

## Sorption Behavior of Mixtures of Glycerol and Starch

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Glycerol is often added to starches to plasticize the product, but the presence of glycerol may also affect the water content of the samples. To evaluate the effect of glycerol on the sorption properties of starches, waxy maize, rice, and wheat starch were thermomechanically extruded in the presence of glycerol. Sorption isotherms of these extruded samples were ascertained using dynamic vapor sorption (DVS). BET and GAB modeling showed a monolayer ( $m_o$ ) significantly higher for waxy maize than for rice and wheat. Glycerol inclusion changed the model values, indicating reduction in sorption energy at the monolayer and restructuring of the multilayer. An interaction factor ( $\xi$ ) based on weight fraction models was calculated. Differences in  $\xi$  were obtained when glycerol was added, varying from  $\sim 0.9$  for 5% glycerol to  $\sim 0.8$  for 20% glycerol, supporting the hypothesis of interactions between starch and this polyol.

**KEYWORDS:** Sorption isotherm; starch; glycerol; modeling; interaction; GAB; BET; DVS

### INTRODUCTION

The dependence of water sorption behavior on water activity ( $A_w$ ) or equilibrium relative humidity (RH) can have a significant effect on the shelf life and quality attributes of starch-based foods.

Van den Berg (*1*) described the water sorption process, at low partial vapor pressures, as “a localized physical adsorption on an initially rigid adsorbent”. Therefore, textural properties, especially if the moisture content range is close to that of the glass to rubber transition, can be markedly affected by storage at different relative humidities (2–5). Polyols are often used to plasticize samples without increasing their water activity.

Measurement and modeling of sorption are therefore important, and accurate predictions of plasticizer behavior in complex foods could markedly reduce the trial and error basis for recipe development. Water is a small and ubiquitous molecule, and its effect on the texture of many food materials can be related to its plasticizing effects by increasing the free volume in the polymer. This causes a reduction in the glass transition temperature ( $T_g$ ). Other small molecule components, such as polyols (e.g., glycerol, glycol, and sorbitol), can also plasticize the polymer matrix. Polyols are commonly used in the food industry as humectants that can maintain the food at a low overall  $A_w$  by absorbing water to the polyol’s hydric structure. It is generally expected that addition of glycerol will reduce the  $A_w$  of a system at any starting moisture level. However, published work has shown that this is not always the case (*1–3*). Working with matrices of dextran, pullulan, or amylose and using polyols, Scandola et al. (*6*) suggested that there were two

types of polymer–water interactions; for plasticizers at concentrations of  $< 10\%$ , the polymer–water system formed by hydrogen bonds was more compact than the polymer–polymer system, but at  $> 10\%$ , a looser network was formed due to the occurrence of plasticizer–plasticizer interactions. It is therefore not clear how the incorporation of polyols with starches would affect the sorption isotherms.

To establish the sorption behavior of starch–glycerol mixtures it is important to have an accurate method of determining the sorption isotherms. Development of very accurate balances and control of air at defined moisture levels has led to the development of dynamic vapor chambers that allow accurate and precise determination of the sorption isotherms. Once established, these isotherms need to be described and understood.

Three models have been commonly used to represent the experimental sorption data: the Brunauer–Emmett–Teller model (BET) (eq 1), the Guggenheim–Anderson–de Boer (GAB) model (eq 2), and the Peleg model (eq 3).

The BET model is commonly used to model relative humidities of up to 50% RHs

$$M = \frac{m_o C_{\text{BET}} \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left(1 - \frac{p}{p_0} + C_{\text{BET}} \frac{p}{p_0}\right)} \quad (1)$$

where water is the solvent,  $M$  the moisture content (% db), and  $m_o$  monolayer value (% db).  $C_{\text{BET}}$  is a temperature-dependent constant (related to the net heat of sorption, between the monolayer and the bulk water), and  $p/p_0$  is the gas partial pressure (i.e., relative humidity in the case of water at thermodynamic equilibrium).

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The GAB model (eq 2) is used for relative humidities of up to 95%

$$M = \frac{m_0 C_{\text{GAB}} K \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left(1 - K \frac{p}{p_0} + C_{\text{GAB}} K \frac{p}{p_0}\right)} \quad (2)$$

where there is a constant  $C_{\text{GAB}}$  that is related to the energy associated with the binding between the water molecules and the matrix primary interactions sites or monolayer. There is also a temperature-dependent value ( $K_{\text{GAB}}$ ) related to the heat of sorption of the multilayer. The gas partial pressure is presented by  $p/p_0$ .

The parameters used in the BET and GAB models such as ( $C_{\text{BET}}$ ,  $C_{\text{GAB}}$ , and  $K_{\text{GAB}}$ ) can give information related to sorption at low relative humidities and the energies (heats of sorption) involved during the sorption process. A detailed description of these two models and their application for food systems can be found in a number of papers (6–14).

Peleg (15) suggested that it was not simple to predict, on the basis of the fit of the BET or GAB models, the molecular events that take place at the solid surfaces. As a consequence, Peleg defined a new sorption isotherm model (eq 3) based on four parameters:

$$M = k_1 \left(\frac{p}{p_0}\right)^{n_1} + k_2 \left(\frac{p}{p_0}\right)^{n_2} \quad (3)$$

$k_1$ ,  $k_2$ ,  $n_1$ , and  $n_2$  are constants, with  $n_1 < 1$  and  $n_2 > 1$ . Although the parameters used in the Peleg model do not have fundamental meaning, it is a precise model to predict sorption isotherms, due to its four fitting parameters. Therefore, the Peleg model has been successfully applied to many food systems for relative humidities of up to 95% (9, 11, 15–18).

Prediction of sorption isotherms for food mixtures becomes important when new recipes need to be produced. Sorption isotherms, based on data from individual components, have frequently been used to estimate sorption curves of complex food mixtures (19–25). In practice, it is assumed that individual components or ingredients do not interact with each other and that the water activity for each moisture content is the same for all of the components (21–23). A simple formula commonly used to predict the equilibrium moisture content for a mixture was proposed by Lang and Stenberg (eq 4) (22)

$$M_{\text{calcd}} = \frac{\sum_{i=1}^n W_i X_i}{\sum_{i=1}^n W_i} \quad (4)$$

where  $M_{\text{calcd}}$  is the calculated total moisture content at specific water activity ( $A_w$ ),  $W_i$  is the individual component weight expressed on a dry basis, and  $X_i$  is the equilibrium moisture content (% db) of each component at the specific  $A_w$ .

Although this approach has been successfully applied to some binary and tertiary mixtures (22), it is usually inaccurate for low moisture contents ( $\pm 16\%$  error) (26, 27). Modeled values obtained were greater than the experimental data values, suggesting some interaction between the mixture constituents. On the basis of derivations, an interaction coefficient,  $\xi_i$ , was introduced (19, 24). If an interaction occurs, the moisture content

of component  $i$  ( $X_{ei}$ ) becomes  $\xi_i X_{ei}$ . For an  $n$ -component mixture the mean moisture content in the mixture  $X_{\text{em}}$  is defined as

$$X_{\text{em}} = \sum_{i=1}^n W_{Si} \xi_i X_{ei} \quad (5)$$

where  $W_{Si}$  and  $X_{ei}$  are the mass fraction and equilibrium moisture content of the  $i$ th component in the mixture and  $\xi_i$  is the physicochemical interaction between particular components.

It is therefore clear that prediction of moisture uptake in the presence of starch and glycerol is not straightforward to predict. To try and establish how glycerol affects the water sorption of starchy materials and to find if the behavior can be predicted, a set of model systems, waxy maize, rice, and wheat starch mixed with different glycerol concentrations, was prepared by thermomechanical extrusion. This method should ensure homogeneous mixing of the samples with breakdown of the native granule structure to form a non-phase-separated system. The extrudates were dried and then ground to a defined particle size so that their sorption characteristics could be followed using dynamic vapor sorption (DVS). The data obtained were used to fit theoretical and empirical models to establish the behavior of the polyol–starch mixtures.

## MATERIALS AND METHODS

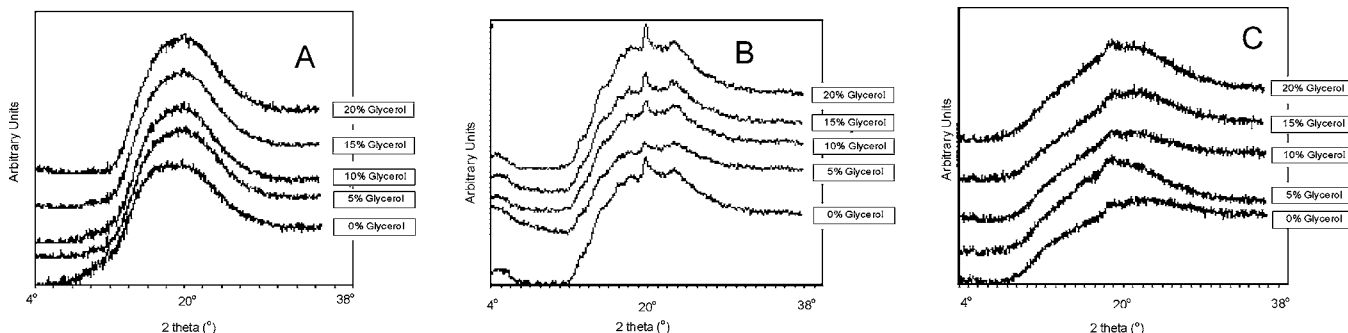
The following starches were used: wheat starch, 13% moisture content (MC), wet basis (wb) supplied by Avebe, Ulceby, U.K.; waxy maize starch, 13%MC (wb), variety Amioca; and rice starch, 10%MC (wb) from Sigma, Dorset, U.K. The plasticizer was glycerol (99% purity, Merck, Dorset, U.K.).

**Sample Preparation.** Native waxy maize (WMS), rice (RS), and wheat starch (WS) were fed into the barrel of a twin-screw, corotating thermomechanical extruder (Cletral BC-21, Firminy, France). The temperatures for the barrel zones (second, third, and fourth) were 90, 150, and 90 °C for WMS and 85, 85, and 65 °C for WS and RS, respectively. This range of temperatures was used to ensure mixing and melting of the materials and to ensure that no puffing of the product occurred on exiting the extruder die. Distilled water and glycerol were directly pumped into the first section of the extruder barrel. The glycerol concentration in the final products was 0 (control), 5, 10, 15, and 20% (dry basis). The feed rates of the solid (starch) and liquids (water and glycerol) were adjusted to obtain a fully translucent ribbon at the exit of the extruder die, keeping a similar specific mechanical energy (SME ~ 55 Wh/kg) for the different mixtures. The final moisture content was ~35% (wb). After extrusion, the ribbons (~15 cm long) were hermetically packed, quenched in liquid nitrogen ( $N_2$ ), and freeze-dried. The freeze-dried extruded starch–glycerol samples were ground and sieved to give fractions with a particle diameter ( $d$ ) of  $d < 150 \mu\text{m}$ ,  $150 \mu\text{m} < d < 212 \mu\text{m}$ , and  $d > 212 \mu\text{m}$ .

**Wide Angle X-ray Diffraction (WAXS).** To assess the crystalline structure of the samples, they were X-rayed using a D5005 X-ray diffractometer (Cu  $K\alpha \rightarrow 0.154 \text{ nm}$ ) (Bruker). Experimental settings were typically step scanning for an angle range of  $2\theta$  from 4° to 38°, an angular step of 0.05 per 3 s, and a rotational speed of 60 rpm. Duplicate samples of particle size fraction diameter  $> 212 \mu\text{m}$  were used for this analysis.

**Dynamic Vapor Sorption.** Sorption isotherms at 25 °C for waxy maize-, wheat-, and rice starch–glycerol extrudates with different glycerol contents were obtained using a dynamic vapor sorption system (DVS-1, Surface Measurements). This technique is based on an ultrasensitive balance capable of measuring changes in the sample mass as low as 0.01 mg. The sample is equilibrated at a constant temperature at different relative humidities. The changes in relative humidity were induced by changing the gas, a mixture of dry and moisture-saturated nitrogen, flowing over the samples.

The sample mass used was ~3 mg, and the programmed relative humidities were from 0 to 90%, divided in 10% increments (10 points). The temperature was set at 25 °C. The samples were considered to be



**Figure 1.** X-ray diffractograms for the different freeze-dried extrudates, coextruded with different amounts of glycerol: waxy maize (A), rice (B), and wheat (C).

at equilibrium when the value  $dm/dt$  (slope of the changing in mass with time) was set to be  $<0.002$  mass %/min.

A sieved fraction of the extruded starchy materials of diameter  $150 \mu\text{m} < d < 212 \mu\text{m}$  ( $\sim 180 \mu\text{m}$ ), stored over  $\text{P}_2\text{O}_5$  for 12 h, was used for the sorption studies. Three replicates were analyzed for each extruded starch–glycerol mixture.

The accuracy of the fitting was evaluated from an error function (EF) (eq 6) using Solver in Excel (Office 2003, Microsoft)

$$\text{error} = \frac{1}{n} \sum_{p/p_0=0}^n \left| \frac{M_{\text{measured}}\left(\frac{p}{p_0}\right) - M_{\text{modeled}}\left(\frac{p}{p_0}\right)}{M_{\text{measured}}} \right| \quad (6)$$

where  $p/p_0$  is the gas partial pressure, relative humidity in the case of water, for the experimental and modeled data, and  $n$  is the number of modeled points. Modeling giving values below 10% for this function is considered to represent accurately the experimental data (17, 27).

## RESULTS AND DISCUSSION

First, the effect of extrusion on the starches, when different levels of glycerol were present, was ascertained. As the water feed rate was reduced when the glycerol feed rate was increased, the resultant specific mechanical energies (SME) were similar for all mixtures (SME  $\sim 53$  Wh/kg). All of the extruded samples appeared to be ribbons of clear material, and no obvious nonhomogeneity was observed.

To establish the conversion from the native starch, the ground extrudates, at 10% moisture (wb), were X-rayed. Diffractograms for the three extruded starches with different glycerol contents are presented in **Figure 1**. Extruded waxy maize starch (**Figure 1A**) showed a completely amorphous pattern for the control sample and the starch–glycerol mixtures. For rice starch–glycerol extrudates (**Figure 1B**), the diffractogram shows the presence of a shoulder at  $\sim 13^\circ$  and a peak at  $\sim 20^\circ$ . The diffraction peaks at these angles represent an ordered-like structure associated with amylose–lipid complexes (28). The peaks at  $\sim 18^\circ$  and  $\sim 23^\circ$  in **Figure 1B** indicate native starch, thus demonstrating that all of the starch had not been fully converted during extrusion. This is especially noticeable for the 20% glycerol mixture. It is possible that for this specific starch, high moisture and glycerol contents could have a lubricating effect, protecting its native structure from shear forces during extrusion.

X-ray diffractograms for extruded wheat starch mixtures (**Figure 1C**) showed a fairly amorphous structure with just some indication of amylose–lipid complexation.

**Dynamic Vapor Sorption.** Sorption isotherms were obtained for all of the starch–glycerol mixtures (particle size  $\sim 180 \mu\text{m}$ ) using the DVS. **Figure 2A** shows the sorption data for waxy maize, rice, and wheat starch extrudates, each with a glycerol

concentration of 0, 5, 10, 15, and 20% (db). The dotted line corresponds to the sorption isotherm for pure glycerol at  $25^\circ\text{C}$  (29).

Glycerol had the same effect on sorption behavior for all three starches. This polyol contributed to an increase in moisture uptake for  $\text{RH} > 70\%$ . For  $\text{RH} < 60\%$ , glycerol did not increase the moisture compared to the control (no glycerol). Moreover, it seems that higher concentrations of this polyol reduced the water uptake during equilibration at the low relative humidities.

Similar behavior has been reported for barley starch (30), potato starch (31), and pure amylose and amylopectin (31). Myllärinen et al. (32) suggested that at low relative humidities, water is displaced from the starch active polar groups by glycerol molecules. The trihydric alcohol structure of glycerol and the solid acting as an adsorbent at these low relative humidities may explain these results (33, 34). At low vapor pressures hydrogen bonding is the main force involved in the adsorption mechanism, suggesting the predominance of glycerol over water.

Completely opposite behavior was detected for  $\text{RH} > 70\%$ , where glycerol facilitated water sorption. At these high water vapor pressures there is an increase in the molecular mobility by the plasticizing effect of glycerol and water.

The effect of glycerol on sorption can be more clearly observed by plotting the moisture content as function of the weight fraction of starch and glycerol (grams of starch/(grams of starch + grams of glycerol)). Plots, up to 70% RH for the sake of clarity, are shown in **Figure 2B**. These show that glycerol does not cause an increase in moisture content for  $\text{RH} < 70\%$ ; for  $\text{RH} < 50\%$  a “drying effect” is evident.

As shown in **Figure 2A**, adding glycerol at moisture contents  $> 15\%$  would contribute to a decrease in the  $A_w$ , and hence the glycerol would act as a humectant. However, for lower moisture contents ( $\text{MC} < 10\%$ ), adding glycerol contributed to an increase in the  $A_w$  and the water chemical potential would increase. This situation might be explained by glycerol molecules interacting with starch, hence increasing the availability of water; this could lead ultimately to a physical and/or chemical instability.

**Modeling of the Sorption Isotherms.** Equations 1–3 were applied to the sorption data obtained from all of the extruded starch–glycerol mixtures. To assess the statistical significance of the difference between the obtained parameters from model fittings, a paired  $t$  test (same variances) was performed on the experimental data obtained from all of the starch–glycerol mixtures.

**Table 1** shows the values for the fitted BET and GAB equations and the associated error function (EF). In the case of BET, the data were modeled up to a relative humidity of 50%. GAB and Peleg equations were fitted to the whole data range

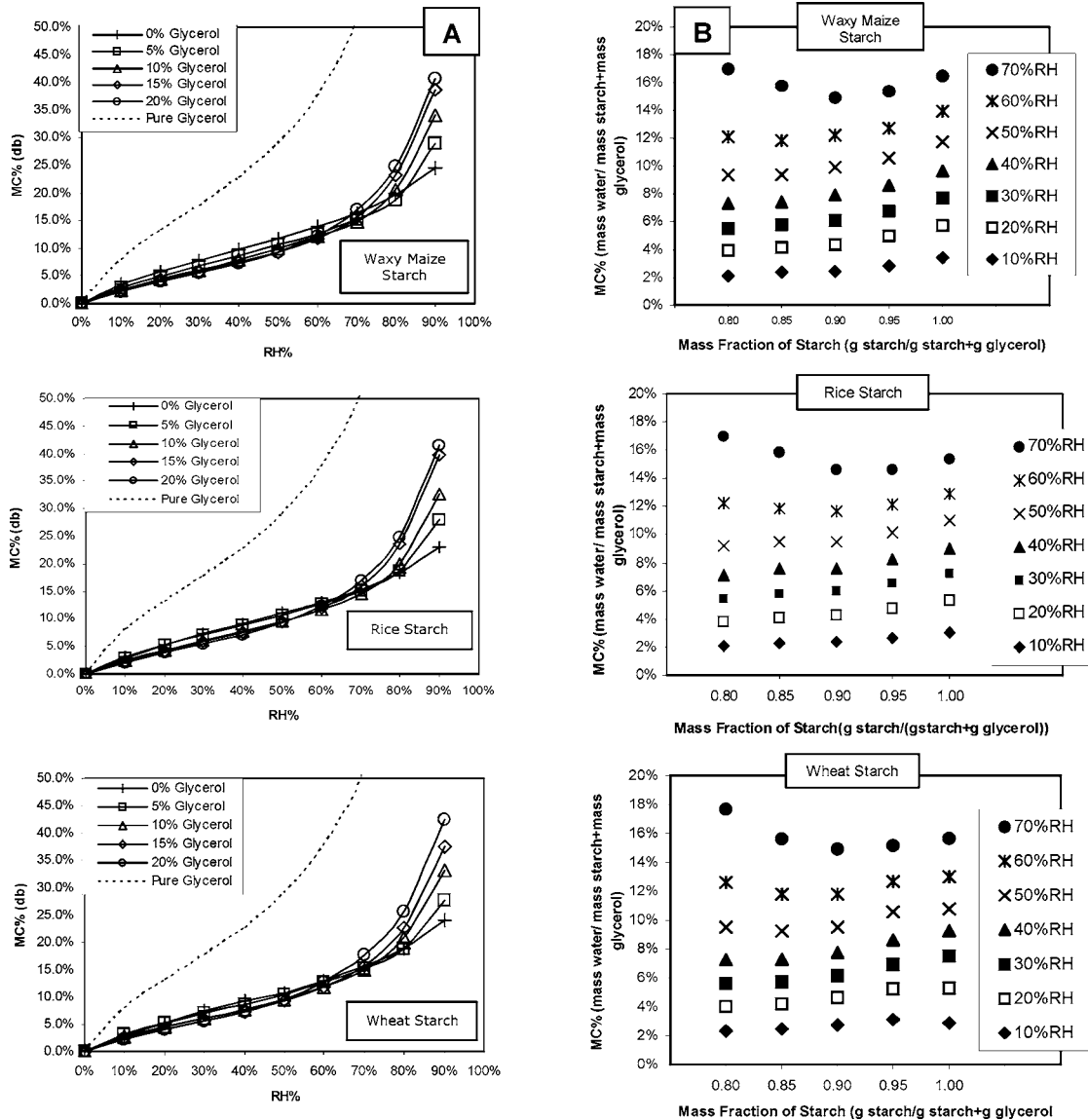


Figure 2. Sorption isotherms for waxy maize-, rice starch-, and wheat starch-glycerol extrudates at 25 °C (A). The moisture content, as a function of weight fraction of starch and glycerol is shown in (B). Depicted data are the calculated mean of three replicates.

Table 1. BET and GAB Modeling Parameters for Waxy Maize-, Rice-, and Wheat Starch-Glycerol Mixtures<sup>a</sup>

starch type	glycerol % (db)	BET			GAB			
		monolayer ( $m_0$ ) % (db)	$C_{BET}$	EF (%)	monolayer ( $m_0$ ) % (db)	$C_{GAB}$	$K_{GAB}$	EF (%)
waxy maize	0	6.7	8.9	1.9	9.4	6.8	0.72	0.7
rice	0	6.3	8.0	2.5	8.9	6.4	0.72	0.9
wheat	0	6.4	7.9	5.1	8.7	6.4	0.73	2.2
waxy maize	5	6.2	7.2	2.4	6.6	9.1	0.86	4.4
rice	5	5.9	7.1	3.0	6.0	9.7	0.88	5.2
wheat	5	6.0	7.6	2.2	6.3	9.5	0.85	3.1
waxy maize	10	5.9	6.8	1.4	5.8	8.0	0.92	4.2
rice	10	5.6	6.1	2.1	5.6	8.1	0.93	3.9
wheat	10	5.4	7.4	2.0	5.6	8.2	0.93	1.9
waxy maize	15	5.5	6.1	1.1	5.8	5.8	0.95	0.9
rice	15	5.7	5.6	8.6	5.9	5.6	0.95	1.7
wheat	15	5.3	6.7	0.8	5.8	6.0	0.94	0.5
waxy maize	20	5.6	4.9	1.8	6.3	3.8	0.95	1.8
rice	20	5.6	4.8	0.8	6.6	3.5	0.94	1.9
wheat	20	5.6	5.4	0.4	6.9	3.5	0.94	3.2

<sup>a</sup> The presented values were obtained from the mean value obtained from three replicates. Error values were calculated using the error function (EF) (eq 6).

(0–90% RH). The EF values obtained were <5%, thus showing accurate fits.

When the starches were compared, differences in their BET monolayer values ( $m_0$ ) were found ( $P < 0.05$ ), with the waxy



maize showing the higher value compared to wheat and rice starches over the range from 0 to 10% glycerol. Similar findings were obtained from GAB, where  $m_0$  was also significantly higher ( $P < 0.05$ ) for waxy maize compared to rice and wheat starches. This may be explained by the higher amylopectin concentration in the waxy sample compared to rice and wheat starch. Amylopectin, being a highly branched molecule, is likely to have active sorption sites readily available for the binding of water molecules compared to the linear structure of amylose. Also, the presence of amylose–lipid complexes in wheat and rice starches formed during/after sample preparation (**Figure 1**) may have hindered water sorption by making the amylose less available.

The differences in the monolayer values from BET and GAB, at glycerol concentrations above 10%, are dominated by the levels of polyol. The variations due to starch types would seem to become less evident at high glycerol levels. This is possibly due to the filling of some of the active sites of the branched amylopectin with the glycerol, thus decreasing the difference in the monolayer between the three starches.

**Table 1** shows that glycerol reduced the monolayer values obtained from the BET equation for all three starches. A value of  $\sim 6.5\%$  for the 0% glycerol samples was decreased to  $\sim 5.6\%$  in the presence of 20% glycerol. In a similar way to BET, monolayer values obtained from GAB decreased significantly ( $P < 0.05$ ) for the three starches when the glycerol concentration increased, from  $\sim 9.4\%$  for the no-glycerol extrudates to a minimum of  $\sim 6.6\%$  for the 20% glycerol samples. It seems that at low relative humidities (i.e., moisture contents of less than the monolayer coverage) glycerol decreases the availability of active sorption sites, hence reducing the surface area available for water molecules and hence the monolayer values. The reasons suggested are the solid starch acting as an adsorbent with glycerol displacing the water (32, 33).

There were differences in the values of  $m_0$  obtained from BET and GAB models for similar compositions. The  $m_0$  values from BET were generally lower than those from the GAB equivalent when modeled across the relative humidity range or only up to 50%. There is no clear explanation of this difference, it is possible that the extra parameter  $K$  in GAB may affect the value of  $m_0$  during model fitting. The GAB model values are closer to the theoretically expected values for the monolayer ( $\sim 11\%$  db for starch) (1).

**Table 1** also gives the thermodynamic parameters  $C_{\text{BET}}$ ,  $C_{\text{GAB}}$ , and  $K_{\text{GAB}}$  obtained after model fitting. There was no clear correlation between the starch type and the values of  $C_{\text{BET}}$ . However, comparison of the same starch type with different glycerol concentrations showed a marked decrease in  $C_{\text{BET}}$  when the glycerol content increased ( $P < 0.05$ ).

Following the definition by Brunauer et al. (7) the value  $C_{\text{BET}}$  is related to the difference in heat of sorption between the monolayer ( $E_1$ ) and the multilayer or bulk water ( $E_L$ ). In other words, a decrease in the  $C_{\text{BET}}$  would suggest a decrease in the value of  $E_1$  (for monolayer), as  $E_L$  (bulk liquid) would remain constant. A lower  $E_1$  would indicate water molecules are less strongly bound to the matrix sorption sites when glycerol is present, suggesting that this polyol might occupy some of the sorption sites of the polymer.

The values for  $C_{\text{GAB}}$  were not starch dependent, but the presence of glycerol had a marked effect ( $P < 0.05$ ). Higher values were obtained for the 0% glycerol sample ( $C_{\text{GAB}} \sim 6.5$ ) and the lowest values ( $C_{\text{GAB}} \sim 3.5$ ) for the 20% glycerol.

Similar to the rationale followed for the BET equation, the constant  $C_{\text{GAB}}$  is also related to the adsorption energies of the

**Table 2.** Peleg Modeling Parameters for Waxy Maize-, Rice-, and Wheat Starch–Glycerol Mixtures<sup>a</sup>

starch type	glycerol % (db)	$K_1$ (%)	$K_2$ (%)	$n_1$	$n_2$	EF (%)
waxy maize	0	19.3	12.4	0.76	6.1	0.9
rice	0	18.6	11.6	0.78	6.4	0.4
wheat	0	18.8	13.1	0.79	6.3	1.5
waxy maize	5	19.8	37.1	0.87	11.7	1.9
rice	5	18.7	38.5	0.87	11.7	1.4
wheat	5	18.5	38.7	0.86	11.4	1.8
waxy maize	10	18.7	45.5	0.91	9.6	1.6
rice	10	17.6	43.4	0.89	9.2	1.3
wheat	10	16.2	43.6	0.89	8.8	1.4
waxy maize	15	16.6	52.4	0.87	7.6	1.1
rice	15	16.9	55	0.88	7.7	0.6
wheat	15	16.2	49.7	0.85	7.5	1.7
waxy maize	20	16.7	55	0.92	7.2	1.1
rice	20	17.5	54.4	0.96	7.2	2.1
wheat	20	17.1	54.5	0.91	6.8	2.4

<sup>a</sup> The presented values were obtained from the mean obtained from three replicates. Error values were calculated using the error function (EF) (eq 6).

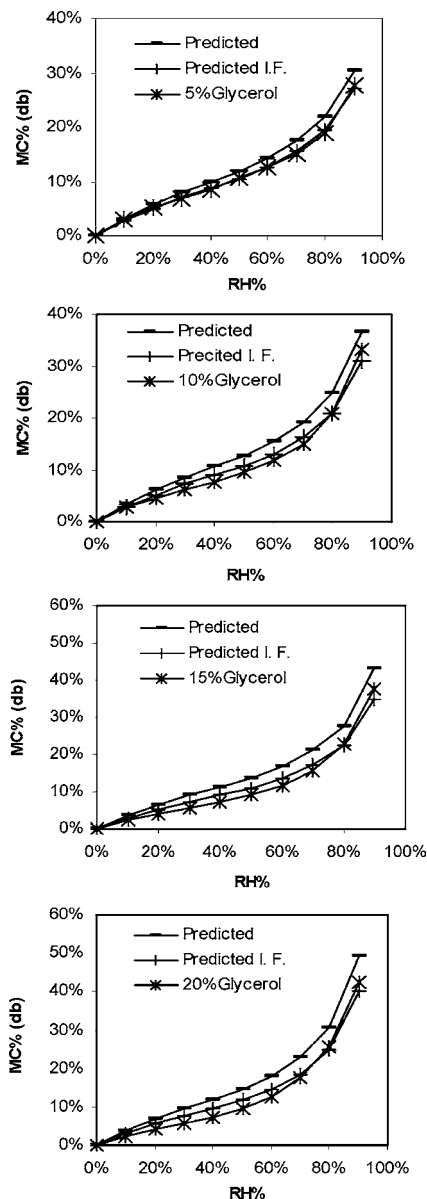
monolayer. Therefore, the decrease in this value would suggest water molecules less strongly bound to the active sites of the matrix when this polyol is present.

The differences in  $C$  from GAB and BET come mainly from the fitting procedure; in the case of GAB it includes the extra parameter  $K_{\text{GAB}}$ , which contributes similarly to  $C_{\text{GAB}}$  in the model fitting. Theoretically, the GAB equation separates the sorption energies in the monolayer and multilayer domains compared to BET, which considers only the heat of sorption for the monolayer, assuming similar energies associated with the multilayer. Therefore, one would expect to obtain smaller values for  $C_{\text{GAB}}$  compared to  $C_{\text{BET}}$ .

When the  $K_{\text{GAB}}$  values were analyzed, differences were not significant between waxy maize, rice, and wheat starches ( $P > 0.05$ ). If glycerol concentrations were compared for the three starches, a clear increase in the values of  $K_{\text{GAB}}$  was observed when the polyol concentration was increased to 20% ( $P < 0.05$ ) (**Table 1**).

Following the definition given in eq 2, an increase in  $K_{\text{GAB}}$  toward a value of 1 would suggest a smaller difference between the energy associated with the heat of sorption of the multilayer and the heat of condensation of pure water. As the latter remains constant, the increase in this value would indicate a reduction in sorption energy of the multilayer, which suggests a destructuring behavior from a multilayer to a bulk liquid-like domain. Therefore, the more the sorbed molecules are structured in a multilayer, the lower the value for  $K_{\text{GAB}}$  (14). It is possible that glycerol molecules, on the sorption sites of the matrix, could reduce the interaction energies between the water molecules, on the second and higher water layers, and the polymer. **Table 1** shows that for the higher concentrations of glycerol (10, 15, and 20%) the  $K_{\text{GAB}}$  values obtained were  $> 0.9$ .

In the case of the Peleg equation, the EF after modeling was generally  $< 2\%$ , proving a better fit than BET and GAB for representing the sorption isotherm for these particular systems, particularly for the high-glycerol samples. The values of the model parameters in **Table 2** for control samples (no glycerol) were similar to the values reported in the literature for starchy materials. Peleg (15) obtained  $K_1 \sim 21\%$ ,  $K_2 \sim 16\%$ ,  $n_1 \sim 0.7$ , and  $n_2 \sim 6$  for potato starch, whereas Al-Muhtaseb et al. (10) obtained  $K_1 \sim 19\%$ ,  $K_2 \sim 9\%$ ,  $n_1 \sim 0.6$ , and  $n_2 \sim 8$  for an amylopectin starch. **Table 2** shows values that are independent of the starch botanical source ( $P > 0.05$ ), but marked changes



**Figure 3.** Comparison of sorption isotherms for wheat starch–glycerol extrudates between predicted moisture contents, the predicted values including the interaction factor (I. F.), and experimental values.

occur when glycerol was present. The decrease in  $K_1$  and increase in  $n_1$  represent a flatter sorption curve at low relative humidities, equivalent to the smaller monolayer values from BET and GAB. Increases in  $K_2$  and  $n_2$  are related to the increase in the sorption behavior at high relative humidities ( $>60\%$ ) for the higher glycerol concentrations.

The Peleg model represents an alternative to the classic BET and GAB models. It can be used to accurately represent sorption isotherms due to the presence of an extra parameter in the equation. The drawback of using this model is the lack of a theoretical background in its development, and thus it does little to improve the fundamental understanding of the differences in sorption behavior.

The prediction of sorption isotherms for starch–glycerol mixtures was also calculated using the component weight fraction contribution approach (eqs 4 and 5). To simplify the interpretation of the data given by eq 5, a unique interaction factor was estimated. Knowing the composition and the

**Table 3.** Interaction Factor  $\xi$  and Error Functions (EF) When Including  $\xi$  (EF  $\xi$ ) and When Not Including  $\xi$ , for Waxy Maize–, Rice–, and Wheat Starch–Glycerol Extrudates

glycerol % (db)	waxy maize starch			rice starch			wheat starch		
	$\xi$	EF $\xi\%$	EF %	$\xi$	EF $\xi\%$	EF %	$\xi$	EF $\xi\%$	EF %
5	0.88	5.7	17.4	0.91	2.5	10.3	0.89	3.0	10.4
10	0.83	13.7	32.7	0.84	11.8	29.8	0.84	8.5	25.2
15	0.81	14.7	32.4	0.88	15.9	28.6	0.81	14.7	37.4
20	0.76	21.9	53.7	0.80	22.4	48.9	0.81	19.7	43.4

complete sorption data of the individual components, the complete sorption profile of the starch–glycerol mixtures was calculated.

**Figure 3** shows the sorption isotherm for wheat starch extrudate–glycerol mixtures and the predicted values given by the eq 4, labeled “Predicted”. Very similar sorption profiles were obtained for the extruded waxy maize– and rice starch–glycerol model systems (data not shown). Values given by the weight fraction model, based purely on the component’s weight fraction and individual sorption isotherms, overestimated the moisture content when compared to the experimental data. Authors have attributed this overestimation to the probable interaction between components, which may decrease the availability of sorption sites (23, 26). To account for this interaction, the factor  $\xi$  was estimated by fitting eq 5 to the same experimental data represented by the curve labeled “Predicted I. F.” in **Figure 3**. **Table 3** summarizes the values obtained for the interaction factors for all starch–glycerol mixtures and their associated EF obtained from each fit. The reduction in the error was by almost 30% for the higher glycerol concentrations when  $\xi$  was used.

As expected, the similar sorption profiles obtained for the three starches studied (**Figure 2A**) gave similar interaction factors  $\xi$  ( $P < 0.05$ ) between these starches. The value of the factor  $\xi$  was  $<1$  when glycerol was present in the extruded starches, and it significantly decreased ( $P > 0.05$ ) when the concentration of this polyol increased. These results support the data given by BET and GAB, showing a reduction in the monolayer value and its associated adsorption energy when the glycerol was present.

In conclusion, this work indicates that reproducible sorption isotherms were obtained using the DVS on all of the starch–glycerol mixtures and that these can be used to detect significant differences when the data are modeled. The control samples (no glycerol), for each of the three studied starches, showed the typical S-shaped curve commonly associated with starch-based materials. The modeling of the experimental data showed that the monolayer value reported from BET and GAB equations was significantly higher ( $P < 0.05$ ) for waxy maize starch compared to rice and wheat starches.

When glycerol was added during extrusion, each starch showed that for  $RH < 60\%$ , the presence of glycerol seemed to decrease the equilibrium moisture content. The low  $m_0$  and  $C$  values from BET and GAB suggest that fewer sorption sites are available for water molecules and hence the reduction in the heat of sorption at the monolayer. At  $RH > 70\%$ , the presence of glycerol in the polymer increased the water sorption. This result follows the concept of glycerol acting both as a plasticizer, contributing to an increase the molecular mobility of the system, and as a hygroscopic compound, contributing to a greater hydration of the system.

Although lacking any theoretical background, the Peleg equation proved to be most flexible in describing the sorption behavior for the control and starch–glycerol samples, giving

the lowest fitting error, the average ER being 1.4% for the Peleg equation compared to 2.4% for the other models (Tables 1 and 2). Hence, the Peleg equation would be the most useful for sorption modeling of complex systems.

The predictions of sorption isotherms based on the component weight fractions not only showed that glycerol not only may interact with starch at the low end of relative humidities but also seem to indicate that there is interaction at higher moisture contents as well.

To improve the understanding on the different levels of energies associated with water sorption in the presence of glycerol, further studies at different temperatures would be required. Also, the study of other polyols (e.g., polyethylene glycols and sorbitol) and starch types (e.g., potato, cassava, and maize) could also be used to validate some of the ideas presented in this work. However, this work shows that the use of glycerol as a general plasticizer for starchy systems needs careful thought if its behavior is to be predictable.

#### ABBREVIATIONS USED

$A_w$ , water activity; RH, equilibrium relative humidity;  $T_g$ , glass transition temperature; BET, Brunauer–Emmett–Teller model; GAB, Guggenheim–Anderson–de Boer model; MC, moisture content; db, dry basis; wb, wet basis;  $m_o$ : monolayer value;  $p/p_0$ , gas partial pressure;  $C_{BET}$ , temperature-dependent constant in the BET model (related to the net heat of sorption between the monolayer and the bulk water);  $C_{GAB}$ , temperature-dependent constant in the GAB model (related to the net heat of sorption between the water molecules and the matrix primary binding sites or monolayer);  $K_{GAB}$ , temperature-dependent constant in the GAB model (related to the heat of sorption of the multilayer);  $k_1, k_2, n_1, n_2$ , constants in the Peleg model;  $M_{calcd}$ , calculated total moisture content at specific water activity;  $W_i$ , component weight of the  $i$ th component expressed on a dry basis;  $X_i$ , equilibrium moisture content on dry basis of the  $i$ th component at the specific water activity;  $W_{Si}$ , mass fraction of the  $i$ th component in the mixture;  $X_e$ , equilibrium moisture content of the  $i$ th component;  $\xi_i$ , physicochemical interaction between components; DVS, dynamic vapor sorption; WMS, waxy maize starch; RS, rice starch; WS, wheat starch; WAXS, wide angle X-ray diffraction; EF, error function;  $E_1$ , heat of sorption in the monolayer;  $E_L$ , heat of sorption bulk water;  $dm/dt$ , slope of changing mass with time.

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