $[a_w/(1-a_w)]$, respectively.

Results and Discussion

Effect of blend composition and plasticizer on water vapour transmission rate and permeability

Effects of blend composition and plasticizer on WVTR and P of CMCp/cornflour were also investigated. WVTR and P (Table 1) significantly increased as the amount of cornflour increased due to the water absorbability of amylopectin in cornflour. These results agreed with data on films from different starch sources [19].

Table 1. Water vapour transmission rate and permeability coefficient of films.

Samples	WVTR ($g \cdot day^{-1} \cdot m^{-2}$)	P ($g \cdot m \cdot m^{-2} \cdot mmHg^{-1} \cdot day^{-1}$)
CMCp/Cornflour 100 : 0	87.68^e	1.391×10^{-4}
CMCp/Cornflour 75 : 25	88.28^d	1.401×10^{-4}
CMCp/Cornflour 50 : 50	89.62^c	1.422×10^{-4}
CMCp/Cornflour 25 : 75	90.61^b	1.438×10^{-4}
CMCp/Cornflour 0 : 100	119.54^a	1.897×10^{-4}

Moisture sorption isotherms

The plot of %EMC versus time at different water activities provided sorption isotherm curves as shown in Figure 1. Moisture sorption isotherm curve of CMCp films with and without cornflour can be classified as type III isotherm which represented the crystalline components of films [21]. The moisture content of CMCp films with and without cornflour increased slowly with increasing in water activity up to 0.668, beyond that a steep rise in moisture content of films was observed. This result agreed with sorption isotherms of corn starch film [22]. Increasing cornflour concentration increased %EMC of CMCp films. Thus it is evident that cornflour concentration affected %EMC of films. Films with higher concentration of cornflour absorbed more moisture at a given a_w due to water absorbability of cornstarch [16]. Similarly, Mahmoud and Savello [23] reported that whey protein films having higher glycerol concentration contained higher moisture content.

Fitting of experimental data to sorption isotherm models

Measured sorption isotherm data were fitted to GAB, BET and Oswin's equations. The relevant factors are shown in Table 2.

For BET and GAB models, the most accepted models for food or edible materials [8], monolayer water content (M_0) of CMCp films with and without cornflour were presented in a range of 1.47-4.27 and 2.37-3.16 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 the number of sorption sites [24]. For 0-50% cornflour, the results showed that GAB gave higher M_0 than the BET model. These results agreed with Timmermann *et al.* [25]. For the GAB model, the C parameter in the GAB model is related to the difference of the magnitude in the upper layers and in the monolayer [26]. M_{0BET} of CMCp films increased with increasing cornflour content.

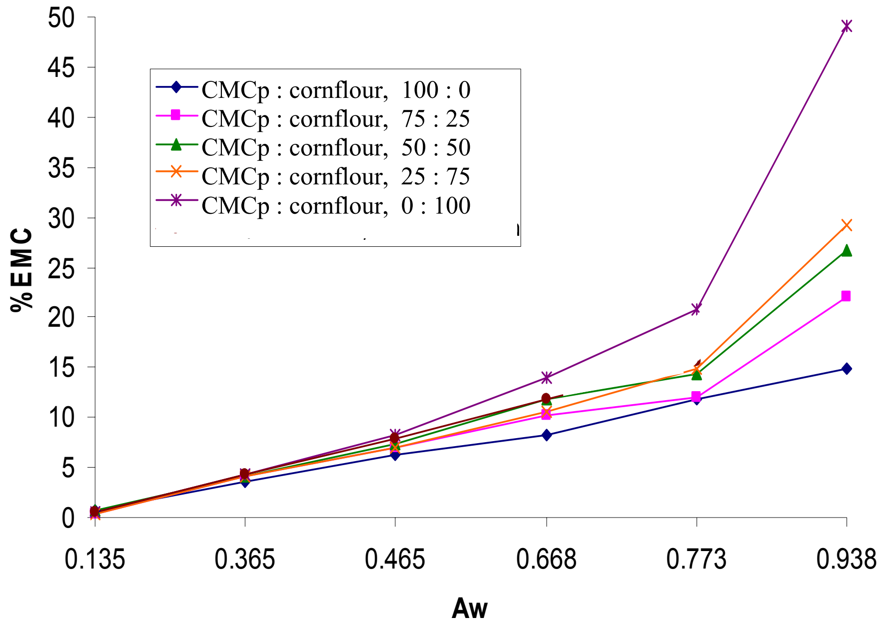

Figure 1. Sorption isotherm of CMC_p/conflour film with different cornflour content at 25ºC.

Table 2. Sorption isotherm model constants of CMC_p/cornflour film with different cornflour content at 25°C.

Films	**GAB**				**BET**			**Oswin**		
	M_0	**C**	**Km**	**%RMS**	**M_0**	**C**	**%RMS**	**k**	**C**	**%RMS**
CMCp:corn flour (0:100)	3.0929	2.7065	1.0870	48.03	4.2735	2.0455	26.47	0.9283	-0.6779	82.50
CMCp:corn flour (25:75)	2.9088	2.7232	1.0433	32.41	3.4868	30.8387	13.11	0.9892	-0.6305	77.87
CMCp:corn flour (50:50)	3.3098	4.2484	1.0017	21.46	2.4438	14.9890	32.73	1.1465	-0.7953	90.78
CMCp:corn flour (75:25)	2.3691	2.0100	1.2132	40.35	2.1791	3.8824	42.75	0.9261	-0.5206	87.18
CMCp:corn flour (100:0)	3.1618	5.6794	0.9129	59.76	1.4743	-12.0266	49.76	1.3338	-0.8226	86.36

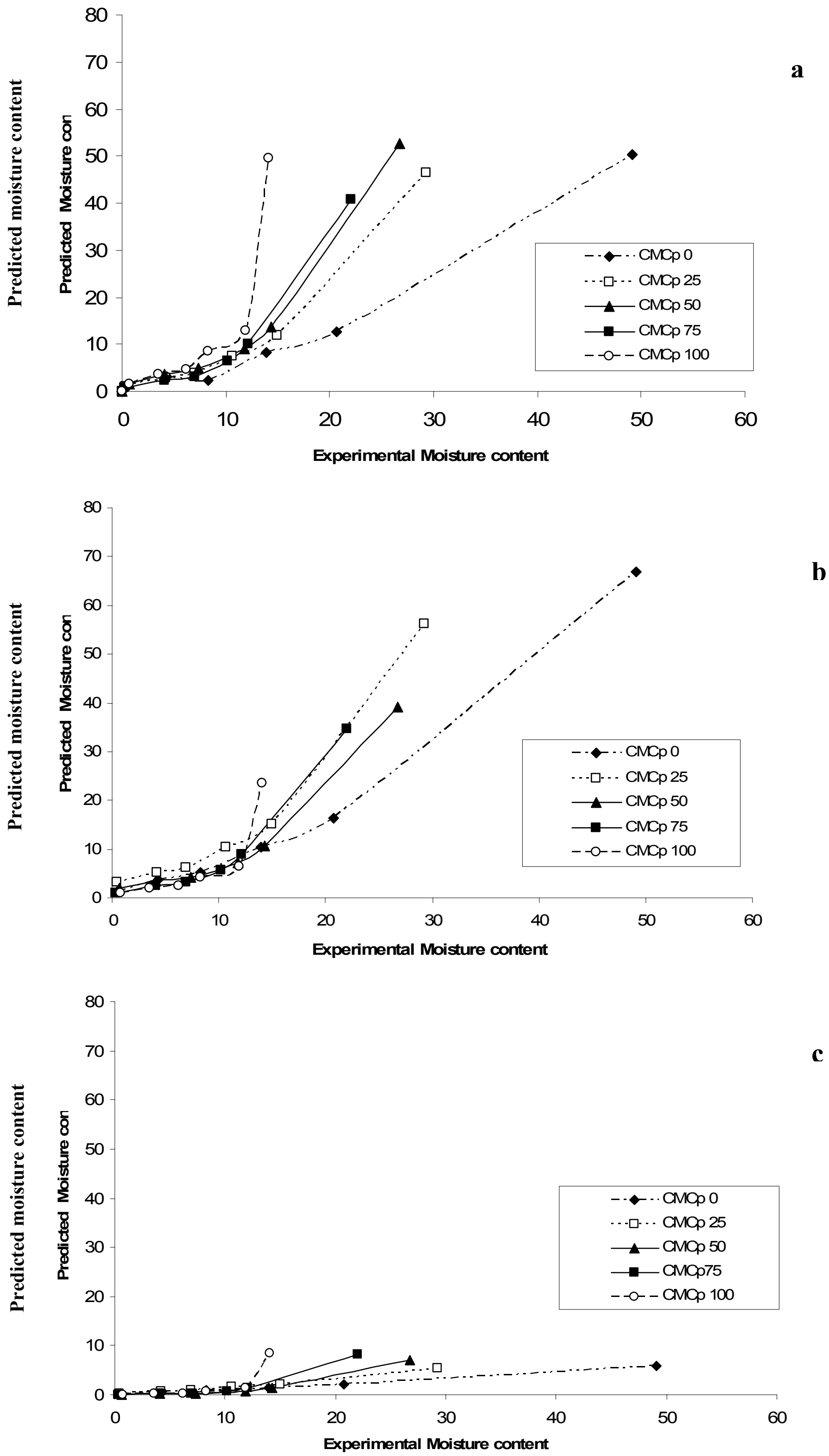

Figure 2. Comparison between experimental moisture content and those predicted by (a) GAB model, (b) BET model and (c) Oswin model of CMC_p films with various cornflour concentrations.

These results may be related to higher hygroscopicity of cornflour which agreed with the M_0 of cassava starch films plasticized with glycerol [27]. The Oswin model usually provides good descriptions of the moisture isotherms throughout the entire range of water activity [28]. However, in this case, maximum %RMS value was obtained for the Oswin model. Thus, the BET model was found to be the better estimator for predicting the EMC of CMCp films with and without cornflour than GAB and Oswin models. This result is in disagreement with the results for cassava flour film plasticized with sorbitol which was best fitted with the GAB model [8].

Figure 2 shows the experimental versus predicted moisture content by GAB, BET and Oswin's models for the CMCp film with and without cornflour which obtained the diagonal lines for low and intermediate a_w levels (0.1-0.8), indicating low interaction between components in accordance with their separation in independent phases as observed during the film drying [29]. At more than 0.8, it can also be observed that the point rapidly increased on the diagonal, as a result of the interaction between the water molecules and the polar groups of the film [11]. These results indicated that all models can be used to predict moisture content of CMCp film with and without cornflour at a_w 0.1-0.8.

Conclusions

In this research the production of CMCp was studied and the effects of cornflour concentration in CMCp films on water vapour transmission rate and sorption isotherm were investigated. WVTR and P increased with cornflour concentration (25-100%) in film solution. The range of WVTR and P of CMCp/cornflour films were 87.68 – 119.54 g/day·m^2 and 1.391×10^{-4} - 1.897×10^{-4} g·m/day m^2·mmHg, respectively. The percent of equilibrium moisture content (%EMC) also rose with increasing conflour. The BET model was found to be the best-fit model for CMCp films at a_w 0.3-0.8.

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