Water vapour permeability and sorption isotherms of cassava starch based films blended with gelatin and carboxymethyl cellulose

Wirongrong Tongdeesoontorn¹, Lisa J. Mauer², Sasitorn Wongruong³ and Pornchai Rachtanapun⁴*

¹Department of Biotechnology, Graduate School, Chiang Mai University, Chiang Mai, 50200 Thailand.
²Department of Food Science, Purdue University, Purdue, IN 47907 USA.
³Department of Biotechnology, Faculty of Agro-Industry, Chiang Mai University, Chiang Mai 50100 Thailand.
⁴Department of Packaging Technology, Faculty of Agro-Industry, Chiang Mai University, Chiang Mai 50100 Thailand.

*Author to whom correspondence should be addressed, email: p.rachta@chiangmai.ac.th

This paper was originally presented at Food Innovation Asia 2009, Bangkok, Thailand.
Received 22 June 2009, Revised 2 November 2009, Accepted 8 December 2009.

Abstract

Water vapour permeability (WVP) and moisture sorption isotherm properties of cassava starch based films blended with gelatin or carboxymethyl cellulose (CMC) were studied. WVPs of cassava starch based films with and without gelatin and CMC were determined at 33 and 54%RH, 22 ± 1ºC, and ranged from 0.05 -0.17 and 0.20 – 0.47 g.mm/day.m².mmHg, respectively. At 33 %RH, the addition of gelatin or CMC to cassava starch films had no effect (P>0.05) on the WVPs of all films. At 54 RH, the WVPs of cassava starch films containing gelatin were higher than WVPs of cassava starch-CMC film blends. The WVPs of cassava starch based films increased with increasing gelatin concentrations above 30% (w/w). Moisture sorption isotherms of cassava starch based films blended with gelatin (0, 10, 20, 30 and 40%w/w) or CMC (0, 10, 20, 30, 40%w/w) were investigated at various relative humidities (0, 33, 54, 75, and 85 %RH). The equilibrium moisture content of films dramatically increased after reaching a_w = 0.54. Cassava starch-CMC film blends had higher moisture sorption than cassava starch-gelatin film blends. Increasing gelatin and CMC concentrations caused an increase in monolayer water content (M₀) of films. Guggenheim-
Anderson-de Boer (GAB), Brunauer–Emmett–Teller (BET) and Oswin sorption models were tested to fit the experimental data. The GAB model indicated a better fit for the data than the BET and Oswin models for cassava starch based films with gelatin or CMC. The sorption isotherms and modelling are necessary to predict the properties of the films in different environments pertinent to their applications.

**Keywords:** cassava starch based film, gelatin, carboxymethyl cellulose, water vapour permeability, sorption isotherm, packaging, Thailand.

**Introduction**

Environmental concerns have been created by the large volumes of plastics produced and used as packaging materials that are deposited in landfills after a short lifecycle use. Scientists have thus begun to seek alternative sources for plastics materials that combine renewability with biodegradability. Among the biopolymers investigated as potential alternative raw material for plastics, starch has drawn a great deal of attention. Starch is a polysaccharide which consists of the linear D-glucan amylose and the highly branched amyllopectin. Although most recent research has focused on the conversion of starch into thermoplastic materials by extrusion processes, other means of preparing films have been studied, including formation from a solution or gel [1, 2]. The hydrophilic properties of starch impart minimal water barrier properties to starch based films and the physical and barrier properties of starch films are significantly influenced by moisture content [3]. Nevertheless, starch films possess good barrier properties to oxygen, carbon dioxide and lipids and protect against lipid oxidation [4]. Films from polysaccharides are also stronger and more extensible than protein films [5].

Cassava is an economically crucial crop in Thailand. Cassava starch is useful in thickeners and binding agents and is widely used in the production of soups, sauces and pastry fillings. In recent studies, cassava starch was used to produce edible films plasticized with glycerol and sorbitol [6, 7]. Cassava film plasticized with glycerol showed interesting mechanical properties, being transparent, clear, homogeneous, flexible and easily handled. Cassava starch films plasticized with glycerol exhibited poor moisture barrier properties compared to LDPE because of the inherent hydrophilicity of the polysaccharides and the plasticizers used in the formulations [6]. However, their WVPs are in the same order of magnitude as WVPs of gluten films [8].

Enhancing moisture barrier properties of starch films could expand their potential uses. Other biopolymers such as polysaccharides, lipids and proteins can be added to starch films to modify their properties. Blending with sodium carboxymethylcellulose (NaCMC) improved tensile strength and reduced WVP and P\textsubscript{O2} of rice starch film at 90%RH, 25°C [9]. Li et al. [10] found that glucomannan (GMN) films blended with gelatin showed the best miscibility, good tensile strength, heat sealability and the least water–vapour transmission rate. All the blended GMN films were water-soluble and could dissolve in less than 30 sec [10].

CMC is an anionic linear polysaccharide derived from cellulose. CMC is used in food applications as a viscosity modifier or thickener and to stabilize emulsions in various products including ice cream. As an amylose with many hydroxyl and carboxylic groups, it can absorb water and moisture forming the hydrogel has many excellent properties such as high water content, good biodegradability and a wide range of applications due to its low cost [11].
Proteins are widely used to form edible films. Park [12] and Cuq et al. [13], indicated that proteins (such as zein, wheat gluten, keratin and gelatin) are better gas barriers than polysaccharides due to their unique structure and high intermolecular binding potential.

Most biodegradable films, except lipid-based films, are sensitive to moisture and their properties change with changes in surrounding relative humidity (RH). The water sorption isotherm of a material represents the equilibrium relationship between its moisture content and the water activity ($a_w$) at constant temperature and pressure. The sorption isotherms obtained from experimental data of equilibrium moisture content versus relative humidity, are necessary to predict the properties of films in different environments pertinent to their applications [14]. Some authors have studied the sorption isotherms of cassava starch films. Mali et al. [15] studied water sorption of cassava film and resulting plasticizing effects. Suppakul [16] reported the sorption characteristics of cassava flour films plasticized with sorbitol. They found that the equilibrium moisture content of film dramatically soared above $a_w = 0.6$ and its experimental data fitted with GAB and Lewicki models.

Few studies have investigated the water sorption of films made from cassava starch [6, 7] and there are no reports on effects of the addition of gelatin or CMC to cassava starch films on WVP and sorption isotherm properties. The aims of this study were to investigate WVPs and moisture sorption isotherms of cassava starch films blended with gelatin or CMC and to fit experimental data to moisture sorption models. Knowledge of sorption isotherms is important for predicting moisture sorption properties of films via moisture sorption empirical models.

**Materials and Methods**

**Materials**

Cassava starch (Bangkok Inter Food Co., Ltd., Thailand) and glycerol (EM Science, Germany) were used to create films. Gelatin and carboxymethyl cellulose (CMC) were purchased from Sigma (Sigma-Aldrich, USA) and Akzo Nobel (Netherlands), respectively.

**Cassava starch based film preparation**

Film solutions were prepared by dispersing cassava starch and gelatin or CMC at different concentrations in distilled water as shown in Table 1. Glycerol (30% w/w solid) was added as a plasticizer. Film solutions were heated to 80°C with constant stirring to gelatinize the starch. Film-forming solutions (200 ml) were cast on flat 30 x 30 cm Teflon plates. The films were dried at room temperature (22 ± 1°C) and ambient RH for 24 hours.

A hand-held micrometer (Gotech, Japan) was used for measuring film thickness. Five readings were taken for each sample, one at the sample centre and four around the perimeter.
Table 1. Composition of film solutions.

<table>
<thead>
<tr>
<th>Film blends</th>
<th>Composition of film solution (g/100 ml water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>starch</td>
</tr>
<tr>
<td>Control</td>
<td>5</td>
</tr>
<tr>
<td>Gelatin 10%</td>
<td>4.5</td>
</tr>
<tr>
<td>Gelatin 20%</td>
<td>4</td>
</tr>
<tr>
<td>Gelatin 30%</td>
<td>3.5</td>
</tr>
<tr>
<td>Gelatin 40%</td>
<td>3</td>
</tr>
<tr>
<td>CMC 10%</td>
<td>4.5</td>
</tr>
<tr>
<td>CMC 20%</td>
<td>4</td>
</tr>
<tr>
<td>CMC 30%</td>
<td>3.5</td>
</tr>
<tr>
<td>CMC 40%</td>
<td>3</td>
</tr>
</tbody>
</table>

Water vapour permeability (WVP)

WVP of films was determined at 22 ± 1°C using the ASTM E96 method [17]. Each film sample was sealed over a circular area (0.00328 m²) of aluminum cup and 10 g of driedrite was placed inside the cup. Cups were stored in a desiccator containing saturated salt solution (MgCl₂ and Mg(NO₃)₂ for 33% and 54% RH, respectively. WVTR and WVP were calculated using the following equations:

\[
\text{WVTR} = \frac{\Delta W \times A}{\Delta t} \quad \text{(g/day.m}^2\text{)} \quad \text{..................(1)}
\]

\[
\text{WVP} = \frac{\text{WVTR} \times L}{\Delta P} \quad \text{(g mm/day.m}^2\text{.mmHg)} \quad \text{..................(2)}
\]

Where \(\Delta W/\Delta t\) is the amount of water gain (g/day), \(A\) is the test area (m²), \(L\) is the film thickness (m), \(\Delta P\) is the partial vapour pressure difference between both sides of the film (mmHg) [18].

Determination of water sorption isotherms

Film specimens (25 x 40 mm) were conditioned in a desiccator containing silica gel beads for 3 days at 22 ± 1°C to eliminate the initial moisture content. Film specimens were then placed in desiccators at 22 ± 1°C over saturated salt solutions (MgCl₂, Mg(NO₃)₂, NaCl and KCl with 33, 54, 75 and 85%RH, respectively). Weight gain of films was determined daily. Equilibrium moisture sorption was reached following 10 days of storage in the desiccators. Moisture contents of the films were determined using an air-oven method [19] at 105°C for 3 h. The drying operation was repeated until the difference in weight between two successive measurements was not greater than 0.1% of sample weight [20]. Equilibrium moisture content was calculated as equation 3 [21, 22]

\[
Me = \frac{We}{Wi} (Mi + 1)^{-1} \quad \text{(g / g dry product)} \quad \text{..................(3)}
\]

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 from the literature [16, 21, 22, 23], were selected for fitting the sorption isotherm experimental data. These models are expressed and rearranged as given below.

GAB (Guggenheim-Anderson-de Boer) model:
\[ M = \frac{M_0 C k a_w}{(1 - a_w)[1 + (C - 1)k a_w]} \]  \hspace{1cm} (4)

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 for GAB models were obtained from its second-order polynomial form \( y = \alpha x^2 + \beta x + \gamma \), as follows:

\[ \alpha = \frac{1}{M_0 [1/c - 1]}, \quad \beta = \frac{1}{M_0 [1 - 2/C]}, \quad \gamma = \frac{1}{M_0} k C \]  \hspace{1cm} (5)

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:
\[ M = \frac{(M_0 + T) C a_w}{(1 - a_w)[(1 - a_w) + C a_w]} \]  \hspace{1cm} (6)

Where \( M_0 \) and \( C = \) constants. Both constants were obtained from the slope and intercept of the linear plots of \( a_w/[1-a_w]*M \) vs. \( a_w \). \( M_0 = 1/ \) (intercept + slope) and \( C = 1/ \) (intercept * \( M_0 \))

Oswin model:
\[ M = k(a_w/(1-a_w))^C \]  \hspace{1cm} (7)

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

Water vapour permeability (WVP)

Water vapour permeability (WVP) of cassava starch based films with and without gelatin and CMC are presented in Figures 1(A) and 1(B), respectively. At 33%RH, the WVP of the films with gelatin and CMC were not significantly different than films without gelatin and CMC (controls) and ranged from 0.05 to 0.18 g mm/day m² mmHg. The amount of gelatin and CMC had no significant effect on WVP of cassava starch based films at 33%RH. When RH increased from 33 to 54%RH, the WVP values for all cassava starch based films increased, probably due to the plasticizing effect of water. Water has been shown to act as a plasticizer, reducing intermolecular forces within the film structures and increasing polymer chain mobility [24].
At 54%RH, the addition of CMC to cassava starch based films had no significant effect on WVP. WVP under this condition ranged from 0.2 to 0.3 g mm/day m² mmHg. This trend is different from previous reports indicating that adding CMC to rice starch films reduced WVP at 90%RH, 25°C [10]. These results may be related to amylose content of cassava starch which is higher than in rice starch. High amylose starch would form more compact and strong film and inhibit the permeability [10]. Chemical structure, ratio of amylose to amylopectin, polymer packing, crystallinity, plasticizer and environmental humidity are all factors related to the permeability of starch films [25].

At 54%RH, the WVP of cassava starch-gelatin films increased with increasing the amount of gelatin above 30%(w/w) from 0.27 to 0.46 g mm/day m² mmHg. This trend corresponds to WVP reported for chitosan-cassava starch film blends [24]. Consequently, water permeability of cassava starch-gelatin films increased mainly due to the high hydrophilic nature of gelatin [26, 27]. The arrangement of the polymers inside the film matrix significantly affects the water vapour transferring property [28].

When comparing cassava starch based films with other films, WVP of films can be ordered from low to high as PVDC< LDPE< PVC < cassava starch based films < whey protein films [29].

**Figure 1.** WVPs of cassava starch based films with various amount of (A) gelatin and (B) CMC at 33 and 54%RH, 22 ± 1°C.

**Moisture sorption isotherms**

**Moisture sorption curves**

Moisture sorption isotherm curves for cassava starch, CMC powder, gelatin powder and glycerol are depicted in Figure 2. This figure shows that water absorbability of film components could be ordered from high to low as 100% glycerol > 100% CMC > 100% gelatin > 100% cassava starch. Moisture sorption isotherm curve of cassava starch is a sigmoid-shaped curve, type II isotherm, whereas moisture sorption isotherm curves of CMC, gelatin and glycerol are type III isotherm, which show crystalline components [30].

For all films stored in controlled RH desiccators and monitored over time, water sorption increased more rapidly in the initial stages and then slowly increased. When moisture contents of the films reached a plateau, this indicated that the films were equilibrated. The
higher the RH, the longer it took for the films to reach equilibrium. Equilibrium was reached within 10 days for films stored at 33% RH and within 7 days for films stored at 85% RH.

![Figure 2. Moisture sorption isotherms of 100% cassava starch, CMC, gelatin and glycerol at 22 ± 1°C.](image)

Moisture sorption isotherms for cassava starch based films with and without gelatin and CMC are shown in Figures 3(A) and 3(B), respectively. All films can be classified as having type III isotherms, the same as the isotherm curve of starting materials (CMC, gelatin and glycerol). The sorption isotherms of studied films were similar to those of cassava starch films [15], keratin films [31] and hydroxypropyl methylcellulose films [32]. Cassava starch based films with gelatin and CMC had higher moisture sorption than control films (without gelatin or CMC). The moisture sorption of cassava starch-gelatin films decreased with increasing gelatin concentration, whereas cassava starch-CMC film moisture sorption increased with increasing CMC concentration. Cassava starch films with 40% CMC had the highest moisture content. This result is consistent with the moisture sorption isotherm of CMC, which absorbed more moisture than gelatin or cassava starch (Figure 2). The unchanged WVP of cassava starch-CMC films may be due to high water absorption of CMC on film surfaces which could be a barrier for water vapour transmission. This result was related to the effect of the high polarity of the plasticizer on the WVTR of cassava starch films [33].

**Fitting sorption isotherm models to experimental data**

The sorption isotherm data were fitted to GAB, BET and Oswin’s models. The constants are shown in Table 2.

For BET and GAB models, the most accepted model for food or edible materials [16], monolayer water contents (M₀) of blended cassava starch films with and without gelatin and CMC from BET and GAB models were in the range of 0.014-0.035 and 0.132-0.226 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 an indicator of the number of absorption sites [34]. The results showed that BET models reported higher M₀ than GAB models, likely because the BET model is based on the monolayer while the GAB model is
based on multiple layer and condensed film water [35]. These results agreed with those of Arevalo-Pinedo et al. [36], who found the similar trend of \( M_0 \) values from BET and GAB models for Inga pulp sorption isotherms. For the GAB model, the \( C \) parameter is related to the difference of the magnitude in the upper layers and in the monolayer [37]. Films with CMC had lower \( C \) values than films with gelatin and control films, respectively. The differences in \( C \) value indicate that cassava starch films with CMC could absorb moisture in monolayer as well as in the upper layers, while moisture absorption of control films and films with gelatin could occur in upper layers more readily than in the monolayer. These results were related to the differences in WVP of cassava starch blended films.

The Oswin model has been reported to provide good descriptions of moisture isotherms throughout the entire range of water activity [37]. However, for the cassava starch film data, a maximum %RMS value was obtained for the Oswin model, which means that differences were found for moisture content values between experimental data and calculating with Oswin equation. At 50-75% RH, the GAB model was found to be the better estimator for predicting the equilibrium moisture content of cassava starch films with and without gelatin and CMC than BET and Oswin models. This result is in agreement with cassava flour film plasticized with sorbitol which was best fitted with GAB model [6, 16].

Figure 4 shows the experimental versus predicted moisture content of the CMCp film with and without cornflour which obtained the diagonal lines for low and intermediate \( a_w \) levels, indicating low interaction between components in accordance with their separation in independent phases as observed during the film drying [38]. At high level of water activity, it can also be observed that the point increased rapidly on the diagonal, as a result of the interaction between the water molecules and the polar groups of the film [16]. These results indicated that all models can be used to predict moisture content of cassava starch film with and without gelatin and CMC at \( a_w \) 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.

<table>
<thead>
<tr>
<th>Cassava Starch Films</th>
<th>GAB</th>
<th>BET</th>
<th>Oswin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_0 )</td>
<td>( K )</td>
<td>( C )</td>
</tr>
<tr>
<td>Control</td>
<td>0.0138</td>
<td>0.2843</td>
<td>123.2235</td>
</tr>
<tr>
<td>Gelatin10%</td>
<td>0.0229</td>
<td>1.1002</td>
<td>38.0716</td>
</tr>
<tr>
<td>Gelatin20%</td>
<td>0.0227</td>
<td>0.8882</td>
<td>42.5592</td>
</tr>
<tr>
<td>Gelatin30%</td>
<td>0.0138</td>
<td>0.1902</td>
<td>147.6013</td>
</tr>
<tr>
<td>Gelatin40%</td>
<td>0.0221</td>
<td>0.8610</td>
<td>44.3321</td>
</tr>
<tr>
<td>CMC10%</td>
<td>0.0243</td>
<td>1.5053</td>
<td>30.8895</td>
</tr>
<tr>
<td>CMC20%</td>
<td>0.0252</td>
<td>1.2895</td>
<td>32.0509</td>
</tr>
<tr>
<td>CMC30%</td>
<td>0.0255</td>
<td>1.2909</td>
<td>31.6435</td>
</tr>
<tr>
<td>CMC40%</td>
<td>0.0352</td>
<td>4.9990</td>
<td>12.1905</td>
</tr>
</tbody>
</table>
Figure 3. Moisture sorption isotherms of cassava starch based films plasticized with 30% (w/w) glycerol with and without (A) gelatin and (B) CMC at 22 ± 1°C.
Figure 4. Comparison between experimental moisture content and those predicted by (a) GAB model, (b) BET model and (c) Oswin model of cassava starch films with various gelatin and CMC concentrations.
Conclusions

The water permeability (WVP) of cassava starch films with and without gelatin and CMC was not significantly different at 33%RH, however, films with gelatin had higher WVP with increasing gelatin concentration at 54%RH. The WVP of all cassava starch based films increased when humidity increased from 33%RH to 54%RH.

Cassava starch based films with gelatin and CMC demonstrated higher water sorption capability than control films. The GAB model was a better fit for the data of these cassava starch based films than the BET and Oswin models.

In addition, cassava starch based films with and without gelatin and CMC show potential for use as biodegradable and edible packaging with moderate WVP. Water barrier properties of the films may be improved by coating or blending with other hydrophobic biopolymers in any further study.

Acknowledgement

The authors wish to thank the Office of the Higher Education Commission, Thailand, for their scholarship and financial support and Chiang Mai University for additional support.

References


