

Modelling and control of moisture transfers in high, intermediate and low a_w composite food

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Abstract

Limitation of moisture transfer in composite food products can be achieved by two main techniques: reduction of a_w difference between components and use of hydrophobic barrier at the interface of the system. Both techniques were tested in a multi-domain model food associating a dry cereal-based component to a wet component using a model based on Fick's second law. Required input modelling parameters were moisture equilibrium and transport properties of the components. The two stabilisation techniques permitted a significant extension of the period of acceptability of the dry component: from 7 min to more than 40 h using solutes addition and up to 12 days using a 300 μm hydrophobic barrier. A further extension of this period of acceptability was achieved by combining the two techniques. However, this had a detrimental effect on the relative efficiency of the barrier due to increased internal resistance of the wet component.

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1. Introduction

Ready-to-eat composite snacks in which distinct water activity (a_w) components are put into contact is a promising trend in new product development. These products present attractive organoleptic profiles, resulting from the association of components characterized by a specific texture and sensorial attributes related to their hydration state (Roudaut, Dacremont, Vallès-Pamiès, Colas, & Le Meste, 2002). Internal moisture transfer, driven by a difference of a_w between the components of the composite food, destroys the sensorial balance of the product and trigger deleterious reactions. Moisture transfers compromise the quality, stability and safety of the product and limit its shelf life (Kester & Fennema, 1986).

The control of moisture transfer between components can first be obtained through the modification of viscosity or porosity of the domains (Labuza & Hyman, 1998) which affect the rate of transport in the system (water diffusion). A second solution is to reduce the a_w difference between the domains, on which depends the total amount of moisture being transferred before the system reaches its equilibrium. This can be achieved by the use of humectants such as salts and sugars. However, there is only a restricted number of safe, effective and palatable a_w lowering agents. Besides, the concentration of humectants that can realistically be added is limited by sensory and nutritional considerations. Lastly, water transfer between components can be delayed using edible films or coatings with good barrier properties at the interface of the components. This last technique has been widely investigated over the last 25 years (Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). Most studies underlined the superiority of hydrophobic barriers, which present a low affinity with water, as long as their mechanical properties are also acceptable.

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Fewer authors tested edible barriers or coatings under real condition of use, i.e. at the interface of a composite model food (Biquet & Labuza, 1988; Bourlieu et al., 2006; Bravin, Peressini, & Sensidoni, 2006; Fennema, Donhowe, & Kester, 1993; Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003d).

Generally, water transfer during storage of composite model foods has been less extensively analysed and modelled than mass transfer phenomena during food processes such as baking, drying, or rehydration (Fahloul, Trystram, Duquenoy, & Barbotteau, 1994; Kayacier & Singh, 2004; Ni & Datta, 1999; Zhang, Datta, & Mukherjee, 2005). Hong, Bakshi, and Labuza (1986) described a model for predicting moisture transfer in dried fruits and almonds mixture; Karathanos, Kostaropoulos, and Saravacos (1995) discussed water diffusion in a dough/raisin system; (Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003a, 2003b, 2003c, 2004) validated a predictive model on several composite foods composed of high water activity agar gels and cereal based-components, possibly separated by barrier films; Roca, Guillard, Guilbert, and Gontard (2006) used successfully the same model to determine the effect of porosity and fat content on the moisture transfer in a composite product (sponge-cake/high a_w gel). As a consequence, the shelf life of composite products is still often determined by long and laborious storage tests which have to be repeated when a parameter of the product manufacturing process is modified. The validation of versatile predictive models to assess moisture transfer in a wide range of food products could thus benefit to most of the sectors of the food industry and help meeting the challenges associated with marketing innovative, long shelf life and nutritionally acceptable products.

The objective of the present study was to compare two common techniques of stabilisation of composite food products (reduction of a_w difference between components and use of edible barrier) using experimental and modelled moisture migration profiles. A model composite food system associating a low a_w moisture sensitive cereal-based component to various wet fillings presenting either high, intermediate or low a_w (ranging from 0.5 to 0.99) and possibly separated by an hydrophobic barrier was selected.

The parameters required for modelling, i.e. moisture equilibrium and transport properties in each components of the model food, are first presented. Moisture transfers in model foods with either high a_w difference, or reduced a_w difference or a barrier film at their interface, are then modelled and discussed.

2. Materials and methods

2.1. Materials

The cereal-based dry component was a thin (2.4 mm) porous dry biscuit (wheat flour, sugars, fat) supplied by Nestlé Product Technology Centre (York, UK).

Four wet components of intermediate water activity (0.75, 0.7, 0.6 and 0.5; 20 °C) were made adding 4.5% agar, water and FRUCTOR 30–85 (glucose–fructose syrup, glucidic profile: fructose 27%, glucose 25%, maltose 27%, maltotriose 8%, higher weight sugars 10%; dry content ~ 85%; DE–67%; Chamtor, Bazincourt, France) in the respective amount of 80, 85, 92.5 and 92.5% for each of the 4 gels. To obtain the 0.5 a_w agar gel, 38 g/100 g crystallized fructose (a_w lowering agent) was added. The agar solution was prepared by mixing the ingredients following the proportions previously given, homogenising the preparation with a magnetic stirrer during 30 min and leaving the solution in a water bath at 100 °C for an hour.

The 0.99 a_w agar gel was prepared according to the method described in a previous study (Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003b).

A 0.64 a_w wet component was obtained by concentrating through boiling a commercial strawberry jam (composition: glucose–fructose syrup, strawberry: 35% w.b., sugar, pectin, citric acid; initial $a_w = 0.86$, 20 °C; Corrèze Conserve, France).

The agar gel solution and concentrated jam were then poured into glass plates 80 mm (external diameter) and 1.8 cm high. The gels were covered with parafilm, wrapped with aluminium foil and used within 24 h.

A commercial blend of white beeswax and Acetic Acid Ester of Mono and Diglycerides (GBS 2000®: MP = 57 °C, fatty acid chain length of ACETEM = C16/C18, white beeswax addition ≤ 20% w/w; Danisco Ingredients, Trappes, France), called hereafter Wax/ACETEM, was tested as a moisture barrier. The fat material was heated for 10 min at 67 °C, i.e. 10 °C above its melting point. The melted material was quickly laminated (target thickness 300 µm) using a film making apparatus (Braive Instrument, Checy, France) onto a steel plate covered with greaseproof paper sheets. Both instruments were pre-warmed (20 min, 100°) before the application of the film. Films were preconditioned in desiccators over MgCl₂ (20 °C) and used within 5 days after their preparation to limit changes in the crystallization state of the fat phase.

2.2. Moisture sorption isotherm and effective diffusivity determination

To gather more experimental data two complementary methods to determine model food components moisture sorption isotherms were used in our study. Moisture isotherms were determined by absorption for the dry component and barrier film, and by desorption for the wet components, in order to minimize errors due to hysteresis.

The static saturated salt methods described by Bell and Labuza (2000) was followed. Samples (1–3 g, in triplicate) were equilibrated at 20 °C over saturated salt solutions in desiccators and weighted every two weeks (Sauter GmbH-D balance, sensitivity = 10⁻⁴ g, Ebingen, Germany).

The sorption isotherms were also determined (duplicates, 20 °C) using a controlled atmosphere microbalance

(Dynamic Vapour Sorption apparatus equipped with a CAHN D-100 balance-Madison, sensitivity = 10^{-6} g, Surface Measurement System Ltd., London, UK). Disc samples (7 mm diameter) were used for the measurement. The dry biscuit and the film were desiccated for one week over P_2O_5 before being loaded in the microbalance. The samples were then equilibrated at successive levels of relative humidity: from 10 to 95% in adsorption with steps of 10% RH in the low water activity range (below 0.7) and of 5% in the high relative humidity range. In desorption, from 75 to 10%, 5% steps were used. The length of the steps at a given humidity differed according to the type of sample. For the dry biscuit and the 0.75 a_w gel, the steps automatically finished when the variation in sample mass was, respectively lower than 0.002% sample weight (d.b.)/min and 0.001% sample weight (d.b.)/min. For the lipidic film, based on more hydrophobic material that absorb significantly lower amounts of water on each RH step, the previous variation of mass criteria did not enable to reach equilibrium. Eight hours and 24 h-long steps, respectively below and above 60% RH were applied. The final average weight variation in the lipid-based films averaged $0.0002 \pm 0.0001\%$ sample weight (d.b.)/min, which corresponded more precisely to 0.004 mg/min considering the average dry weight of the two lipid samples of 16.24 mg.

The Ferro-Fontan Eq. (1) was used to model the agar gel, barrier film and dry biscuit sorption isotherm curve for a_w ranging from 0.10 to 1 (20 °C).

$$X = \left[\text{Ln} \left(\frac{a}{a_w} \right) \cdot \left(\frac{1}{b} \right) \right]^c \quad (1)$$

where X is the moisture content in g/g (d.b.) and a , b and c are unknown parameters.

The Guggenheim-Anderson-de Boer (GAB) Eq. (2) was used to model the FRUCTOR agar gels, concentrated jam, barrier film and dry biscuit sorption isotherm curve for a_w ranging from 0.1 to 0.75 (20 °C).

$$X = \frac{X_m \cdot K \cdot C_g \cdot a_w}{(1 - Ka_w)(1 - Ka_w + C_g Ka_w)} \quad (2)$$

where X is the moisture content in g/g (d.b.), X_m the monolayer value (g/g d.b.), C_g a constant related to the heat of sorption of the first layer, K a constant related to the heat of sorption of the multilayer.

The models parameters were determined by minimising the sum of squared error between experimentally measured and predicted values of moisture content using the Levenberg and Marquart algorithm of MATLAB[®] software (The Mathwork Inc., Natick, MA, USA).

Water diffusivity values in the various components were estimated at 20 °C for each relative humidity range from moisture content kinetics data obtained using DVS balance by minimising the root mean square of deviations between simulated and measured moisture content values. To do so, an iterative process taking into account sample volume deformation and external air resistance (Roca, Guillard, Broyart, Guilbert, & et Gontard, 2007) was used.

2.3. Dry component structure observations

Magnifying glass cross-section observations of the dry component were conducted (using 10× to 50× magnification; Sterni 2000-C, Zeiss, Le Pecq, France). The dry component had been previously conditioned at 0.11, 0.33, 0.54 and 0.75 a_w over saturated salt solutions (3 weeks, using LiCl, MgCl₂, MgNO₃, NaCl; 20 °C).

2.4. Moisture migration experiments

Moisture migration experiments were conducted following the methodology previously detailed by Bourlieu et al. (2006). The two component cells (dry component/wet component) were opened at 2, 4, 6, 12 h and 1, 6, 10 and 22 days. The cells with moisture barriers were opened after 1, 4, 6, 10 and 22 days. After opening, the moisture content of the dry component and wet components of the model food were determined by weighting before and after complete desiccation: 24 h in an oven at 103 °C and cooling down stage of 2 h over P_2O_5 for the dry component and 0.99 a_w agar gel, 16.5 h vacuum drying at 70 °C and 50 mmHg for the intermediate a_w gels and jam (A.O.A.C. method No. 925.45A, 2000).

2.5. Simulations

Simulations of moisture transfer were performed using the model developed by Guillard et al. (2003b) with MATLAB[®] software (The Mathworks Inc., Natick, MA, USA). Input parameters were for each component: initial water activity, initial moisture content, water sorption equation, moisture effective diffusivity value and the material apparent density.

The root mean square error (RMSE) was used to estimate the quality of model fitting and was calculated as follows:

$$\text{RMSE} = \sqrt{\frac{(\hat{y} - y)^2}{(N - p)}} \quad (3)$$

where y , \hat{y} , N and p are respectively, the experimental and predicted values (g/100 g d.b.), the number of experimental moisture content measurements and the number of estimated model parameters.

3. Results and discussion

3.1. Moisture sorption isotherm

The biscuit moisture sorption isotherm over 0.10–0.99 a_w range (20 °C) is presented on Fig. 1a. The Ferro-Fontan model [Eq. (1)] gave accurate fitting of the sorption curve with 1.0649, 0.1457, and -1.5251 values for a , b and c parameters, respectively (RMSE = 0.15 g/100 g; Confidence Interval: $0.9844 < a < 1.1454$, $0.060 < b < 0.2313$; $-2.4096 < c < -0.6406$). This model was initially developed

to describe moisture sorption over the high a_w range (>0.90) and was later on described by Iglesias and Chirife (1995), as a good alternative to the GAB model over a wide range of a_w (0.10–0.90). The GAB model was used over the intermediate and low a_w range (Fig. 1b), as advocated since the 1983 ‘International Symposium on the Properties of Water’. This latter model allowed a more accurate fitting

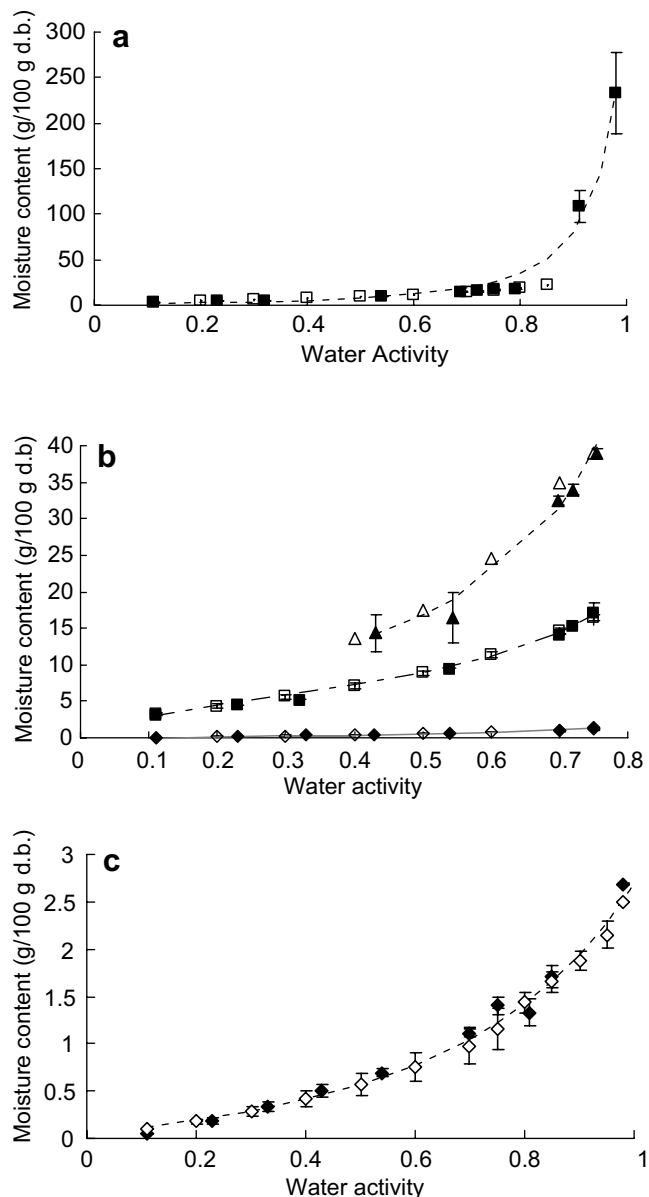


Fig. 1. (a) Dry biscuit moisture sorption isotherm and corresponding Ferro-Fontan fitting over a 0.1–0.99 a_w range (20 °C): DVS experimental data (\square), SS experimental data (\blacksquare), Ferro-Fontan fitting (—). (b) Comparison between experimental and GAB fitted water vapor sorption isotherms for the 0.75 a_w FRUCTOR gel (desorption), for the dry biscuit and hydrophobic barrier (adsorption) at 20 °C: 0.75 a_w FRUCTOR gel experimental data (Δ , \blacktriangle), dry biscuit experimental data (\square , \blacksquare), hydrophobic barrier experimental data (\diamond , \blacklozenge). Open symbols: DVS data, filled symbols: SS data, lines: GAB fittings. (c) Comparison between experimental and GAB fitted water vapor sorption isotherms (adsorption) for the Wax/ACETEM barrier at 20 °C: DVS experimental data (\diamond), SS experimental data (\blacklozenge), Ferro-Fontan fitting (—).

of the data than the Ferro-Fontan model (RMSE Ferro-Fontan model = 0.24 g/100 g (d.b.) vs. 0.66×10^{-2} g/100 g d.b with the GAB model). The dry biscuit isotherm presented the typical sigmoid shape curve of a type II isotherm according to the Brunauer classification (Bell & Labuza, 2000) with a discreet monolayer formation (up to 5.5 g/100 g d.b.) followed by multilayer build up of water molecules. Above 0.75 a_w , the curve showed a steep rise, which was attributable to the dissolution of sugars in the product aqueous phase. Similar high equilibrium water uptake for a_w ranging from 0.75 to 1, were reported in dry biscuits (Arogba, 2001; Guillard, Broyart, Guilbert, Bonazzi, & Gontard, 2004), and in various cookies and corn snacks (Palou, Lopez-Malo, & Argaiz, 1997). The difficulty in measuring accurate equilibrium water content for high a_w is well illustrated by the important variability on experimental data obtained with the saturated salt solutions method above 0.80 a_w .

On the contrary, WAX/ACETEM presented an extremely low sorption of water, typical of hydrophobic partially crystalline material (Fig. 1c). Its equilibrium moisture content reached only 2.5 g/100 g (d.b.) at 0.98 a_w .

The FRUCTOR agar gels were characterized by the highest isotherms over the intermediate a_w range, with none or small differences in moisture content at equilibrium (Table 1), which is consistent with their very similar dry basis composition. Apart from honey, fruits and their derivatives, few moisture sorption isotherms of complex sugar-based products have been reported in literature. Kim, Kim, Kim, Shin, and Chang (1999) presented the sorption isotherm of a commercial strawberry jam characterized by higher moisture sorption isotherm than the FRUCTOR gels of the present study. These authors reported a moisture content of 48.5 g/100 g (d.b.) at 0.75 a_w (20 °C) and a monolayer value of 13.5 g/100 g (d.b.) instead of, respectively 38.2 g/100 g and 8.8 g/100 g (d.b.) in the 0.75 a_w FRUCTOR gel. These higher values can be related to the different glucidic profile of the strawberry jam (saccharose, fructose and glucose) compared to the presently studied FRUCTOR gels (fructose, glucose, maltose and maltotriose). A comprehensive work was also recently undertaken by Zamora et al. (Zamora, Chirife, & Roldan, 2005) on the relationship between a_w and moisture in honey. These authors validated a simple regression model between a_w and moisture on supersaturated sugars solutions having either a composition similar to honey (fructose, glucose, maltose and saccharose) or based on glucose/fructose (25 °C). Supersaturated solutions of glucose/fructose (1:1) presented 0.70 and 0.60 a_w for moisture content of 33.7 g/100 g and 23.7 g/100 g (d.b.) The moisture content of such blends is thus slightly higher than the one encountered in our FRUCTOR gels including higher sugar weight (diiose and triose) in their glucidic profile.

The dry biscuit isotherm presented on Fig. 1 allows the prediction of the thermodynamic equilibrium moisture content when the dry component is put in contact with

Table 1
Material characteristics of the model food components used for modelling purpose in the intermediate and low a_w systems (20 °C)

	Apparent density (kg/m ³)	Initial moisture content (g/100 g d.b)	GAB parameters			RMSE of fitting (g/100 g d.b)	Effective diffusivity identified on moisture migration data (10 ⁻¹¹ m ² s ⁻¹)
			X_w	C_g	K		
Biscuit	230 ± 17 ^a	3.0 ± 0.3	0.0545	8.6747	0.9635	6.6 × 10 ⁻³	10.00
0.75 a_w Gel	1451 ± 9	38.4 ± 1.1	0.0877	10.5374	1.0440	2.4 × 10 ⁻²	8.81 ± 4.48 ^b
0.70 a_w Gel	1490 ± 54	29.2 ± 0.7	0.0877	10.5374	1.0440	2.4 × 10 ⁻²	2.43 ± 0.37 ^b
0.60 a_w Gel	1576 ± 19	21.7 ± 0.4	0.0877	11.4021	1.0385	8.1 × 10 ⁻²	0.15
0.50 a_w Gel	1754 ± 53	13.3 ± 0.2	0.0809	11.5317	0.9497	3.3 × 10 ⁻²	0.10
0.64 a_w jam	1370 ± 5	23.8 ± 0.5	0.0845	4.0724 × 10 ⁶	0.9826	9.2 × 10 ⁻²	0.15
Wax/ ACETEM barrier	1010 ± 9	0.3 ± 0.1	0.0085	1.2351	0.7893	4.1 × 10 ⁻²	0.05

^a ± values are standard deviations.

^b Standard deviations could be indicated only for D_{eff} identified from DVS balance kinetics data whose value was maintained in moisture migration modelling.

higher a_w wet components. Determination of the moisture transfer rate in the biscuit and wet component remains necessary to make accurate modelling of moisture transfer in the composite systems.

3.2. Effective diffusivity deduced from water vapour sorption kinetics

The water sorption kinetics were used in preliminary tests to identify D_{eff} and its variation with moisture content in the dry biscuit, 0.75 a_w gel and hydrophobic film. Using the DVS balance, kinetics data were obtained over a wide range of a_w with low levels of a_w variation corresponding to transient-state of moisture content in the product. The dry biscuit D_{eff} values obtained from the DVS balance transient-state moisture content of the sorption kinetics are plotted on Fig. 2a. The dry biscuit D_{eff} presented a moisture concentration dependence with three main regions of variation: (i) a steady state around 4.00×10^{-10} m²/s for moisture content ranging from 3 to 15 g/100 g (d.b.) corresponding to low and intermediate a_w ; (ii) an increase from 4.00×10^{-10} to 12.20×10^{-10} m²/s between 15 and 21 g/100 g (d.b.). This increase starts at 0.75 a_w at which dissolution of sugar can occur; (iii) a decrease between 21 and 30 g/100 g (d.b.) which can be linked to the closure of porosity starting after 0.75 a_w and subsequent collapse of the cereal matrix. The first zone of steady state of D_{eff} can be linked to the stable initial porosity of the material. It was checked experimentally using magnifying glass cross-observations of the cereal-based matrix, preconditioned at variable a_w , that its porosity was almost not affected by moisture content increase up to 0.75 a_w . Similar moisture concentration influence and D_{eff} range of values had been reported in dry biscuits by Guillard et al. (2004): from 3.53 to 6.59×10^{-10} m²/s for moisture content increasing from 1.70 to 11.10 g/100 g (d.b.) and down to 0.63×10^{-10} m²/s for a moisture content of 47.7 g/100 g (d.b.). These variations could reflect variable contributions from liquid

diffusion in the solid matrix of the food and vapour diffusion in pores, which have diffusivity values differing by several orders of magnitude. Typical values are 10^{-9} and 10^{-5} m²/s for liquid and vapour-phase diffusion, respectively (Saravacos & Maroulis, 2001).

The moisture effective diffusivity identified on the 0.75 a_w gel dynamic desorption data are presented on Fig. 2b. A continuous decrease of the gel D_{eff} values, from 1.01 to 0.14×10^{-10} m²/s, was observed over the range moisture content investigated (39–22 g/100 g d.b.). A similar water concentration dependence of the moisture D_{eff} of gelled sugar matrix or sugar solutions has been highlighted by Biquet and Guilbert (1986) and by Adhikari, Howes, Bhandari, Yamamoto, and Truong (2002). Moisture D_{eff} values identified by Biquet and Guilbert at 50 °C in agar/sugar gels (maltodextrin, glucose syrup or saccharose) ranged between 0.30 and 0.80×10^{-10} m²/s at a moisture content of 25 g/100 g (d.b.). These values were two to five times higher than the one identified in the 0.75 a_w gel at the same moisture content but lower temperature (20 °C). At a temperature closer to the one of our experiments, i.e. 35 °C, Adhikari et al. (2002) reported D_{eff} values close to the one presently identified. In fructose solutions, these values decreased from 0.79×10^{-10} m²/s to 0.02×10^{-10} m²/s for moisture content ranging from 39 g/100 g to 11.1 g/100 g (d.b.). In more complex sugar blend solutions (sucrose, glucose, fructose/maltodextrins, 4:1), presenting a composition close to the FRUCTOR gelled matrix used in this study, a D_{eff} value of 0.52×10^{-10} m²/s, comparable to the one identified on the 0.75 a_w gel, was identified for a moisture content of 36.6 g/100 g (d.b.).

Conversely, almost constant effective moisture diffusivity ($\sim 0.05 \times 10^{-10}$ m²/s) was determined in the hydrophobic material (Fig. 2c). This low D_{eff} value is in line with its hydrophobic partially crystalline nature (Solid Fat Content at 20 °C $\sim 88\%$). At high a_w , the sorption of water did not induce plasticization of the hydrophobic film and modification of its barrier properties.

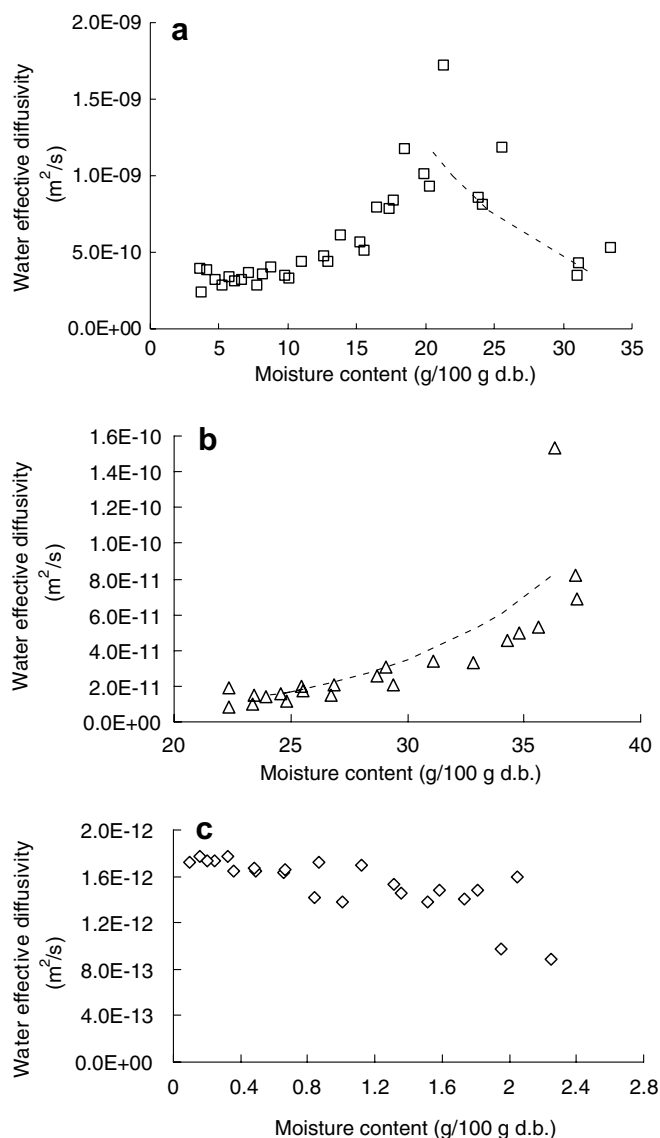


Fig. 2. (a) Moisture diffusivity in the dry biscuit at 20 °C identified from DVS balance sorption kinetics data: experimental data (\square , 3 Replicates), fitting (---, RMSE = 4.99×10^{-10} m^2/s) of the moisture effective diffusivity dependence with moisture content using the empirical form $D_{\text{eff}} = D_0 \cdot e^{(-K \cdot X)}$ with D_{eff} the moisture effective diffusivity (m^2/s), D_0 the pre-exponential factor (m^2/s), K a constant, X the moisture content (g/g d.b.). (b) Moisture diffusivity in the 0.75 a_w gel at 20 °C identified from DVS balance sorption experiments: experimental data (\triangle , 3 Replicates), fitting (---, RMSE = 1.49×10^{-11} m^2/s) of the moisture effective diffusivity dependence with moisture content using the empirical form $D_{\text{eff}} = D_0 \cdot e^{(-K \cdot X)}$ with D_{eff} the moisture effective diffusivity (m^2/s), D_0 the pre-exponential factor (m^2/s), K a constant, X the moisture content (g/g d.b.). (c) Moisture diffusivity in the Wax/ACETEM barrier at 20 °C identified from DVS balance sorption experiments (2 replicates).

3.3. Moisture transfer in a 0.11–0.99 a_w system

The hydration of the dry biscuit put in contact with a 0.99 a_w agar gel was experimentally observed through moisture content measurements of the biscuit and the agar gel over time. These moisture migration experiments were fitted with the model based on Fick's 2nd law using as

input data the Ferro-Fontan fitted moisture sorption isotherms of the two components and by identifying a variable effective diffusivity in the dry component. An empirical expression in agreement with the models used by Roca et al. (2006) was used to describe the moisture concentration dependence in the dry component:

$$D_{\text{eff}} = \alpha \cdot D_0 \cdot e^{(-K \cdot X)} \quad (4)$$

With $\alpha = 0.30$, $D_0 = 3.43 \times 10^{-10}$ (m^2/s), $K = -9.84$, X = moisture content (g/g d.b.).

With this fitted parameters, the model presented accurately the moisture migration results with RMSE in the same range than experimental errors (Table 2).

The hydration of the cereal-based matrix in the model product was drastic (Fig. 3). A a_w critical limit of 0.40 was selected in our cereal-based matrix in accordance with various studies (Hsieh, Hu, Huff, & Peng, 1990; Katz & Labuza, 1981) that suggested a change in crispness of cereal-based product between water activity values of 0.35 and 0.50 (20 °C). This critical limit was obtained after 7 min of contact in the 0.11–0.99 a_w system. Extremely high equilibrium moisture content (380 g/100 d.b.) was reached after 22 days of storage.

3.4. Limitation of moisture transfer induced by reduction of a_w difference between components

Controlled reduction of moisture transfer was achieved using FRUCTOR syrup as lowering water activity agent in the wet component of the system. The a_w difference between components was then reduced from 0.11–0.99 to differences ranging from 0.11–0.75 to 0.11–0.50. The high concentration in fructose of the FRUCTOR syrup, presenting a higher solubility than other commonly used solutes (sucrose, glucose), permitted formulations of intermediate to low a_w wet components. FRUCTOR gels contained fructose, glucose and maltose as major components and in comparable amount, except for the 0.50 a_w gel where fructose was the major compound. This glucidic profile allowed a good stabilization of the amorphous sugar blend, avoiding crystallization of higher weight sugars, thanks to plasticization by lower weight solutes such as glucose and fructose (Arvanitoyannis, Blanshard, Ablett, Izzard, & Lillford, 1993). The glucidic profile of the FRUCTOR gel differs slightly from the most natural sugar composition (fructose/glucose/sucrose) which is typical of fruit and vegetable and which was encountered in the concentrated jam.

The predictive model was first run using as input data the moisture sorption isotherms and D_{eff} identified in each component over the range of a_w of interest, i.e. constant on the 0.11–0.75 a_w range in the dry matrix and constant in the intermediate a_w gel. Indeed, wet components presented almost constant moisture content during moisture migration experiments. Since the components were in direct contact, no air resistance to moisture transfer was considered at the interface. It was also checked experimentally that

Table 2
Results of moisture migration tests including errors of prediction and experimental errors

Model system	Period of time ^a (h)	Experimental error (g/100 g d.b.)		RMSE of the prediction (g/100 g d.b.)		
		Dry component	Wet component	Dry component	Wet component	
2 Component-system dry component/wet component	0.11–0.99 a_w system	0.11	9.26	131.94	25.38	104.57
	0.11–0.75 a_w system	2	0.47	1.02	1.34	2.28
	0.11–0.70 a_w system	3	0.72	0.86	0.51	1.01
	0.11–0.64 a_w system	4	0.23	0.63	0.79	1.93
	0.11–0.60 a_w system	7	0.83	1.22	0.64	1.51
	0.11–0.50 a_w system	43	0.55	0.67	0.86	2.31
3 Component-system dry component/barrier film (300 μm)/wet component	0.11–0.99 a_w system	300 (315) ^b	0.74	67.07	0.49	74.33
	0.11–0.75 a_w system	320 (270)	0.32	1.01	0.38	0.57
	0.11–0.60 a_w system	1010 (308)	1.30	0.77	0.33	0.98

^a Period of time before the dry component reaches the a_{wc} of 0.4 (20 °C).

^b Figure between brackets stands for average film thickness (μm).

volume deformation of the components was negligible and did not influence moisture transfer prediction. Taking into account the previous hypothesis and input parameters, a slight overestimation of the rate of transfer in the model foods presenting intermediate to low a_w wet component (e.g. RMSE dry component in the 0.11–0.75 a_w system = 2.7 g/100 g (d.b.) vs. experimental error = 0.47 g/100 g (d.b.)) was obtained. Identification of moisture effective diffusivity values in the dry and wet components more representative of the real transfer in the model foods was thus necessary. ‘Optimal’ values of effective diffusivity corresponding to a global minimum of RMSE were obtained by screening a wide range of effective diffusivity values around the values (± 10 times) identified from the DVS bal-

ance sorption kinetics. A restricted influence of the wet component moisture D_{eff} , on the transfer in the 0.11–0.75 and 0.11–0.70 a_w difference model food was noticed: the global minimum of RMSE was obtained for a given value of the dry component D_{eff} and for a range of values of the wet component D_{eff} . In this case, the wet component D_{eff} was considered as equal to the one identified from DVS balance kinetics data and only the moisture D_{eff} in the dry component was optimized on moisture migration data. DVS balance sorption kinetics data permitted determining D_{eff} moisture concentration dependence in the various components. However, the moisture D_{eff} values identified from the DVS balance experiments could not be directly used as input data to model moisture migration results. This discrepancy can be explained by differences between the moisture DVS balance sorption and migration experiments (contact direct or indirect/additional solutes transfer in moisture migration experiments).

In all the systems, the optimal value of moisture D_{eff} in the dry component was $1.0 \times 10^{-10} \text{ m}^2/\text{s}$ (20 °C). In 0.60, 0.50 a_w gels and 0.64 a_w jam much lower D_{eff} values were identified than in the 0.75 and 0.70 a_w gels. These lower values were consistent with the lower water content of the wet components and with the higher solutes concentration, which affect water mobility (Table 1).

The reduction of internal water molecular mobility induced by increasing addition of FRUCTOR syrup was extremely important: moisture D_{eff} averaging $1 \times 10^{-9} \text{ m}^2/\text{s}$ in the non rate limiting 0.99 a_w agar gel was reduced by 10 in the 0.75 a_w gel and by 1000 in the 0.5 a_w gel. A significant extension of the dry component shelf life was consequently allowed by increasing FRUCTOR syrup

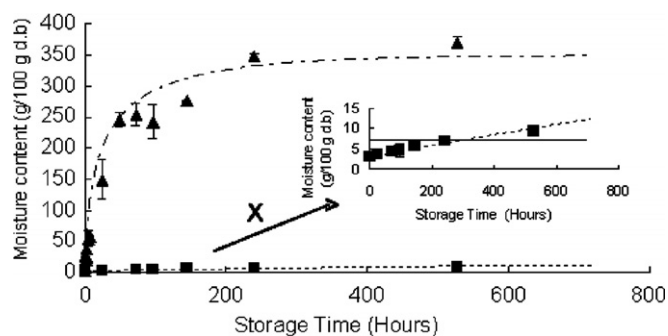


Fig. 3. Moisture uptake of dry component when put in direct contact with 0.99 a_w agar (\blacktriangle), corresponding model fitting (---), dry component moisture uptake when put in indirect contact with 0.99 a_w agar with hydrophobic barrier at the interface (\blacksquare), corresponding model fitting (- - -). Inset: dry component moisture uptake when put in indirect contact with 0.99 a_w agar with hydrophobic barrier at the interface (\blacksquare), corresponding model fitting (—).

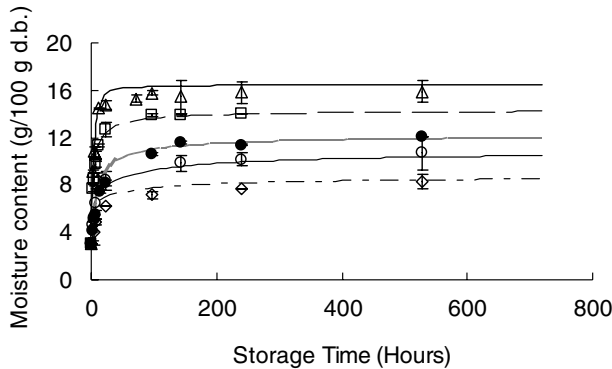


Fig. 4. Moisture uptake of dry component when put in direct contact with 0.75 a_w agar (Δ), corresponding model fitting (—), dry component moisture content when put in direct contact with 0.7 a_w agar (\square), corresponding model prediction (—), dry component moisture content when put in direct contact with 0.64 a_w concentrated jam (\bullet), corresponding model fitting (.....), dry component moisture content when put in direct contact with 0.6 a_w agar (\circ), corresponding model prediction (—), dry component moisture content when put in direct contact with 0.6 a_w agar (\diamond), corresponding model fitting (---).

content in the wet component: of 2, 3, 7 and 43 h, respectively in the systems based on 0.75, 0.7, 0.6 and 0.5 a_w gel compared to 7 min in the 0.11–0.99 a_w system (Fig. 4).

3.5. Reduction of transfer using lipid-based barriers

The effect of a hydrophobic barrier (300 μm) addition at the interface of the 0.11–0.99 a_w system was determined experimentally and correctly fitted with the model (Table 2). The barrier film allowed an important extension of the period of acceptability of the dry component: from 7 min to 12.5 days (Fig. 3). According to the model simulation, a 80 μm barrier film permits the same extension of the period of acceptability of the 0.11–0.99 a_w food system than a reduction from 0.99 to 0.50 a_w of the wet component.

The effect of the barrier in some of the systems presenting intermediate a_w wet components, was also determined

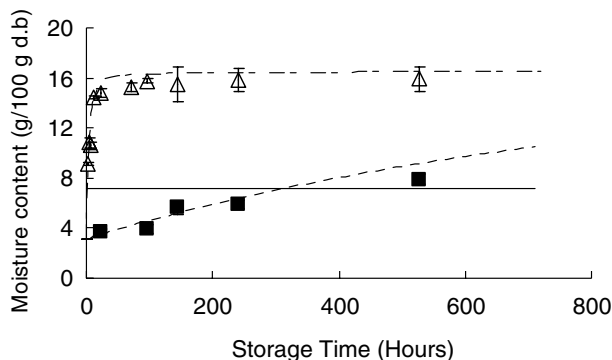


Fig. 5. Moisture uptake of dry component when put in direct contact with 0.75 a_w agar (Δ), corresponding model fitting (---), moisture uptake of dry component when put in indirect contact with 0.75 a_w agar with hydrophobic barrier at the interface (\blacksquare), corresponding model fitting (—).

experimentally and with the predictive model (Fig. 5). The addition of a 300 μm film in a model composite food presenting gels of 0.75, 0.7 and 0.6 a_w permitted an extension of the period of acceptability of the dry component, respectively, from 2, 3 and 7 h to 14, 18 and 42 days. The lower relative efficiency of the barrier film applied on intermediate a_w gels compared to high a_w gel was explained by a lower difference between the internal resistance of the intermediate FRUCTOR gels and the barrier film, than between the high a_w gel and the film (Taoukis, Meskine, & Labuza, 1988).

4. Conclusions

Moisture sorption and transfer rate in the various components of multi-domain food products, presenting high, intermediate or low a_w wet component and possibly protected by a hydrophobic film have been determined. The dry biscuit and sugar-based wet components studied presented high moisture D_{eff} concentration dependence. Conversely, the hydrophobic film presented almost constant and much lower moisture D_{eff} along with low moisture sorption on all the range of a_w , accounting for its interesting barrier properties.

Effective control of moisture transfer was achieved in the model cells by addition of solutes within the wet component, application of a hydrophobic barrier film at the interface of the dry and wet component, and above all, by a combination of the two techniques. The efficiency of both techniques was accurately fitted using a predictive model based on Fick's second law. The addition of solutes induced a significant reduction of water mobility in the wet component: of an 10-fold order of magnitude between the high and first intermediate a_w wet component (0.75 a_w), of an 100-fold order between this latter and the low a_w wet component. The period of acceptability of the cereal-based product was consequently extended from 7 min, when put in contact with a high a_w gel, to more than 40 h, when a low a_w wet component was used. The use of a hydrophobic partially crystalline film was more effective, in term of extension of the period of acceptability of the dry component: up to 12 days when in contact with a high a_w gel.

Such modelling approach permits a controlled formulation of composite food product and a comparison of the efficiency of techniques of stabilization of products.

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