Research Article

Effect of glycerol concentration on sorption isotherms and water vapour permeability of carboxymethyl cellulose films from waste of mulberry paper

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Abstract

The effect of glycerol concentration on the sorption isotherms and water vapour permeability (WVP) of carboxymethyl-cellulose (CMC) films from waste mulberry paper (CMCm) was investigated. The knowledge of sorption isotherms is also important for predicting moisture sorption properties of films via moisture sorption empirical models. The moisture sorption isotherms of CMCm films plasticized with glycerol (0, 0.1, 0.2, 0.3 and 0.4 %v/v) were studied at various relative humidities (13.5, 36.5, 46.5, 66.8, 77.3 and 93.8 %RH), at 25 ± 1°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 glycerol concentration caused an increase in the monolayer water content (M0) of films. The GAB model was found to be the best-fit model for CMCm films at \( a_w = 0.1-0.8 \), 25 ± 1°C. WVP of CMCm film was higher than WVP of commercial CMC film, and WVP of CMCm film increased from \( 10.383 \times 10^{-5} \) to \( 10.826 \times 10^{-5} \) g.m/m².mmHg.day with increasing glycerol concentration.

Keywords: Carboxymethyl cellulose, CMCm, GAB, BET, Oswin, WVP, WVTR, Thailand
Introduction

Cellulose is a main component of plants and wood and may be converted to useful derivatives by etherification [1]. Carboxy methyl cellulose (CMC) is the most important water-soluble cellulose derivative, with many applications in food, cosmetics, pharmaceuticals and detergents [2]. Production of CMC is carried out by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt [3]. The substitution of the hydroxyl groups by the carboxy methyl group is slightly preponderant at C-2 of the glucose [4]. Cellulose, which is modified to be CMC, can be extracted from many sources such as banana pseudo stems [5], sticky rice husk and cotton [6], sugar beet pulp [7], orange peel [8], papaya peel [9, 10, 11] and waste of mulberry paper [12].

In the northern part of Thailand, there are many industries, which use natural materials as raw materials in their production process. After the production process, the natural materials such as mulberry paper, corncob and bamboo are discarded as waste. These wastes of natural materials have cellulose as a component. Especially, waste of mulberry paper has a lot of cellulose due to the production process, which extracts cellulose from mulberry bark to make paper [13]. Extracting cellulose from the waste of mulberry paper and modifying it to CMC for biodegradable film production is potentially a good way to utilize and reduce the waste. Also, it can provide a value for the waste and waste recovery is beneficial to the environment.

Most biodegradable films, except lipid-based, are sensitive to moisture and their properties change with changes in 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, increasing the permeation for water vapour [14]. The water sorption isotherm of a material represents the equilibrium relationship between their moisture content and the water activity (a_w) at constant temperature and pressure. The sorption isotherms obtained from experimental data result in an estimation of equilibrium moisture content, which is necessary to predict the properties of films in different environments pertinent to their applications [15]. Some authors have studied the WVP and sorption isotherms of biodegradable films. Li et al. [16] studied WVP of rice starch/CMC blended film. Suppakul [17] reported the sorption characteristics of cassava flour film plasticized with sorbitol.

The object of this research was to study the effects of the amount of glycerol concentration as a plasticizer in CMC films on water vapour transmission rate (WVTR), permeability coefficient (P) and moisture sorption isotherms of carboxy methyl cellulose films.

Materials and Methods

Materials
Waste of mulberry paper was purchased from Bankradassa (Chiang Mai, Thailand). NaOH, isopropyl alcohol (IPA), chloro acetic acid, methanol, ethanol, acetic acid, glycerol, carboxy methyl cellulose (CMCc), distilled water were purchased from Northern Chemical Co., Ltd. (Chiang Mai, Thailand).
CMCm film preparation
CMCm films were prepared as described in a previous study [12]. Glycerol (0, 0.1, 0.2, 0.3 and 0.4 %v/v) was added as plasticizer.

Water vapour transmission rate (WVTR) and permeability coefficient (P)
Water vapour transmission of films was measured using the ASTM E96-93 [18]. Aluminum cups with a diameter of 8 cm and depth 2 cm were employed. 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 were weighed along with their content 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.m²) was calculated from slope of weight gain and time per area of film sample as follows [19, 20, 21]:

\[ \text{WVTR} = \frac{\text{weight gain (g)}}{\text{time (day) \times area of film sample (m²)}} \]  

Permeability coefficient (P) (g.m/m².mmHg.day) was calculated from [15, 16]:

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

WVTR is the measured water vapour transmission rate (g/day.m²) through the film specimen, \( L \) is the mean film thickness (m), and \( \Delta p \) is the partial water vapour pressure difference (mmHg) across two sides of the film specimen.

The partial water vapour pressure difference (\( \Delta p \)) across two sides of the film specimen was calculated by using the following equation [19, 20, 21]:

\[ \Delta p = P_S \left( \frac{RH_{out} - RH_{in}}{100} \right) \]

\( P_S \) is saturated water vapour pressure, \( RH_{out} \) is relative humidity outside the cup, \( RH_{in} \) is relative humidity inside the aluminum cup.

Moisture sorption isotherms
Various film specimens were pre-dried in a hot air oven for 3 hours and placed in a desiccator for 2 days. Next, films were placed in the desiccator over saturated solution having 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, and equilibrium period of 7 days was sufficient to establish moisture equilibrium. Percent equilibrium moisture content (%EMC) was calculated by equation 4 [21, 22]:

\[ \%EMC = \frac{W_{eq} - W_0}{W_0} \times 100 \]
\[
Me = \frac{We}{Wi} (Mi + 1) - 1 \quad (g / g \text{ dry product})
\] (4)

Where; \( We \) is the equilibrium weight of carboxymethyl cellulose films from waste of mulberry paper (g), \( Wi \) is the initial weight of carboxymethyl cellulose films from waste of mulberry paper (g), and \( Mi \) is the initial moisture content of carboxymethyl cellulose films from waste of mulberry paper (g/g).

**Moisture sorption isotherm curve fitting**

Isotherm models from the literature \[17, 22\] were selected for fitting the experimental data of sorption isotherms of cassava flour film and instant noodles with rice flour, respectively. Those models are expressed and rearranged as given below.

**GAB (Guggenheim-Anderson-de Boer) model:**

\[
M = \frac{M_0 \cdot C \cdot a_w}{(1-a_w)(1+(C-1)\cdot k \cdot a_w)}
\] (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 multiplayer 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:

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

This model was solved using linear regression analysis with the least sum of squares method to obtain \( \alpha, \beta \) and \( \gamma \) and subsequently the parameter values \( M_0, C \) and \( k \).

**BET model:**

\[
M = \frac{(M_0 + T) \cdot C \cdot a_w}{(1-a_w)(1-a_w) + C \cdot a_w}
\] (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. \( a_w \). \( M_0 = 1/ \) (intercept + slope) and \( C = 1/ \) (intercept. \( M_0 \))

**Oswin model:**

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

Where \( k \) and \( C = \) constants. Both constants were obtained from the slope and intercept of the linear plots of \( \log M \) vs. \( \log [a_w/(1-a_w)] \).

**Results and Discussion**

**Effect of amount of glycerol in CMC\(_m\) films on water vapor transmission rate (WVTR) and permeability coefficient (P)**

Effect of amount of glycerol in CMC\(_m\) films on water vapour transmission rate (WVTR) and permeability coefficient (P) was studied. WVTR could be calculated from the slope of weight gain and time per area of film samples.
WVTR and P increased with increasing amount of glycerol (Table 1) because addition of glycerol as a plasticizer in film could increase free volume between polymer chains, reduce cohesive energy and lower Tg [23]. Therefore, water vapour could easily pass through the film [24].

Table 1: Water vapour transmission rate (WVTR) and permeability coefficient (P) of films.

<table>
<thead>
<tr>
<th>Films</th>
<th>WVTR (g/day.m²)</th>
<th>P (g.m².mmHg.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMCc</td>
<td>61.34</td>
<td>9.733 x 10⁻⁵</td>
</tr>
<tr>
<td>CMCm non glycerol</td>
<td>65.44</td>
<td>10.383 x 10⁻⁵</td>
</tr>
<tr>
<td>CMCm + 0.1 ml glycerol</td>
<td>66.36</td>
<td>10.529 x 10⁻⁵</td>
</tr>
<tr>
<td>CMCm + 0.2 ml glycerol</td>
<td>67.32</td>
<td>10.682 x 10⁻⁵</td>
</tr>
<tr>
<td>CMCm + 0.3 ml glycerol</td>
<td>67.49</td>
<td>10.709 x 10⁻⁵</td>
</tr>
<tr>
<td>CMCm + 0.4 ml glycerol</td>
<td>68.23</td>
<td>10.826 x 10⁻⁵</td>
</tr>
</tbody>
</table>

**Moisture sorption isotherms**

Plotting between %EMC and time at different relative humidity provides the sorption isotherm curve as shown in Figure 1. The sorption isotherms gave the characteristic sigmoid-shaped type II isotherm curve of normal moisture adsorption isotherm [25] similar to those observed for salted crackers [21], potato flakes [26] and starches [27, 28]. Glycerol concentration affected the %EMC of films. Films with a higher concentration of glycerol absorbed more moisture at a given Aw due to glycerol being a hydrophilic plasticizer that loosened the structure of films [29]. The addition of plasticizer increased hydrophilicity of films by exposing their hydroxyl groups. Similarly, Mahmoud and Savello [30] reported increase of moisture content in whey protein films as the glycerol concentration in the film formulation increased.

![Figure 1. Sorption isotherm of CMCm film with different glycerol content.](image-url)
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 food or edible materials [17], monolayer water content (M) of CMCm films with and without glycerol were presented in a range of 5.99-8.25 and 2.45-3.76 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 [31]. The results showed that GAB gave higher M than the BET model. These results agreed with Timmermann et al. [32]. 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 [33]. M and M of CMCm films increased with increasing glycerol content. These results may be related to higher hygroscopicity of glycerol which agreed with the M of cassava starch films plasticized with glycerol [34].

Oswin model provided good descriptions of the moisture isotherms throughout the entire range of water activity [35]. However, in this case, maximum %RMS value was obtained for the Oswin model. Thus, the GAB model was found to be the better estimator for predicting the equilibrium moisture content of CMCm films with and without glycerol than BET and Oswin models. This result agreed with cassava flour film plasticized with sorbitol which was best fitted with the GAB model [17].

Figure 2 shows experimental versus predicted moisture content by GAB, BET and Oswin’s models of the CMCp film with and without cornflour which obtained the diagonal lines for low and intermediate aw levels (0.1-0.8), indicating low interaction between components in accordance with their separation in independent phases as observed during the film drying [36]. 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 [17]. These results indicated that all models can be used to predict moisture content of CMCp film with and without cornflour at aw 0.1-0.8.

Table 2. Sorption isotherm model constants of cassava starch based film with gelatin and CMC plasticized with 30% (w/w) glycerol at 22 ± 1°C.
Figure 2. Comparison between experimental moisture content and those predicted by (a) GAB model, (b) BET model and (c) Oswin model of CMCm films with various glycerol concentrations.
Conclusions

In this research, the production of carboxymethyl cellulose from waste of mulberry paper was studied and the effects of the amount of glycerol concentration as plasticizer in CMC films on water vapour transmission rate and sorption isotherms were investigated. Water vapour transmission rate (WVTR) and permeability coefficient (P) increased with increasing glycerol concentration in film solution. The percent of equilibrium moisture content (%EMC) also increased with increasing glycerol. The GAB model was found to be the best-fit model for CMCm films at aw 0.1-0.8.

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References


