Moisture Sorption Characteristics of Composite Foods Filled with Chocolate

S. S. Kim, S. Y. Kim, D. W. Kim, S. G. Shin, and K. S. Chang

ABSTRACT

We compared the moisture sorption isotherms (MSI’s) and their temperature dependence of composite foods with those of crust and filling. The MSI were determined on cracker, cookie, chocolate, and two types of composite foods such as CFI (cracker/chocolate/cracker) and CF2 (cookie/chocolate/cookie) at 20, 30, and 40°C and 11–85% relative humidity, and fitted into the Guggenheim-Anderson-de Boer (GAB) equation. Chocolate had the lowest monolayer (m0) value, equilibrium moisture content (EMC), and sorption energy levels, followed by cookie and cracker. The CFI had higher EMC values and sorption energy than CF2. The GAB m0 values and C0 values decreased with temperature, while C1 values increased with temperature.

Key Words: moisture sorption isotherms, composite foods, chocolate, cracker, cookie

INTRODUCTION

COMPOSITE FOODS SUCH AS PIE AND cream-filled pastry consist of different food layers. A pie-style composite food has a soft center filling of high water activity (aw) and a crispy crust of low aw. The crust may gain moisture from the filling and lose its crispiness and/or develop off-flavors. The filling may dry out and become gummy, sticky, and/or undesirably hard. Moisture exchange may also continue until crust and filling reach equilibrium with environment inside or outside of packaging (Labuza, 1984).

The moisture sorption isotherm (MSI) or the equilibrium moisture content (EMC) of a composite food is one of the most important measures affecting acceptability, shelf-life, and packaging and storage requirements (Bruijn and Luyben, 1980; Kapsalis, 1987). Prediction of EMC values (or MSI) of a composite food from the predetermined EMC values (or MSI) of crust and filling may speed up product development and help determine whether potential problems such as textural changes and reduced storage stability may exist (Labuza, 1984). This may also be useful for package design or shelf-life estimation.

Several researchers (Ross (1975) for intermediate foods; Lang and Steinberg (1981) for mixed food powders; Hardy and Steinberg (1984) for NaCl and parcasein; Busisier and Serpelloni (1985) for confectionery; Hong et al. (1986) for mixed food powders; Chimachoti (1990) for starch, sucrose, and salt; Bakhit and Schmidt (1992) for NaCl/casein mixtures) have developed mathematical models that would enable such prediction. However, the works concerned intimately mixed ingredients. Little information is available on multilayered composite foods except for the works of Sakai and Hayakawa (1992; 1993). Heat and moisture transfer analysis was validated by using model composite foods composed of starch and sucrose. Our objective was to determine the MSI of cracker, cookie, chocolate, and two types of composite foods CFI (cracker/chocolate/cracker) and CF2 (cookie/chocolate/cookie) at 20–40°C and 11–85% relative humidity. The MSI values were fitted to the GAB equation and their temperature dependence was evaluated using the temperature-dependent GAB parameters and the Clausius-Clapeyron equation.

MATERIALS & METHODS

Preparation of composite foods

Two types of crust (cracker and cookie) were prepared. The formulation for cracker was as follows: flour 100g (49.0%), sugar 35g (17.2%), salt 0.25g (0.1%), margarine 7.5g (3.7%), baking powder 1.25g (0.6%), and water 60g (29.4%). The formulation for cookie was as follows: flour 100g (41.6%), sugar 35g (14.6%), salt 0.25g (0.1%), margarine 75g (31.2%), and egg 30g (12.5%). The cracker and cookie samples (cracker: 12 mm × 12 mm × 3 mm, moisture 2.0±0.5%; cookie: 12 mm × 12 mm × 4 mm, moisture 4.0±0.5%) were packaged in foil-laminated pouches and stored in a refrigerator (5°C) up to 2 mo until used. Whipping cream (milk fat 35%) and dark chocolate containing cocoa mass, sucrose, and lecithin were purchased at a local market to prepare chocolate fillings. Disintegrated dark chocolate 100g was melted in 100g whipping cream prewarmed to 50°C, and then cooled in a refrigerator. The dimension of the chocolate filling was 12 mm × 12 mm × 2 mm, and its moisture content was 14.5±0.5%. Using the crust and filling, two kinds of composite food such as CFI (cracker/chocolate/cracker) and CF2 (cookie/chocolate/cookie) were prepared.

Determination of moisture sorption isotherms

MSI’s were determined using the principles described by Labuza et al. (1985). At least triplicate determinations were made for each of the samples “as prepared” were used for the sorption experiment (Hardy and Steinberg, 1984). The term “sorption isotherm” as used here indicates a combination of desorption (in case of saturated salt slurries at aw below initial aw of the sample) and adsorption (in case of saturated salt slurries at aw above the initial aw of the sample). Samples of 12 mm × 12 mm were placed in desiccators containing saturated salt slurries showing the following aw values at 20°C: LiCl 0.1131; CH3COOK 0.2311; K2CO3 0.4316; MgNO3 0.5438; NaCl 0.7547; and KCl 0.8511 (Labuza, 1984) or calculated using regression equations reported by Labuza et al. (1985). At least triplicate determinations were made for each of triplicate samples (9 replicates). When the difference between the weight of the sample was less than 1 mg/g solids for two consecutive weeks, the sample was considered to have reached equilibrium. Moisture content of each sample was determined by a vacuum drying for 24h at 70°C and 50 mmHg.

Fitting of moisture sorption isotherms

The GAB model was used to describe MSI’s (Kapsalis, 1987; Labuza, 1984):

\[
m/\text{m}_0 = (c_1 c_2 c_{aw})/[ (1 - c_{aw}) (1 - c_{aw} + c_1 c_2 c_{aw})] \tag{1}
\]

where m = moisture content (kg water/kg solids), m0 = initial moisture content (kg water/kg solids), c1 = c0 = 0, and c2 = 1.5.
solid); \(m_0\) = monolayer moisture content (kg water/kg solid); \(c_1\) = GAB constant related to monolayer properties; \(c_2\) = GAB constant related to multilayer properties.

The GAB equation was transformed into a quadratic equation to obtain coefficients \(b_1\), \(b_2\), and \(b_3\), from which the GAB constants \((m_0, c_1, c_2)\) could be calculated:

\[
a_{w}/m = b_1 + b_2 a_w + b_3 a_w^2
\]

where \(b_1 = 1/(m_0 c_2(c_2));\) \(b_2 = (1 - 2/c_1)m_0;\) \(b_3 = (c_2/c_1)(1/c_1 - 1)\).

The temperature dependence of the GAB constants was evaluated using the following Arrhenius-type equations:

\[
m_0(T) = m_0^\prime \exp(\Delta H^\prime/RT)
\]

\[
c_1(T) = c_1^\prime \exp((H_1 - H_m)/RT)
\]

\[
c_2(T) = c_2^\prime \exp((H_2 - H_m)/RT)
\]

where \(m_0^\prime, c_1^\prime,\) and \(c_2^\prime\) = pre-exponential factors; \(\Delta H^\prime\) = Arrhenius-type energy factor (kJ/mol); \(H_1\) = heat of sorption of first layer (kJ/mol); \(H_2\) = heat of sorption of multilayer (kJ/mol); \(H_m\) = heat of condensation of pure water vapor (kJ/mol).

The temperature dependence of each MSI was also evaluated by applying the following Clausius-Clapeyron equation (Kapsalis, 1987; Labuza et al., 1985).

\[
\ln(a_w) = (Q_s/R)(1/T) + \text{constant}
\]

where \(Q_s\) = excess heat of sorption (kJ/mol).

Statistical analysis

Linear regressions and quadratic regressions were done by using statistical software (Cricket Graph 1.3, Cricket Software, Inc., Philadelphia, PA; StatWorks™ 1.2, Cricket Software, Inc., Philadelphia, PA). Significance of differences was defined at \(p<0.05\).

RESULTS & DISCUSSION

Isotherms of crusts and a filling

The experimental MSI of crust and filling was determined at 20, 30, and 40°C, and fitted to the GAB model (Fig. 1A) for cracker, cookie, and chocolate. Chocolate had the lowest EMC values which may be due to the hydrophobic nature with high fat content. Cracker had higher EMC values than cookie, indicating its less hygroscopic nature. This may be due to the higher amount (ten times) of margarine in cookie than that in cracker.

Isotherms of chocolate at different temperatures showed temperature shifts i.e., increase of \(a_w\) with temperature at constant moisture. At constant equilibrium relative humidity, the higher the temperature, the lower the EMC value (sorbed water content) of a sample. As pointed out by Kapsalis (1987), this is generally applicable to foods except certain sugar products which become more hygroscopic at higher temperatures because they dissolve in water.

Isotherms of composite foods

The isotherms of two composite foods, CF1 (Fig. 1C) and CF2 (Fig. 1D), were also compared. The isotherms shifted with temperature increase from 20 to 40°C, and CF1 showed a greater temperature dependence than CF2. The isotherms of composite foods were also compared with those of crust and filling (Fig. 2A, B). As shown the isotherms of the composite foods were between those of the crust and the filling, especially near to those of the crust. This may be due to the relatively smaller amount of filling than crust. The crust was double-layered and almost twice as thick as filling (chocolate). The balance equation used by several researchers (Lang and Steinberg, 1981; Hardy and Steinberg, 1984; Chinachoti, 1990; Bakheit and Schmidt, 1992), although applicable only after reaching equilibrium, seemed useful for predicting EMC values from those of the crust and filling. In addition, the composite foods CF1 composed of cracker showed at every temperature higher EMC values than CF2 composed of cookie mainly due to the higher EMC values of the cracker. This suggested that the EMC values (or MSI) of composite foods composed of the same filling depend mainly on the EMC values (or MSI) of the crust.

GAB parameters and their temperature dependence

GAB parameters \((m_0, c_1,\) and \(c_2)\) of cracker, cookie, chocolate, and composite foods (CF1 and CF2) were compared (Table 1) at 20, 30, and 40°C. Chocolate had the lowest monolayer values, followed by cookie and cracker. The cracker \(m_0\) value was similar to the published value (4.23%, 0.044 kg water/kg solid) reported by Saravacos (1986). The composite food CF1 (composed of cracker) showed higher \(m_0\) values than CF2 (composed of cookie). This suggested that the \(m_0\) values of composite foods composed of the same filling but with different crusts depend on those of the crust. The \(m_0\) values of composite foods CF1 and CF2 were between those of cracker (or cookie) and chocolate.

![Fig. 1](image-url)  
Moisture sorption isotherms of cracker, cookie, chocolate, CF1 (cracker/chocolate), and CF2 (cookie/chocolate/cookie) at different temperatures (lines: calculated using GAB model, legends: experimental values).
Table 1—GAB parameters for sorption isotherms of single component foods and composite food products

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temp (°C)</th>
<th>m₀ (kg/kg)</th>
<th>c₁ (kJ/mol)</th>
<th>c₂ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracker</td>
<td>20</td>
<td>0.050</td>
<td>9.012</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.044</td>
<td>5.051</td>
<td>0.974</td>
</tr>
<tr>
<td>Cookie</td>
<td>20</td>
<td>0.034</td>
<td>5.866</td>
<td>0.982</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.032</td>
<td>4.204</td>
<td>1.011</td>
</tr>
<tr>
<td>Chocolate</td>
<td>20</td>
<td>0.016</td>
<td>4.321</td>
<td>1.050</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.014</td>
<td>3.217</td>
<td>1.051</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.013</td>
<td>2.433</td>
<td>1.052</td>
</tr>
<tr>
<td>CF1</td>
<td>20</td>
<td>0.041</td>
<td>1.891</td>
<td>0.969</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.037</td>
<td>6.050</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.033</td>
<td>4.042</td>
<td>0.995</td>
</tr>
<tr>
<td>CF2</td>
<td>20</td>
<td>0.030</td>
<td>4.823</td>
<td>1.011</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.027</td>
<td>3.896</td>
<td>1.021</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.025</td>
<td>2.283</td>
<td>1.028</td>
</tr>
</tbody>
</table>

The GAB m₀ values and c₁ values decreased with increases in temperature; while c₂ values increased with temperature. The same tendency was reported for yogurt powder by Kim and Bhowmik (1994). The GAB parameters at different temperatures (Table 1) were regressed to calculate their temperature dependence (Table 2). Such temperature dependence data may be used for predicting GAB parameters at given temperatures.

**Heat of sorption of crusts, filling, and composite foods**

The excess heats of sorption (Qₑ) calculated by applying Clausius-Clapeyron equation were plotted (Fig. 3). The Clausius-Clapeyron equation (6) could be applied only when the moisture content remained constant (Labuza et al., 1985). In addition, the excess heat of sorption data were so nonlinear that they could not be applied to predict the MSI under different relative humidity conditions. Therefore, only the sorption energy levels were considered with respect to moisture content. As shown chocolate had the lowest sorption energy levels, followed by cookie and cracker. In general, the different sorption energy reflects the difference in sorption capacity which is closely related to the hydrophilic affinity of a material. In the case of composite foods, CF1 showed higher sorption energy levels than CF2 under normal storage or distribution conditions. This indicates that the sorption capacities of composite foods probably depends on both the sorption capacity of each layer and the relationships between layers.

**CONCLUSION**

MOISTURE SORPTION ISOTHERMS of cracker, cookie, chocolate and composite foods CF1 and CF2 were determined at different temperature and relative humidity conditions. The MSI’s were fitted into the GAB model using the temperature-dependent GAB parameters. The m₀, EMC values, and sorption capacities of the composite foods were affected to some extent by the filling but mainly by the crust.

**REFERENCES**


Lang, K.W. and Steinberg, M.P. 1981. Linearization of the water sorption isotherm for homogeneous ingredi- ents over a 0.30-0.95. J. Food Sci. 46: 1450-1452.


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Table 2 — Temperature dependent GAB parameters of single component foods and composite food products

<table>
<thead>
<tr>
<th>Samples</th>
<th>m₀(T) (kg/kg)</th>
<th>ΔH (kJ/mol)</th>
<th>C₁(T) (kJ/mol)</th>
<th>C₂(T) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracker</td>
<td>1.5×10⁻³</td>
<td>8.53</td>
<td>1.82×10⁻⁴</td>
<td>37.51</td>
</tr>
<tr>
<td>Cookie</td>
<td>4.8×10⁻³</td>
<td>4.77</td>
<td>1.46×10⁻⁴</td>
<td>25.84</td>
</tr>
<tr>
<td>Chocolate</td>
<td>6.18×10⁻⁴</td>
<td>5.37×10⁻³</td>
<td>1.08</td>
<td>-0.07</td>
</tr>
<tr>
<td>CF1</td>
<td>1.38×10⁻³</td>
<td>8.28</td>
<td>1.40×10⁻⁴</td>
<td>26.81</td>
</tr>
<tr>
<td>CF2</td>
<td>1.71×10⁻³</td>
<td>6.97</td>
<td>2.97×10⁻₃</td>
<td>18.04</td>
</tr>
</tbody>
</table>

**Fig. 2—Moisture sorption isotherms of cracker, cookie, chocolate, and CF1 (cracker/chocolate/cracker), CF2 (cookie/chocolate/cookie) at 20°C (lines: calculated using GAB model, legends: experimental values).**

**Fig. 3—Excess heat of sorption curves for cracker, cookie, chocolate, and composite foods (CF1 and CF2).**