Edible Acetylated Monoglyceride Films: Effect of Film-Forming Technique on Moisture Barrier Properties

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ABSTRACT: The influence of film-forming techniques on the moisture barrier efficiency of acetylated MG (AMG) films tested in real conditions at the interface between an agar gel (AG) and sponge cake (SC) was investigated. Three systems were studied: self-supporting films, sprayed films, and cast films. The moisture distribution profiles of the AG/AMG/SC systems were determined experimentally and by using a predictive model for both self-supporting films of various thicknesses and formed-in-place (sprayed or cast) films. Increasing the thickness of the self-supporting films had no influence on moisture barrier efficiency, probably due to the high stability of the AMG material. Formed-in-place films were 40% less efficient than the self-supporting films whatever the application procedure used (spraying or casting) because of their poor integrity due to the roughness of the SC surface.

Paper no. J10641 in *JAOCS 81,* 1053–1058 (November 2004).

KEY WORDS: Acetylated monoglyceride films, casting, moisture transfer, self-supporting film, spraying.

Edible lipid films have been widely used for their important moisture barrier properties (1,2). A variety of lipid compounds, including acetylated MG (AMG), natural waxes, and surfactants, have been used as protective coatings to block moisture transfer between compartments of a composite food (3–5). These lipid films were found to be efficient in delaying the moistening of a "dry" compartment in contact with a "wet" compartment but only in the restrictive conditions encountered in laboratories, where films were deposited on a smooth surface to form self-supporting layers. In commercial situations, formed-in-place films produced by spraying appear to be the best means of applying a fatty layer on a food surface. However, the moisture barrier performance of these films has received little attention. The moisture barrier properties of lipid layers have most often been characterized by permeability measurements on freestanding films; consequently, they cannot be easily realized on formed-in-place films in direct contact with food. Moreover, permeability characterizes film barrier performance in the restrictive conditions of film thickness, temperature and humidity (6–8). In

most cases, this value cannot be extended to different sets of conditions and film thicknesses (9).

The barrier performance of lipid-based films is sensitive to parameters such as their chemical group, aliphatic chain length, the presence of unsaturation, and polymorphism. The chemical group influences moisture barrier efficiency through the hydrophobicity of the molecules that interact more or less with water. For example, hydroxyl groups have less affinity for water than carbonyl and carboxyl groups. For groups having the same chemical nature, carbon chain length modifies the barrier properties, usually with a decrease in permeability with an increase in carbon number (from 14 to 18) (10). When the degree of unsaturation increases, the m.p. of the lipid decreases, and as a consequence, so does the barrier efficiency. Polymorphism also strongly influences barrier performance: Kester and Fennema (11) found that crystallization in the β form increased the moisture transfer resistance of soy and canola oil films compared with crystallization in the β′ form, but that the β form gave similar water resistance compared with crystallization in the α form. The film-forming technique and thickness used are also two parameters influencing moisture barrier performance.

Films can be formed either from a film-forming solution cast or extruded to yield freestanding, self-supporting films that can be then applied on the food surface or from a molten fatty material or suspension applied directly onto the food surface by spraying, falling-film enrobing, or immersion (12). Evaluating films applied directly on the food surface raises severe thickness and homogeneity control problems (e.g., the presence of breaks or pinholes). For hydrocolloid films, this poor integrity may be related to the greater potential for premature immobilization of the polymer chains in sprayed films than in self-supporting films. Furthermore, hypotheses proposed for hydrocolloid films remain difficult to apply to to lipid films. Poor film integrity, mainly due to the roughness of food surfaces, drastically decreases barrier performance. For example, Greener and Fennema (13,14) found that the permeability of a formed-in-place wax layer on a brownie surface was about fourfold greater than that of the same type of film formed on a smooth surface, probably because of small ruptures that occurred in the formed-in-place layer during application.

The barrier properties of edible lipid films are generally

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very sensitive to film thickness. Martin-Polo *et al.* (15) noted that the permeability of cellophane films coated with paraffin wax or oil increased with thickness. Debeaufort and Voilley (7) showed that permeability decreased exponentially when the thickness of the TG layer increased from 0 to 60 μm and remained constant for films of greater thicknesses. In chocolate, Biquet and Labuza (16) observed an increase in permeability at thicknesses between 0.9 and 1.2 mm. Landmann *et al.* (9) also found an increase in the permeability of cocoa butter to water vapor when the film thickness rose. In many cases, the microstructure of the film and discontinuities in it are the main explanations suggested for increases in permeability. Nonetheless, the influence of film thickness on moisture barrier properties has never been studied under industrial conditions. Our objective was to determine, through the use of a predictive model of moisture transfer, the effect of film thickness and the film-forming technique on the moisture barrier properties of AMG films used in real conditions at the interface between two food compartments of different a_w (water activities).

MATERIALS AND METHODS

Materials. The solution used for agar gel (AG) preparation was obtained by adding 3 g of agar powder to 97 g of water. The initial a_w of the gel was 0.999. To prepare AG of initial a_w of 0.950, 49 g of glucose syrup [dextrose equivalent = 67, moisture content = 12 g/100 g wet basis (w.b.); Chamtor, Bazincourt, France] were added to a mix of 48 g of water and 3 g of agar. A total of 0.4 g of sodium azide was added in each solution to limit microbial development in the gel. The cylindrical AG samples were prepared as described in previous studies (5) by pouring the warm liquid gel into a plastic tube (∅ = 2.5 cm and height = 2.5 cm) and storing it at 20°C and in a jar with controlled relative humidity (RH); the RH was adjusted to nearly 100% by using pure water or to 97.59% by using K_2SO_4.

Sponge cakes (SC) were prepared by the CTCPA (Auch, France) from a premix composed of sucrose (28.8 g/100 g w.b.), wheat flour (30.3 g/100 g w.b.), whole egg (29.3 g/100 g w.b.), salt (0.4 g/100 g w.b.), water (8.5 g/100 g w.b.), glycerol (2.4 g/100 g w.b.) and emulsifier (0.3 g/100 g w.b.) as described previously (5). The SC (∅ = 17 cm, thickness = 3.5 cm) were packaged in water-impermeable film and frozen at −18°C for long-term storage. Before the experiments, the cakes were slowly thawed at 4°C and kept for 7 d at 4°C to allow moisture redistribution through the staling phenomenon. Moisture content of the SC was 23.0 ± 2.0 g/100 g w.b. and SC a_w was 0.840.

The AMG used in this study was acetomonopalmitin (Danisco, Trappes, France), which was chosen from among four AMG as the film-forming material for its important moisture barrier properties and its low m.p., which allows relatively easy spraying (5). The AMG is based on a hydrogenated raw vegetable oil material and is characterized by a m.p. of 30°C, an acetylation degree of 70%, an acid value of 2, and a saponi-

fication value of approximately 340. The density of the AMG was equal to 890 ± 43 kg (mean ± SD) of dry matter per m^3 of bulk product. The AMG used is stable in its α-polymorphic form; it is translucent and displays good flexibility, and thus good film-forming properties.

Self-supporting films. The AMG material was melted at 50°C for 10 min to obtain an adequate application viscosity. The molten fatty material was then laminated using a film-making apparatus (Braive Instruments, Chécy, France) adjusted to various heights (0.3, 0.6, 0.7, and 1.0 mm height) to produce various film thicknesses (from 200 to 1500 μm) on a hot steel plate (50°C) that was previously covered with greaseproof paper sheets, and the sheets were then solidified at room temperature. Preformed lipid-based film disks of 25 mm in diameter were stamped out and removed from the greaseproof paper, and the disk thickness was measured at room temperature with a hand-held micrometer (Braive Instruments). AMG film disks were stored for 24 h at 20°C in a tightly closed jar in which a RH equal to 0.75% was adjusted by using a NaCl-saturated solution.

Application of films "in-place" on the SC surface. Sprayed films were applied on frozen SC without crust by using a spraying system. The spraying system (Legallais, Montferrier, France) was composed of a heated flask (50°C) containing the molten AMG material and was pressurized by using air at 1.2 bar to push the molten fatty material up to a pinhole. Before application, the fatty material was colored using oil red O (ICN Pharmaceuticals France S.A., Orsay, France) (1 g/100 g of fatty product). The molten AMG at 50°C was nebulized and sprayed onto the surface of the frozen SC for 10 s. The inlet air temperature was equal to the ambient temperature (20°C).

Cast films were formed on the frozen SC surface by applying the molten fatty material with a 3-cm-wide paintbrush. For both cast and sprayed film, the quantity of fatty material laid down on the sponge-cake surface was 0.445 ± 0.045 kg/m^2.

Following cooling, the formed-in-place films with SC were stored and kept for 7 days at 4°C to allow moisture redistribution through staling phenomenon, then kept for 2 days at 20°C before the experiment.

Thicknesses of the formed-in-placed films were evaluated using a light microscope with video output (Nikon; Microvision Instruments, Evry, France) to which a camera (CCD Kappa $^1/_2$", Microvision Instruments) was connected. Scans could be analyzed using Archimed Pro software (Microvision Instruments). The coated SC were frozen for easier cutting, and thin slices of SC covered with the colored AMG material were obtained using a razor blade. The thickness of the coating was measured using Archimed Pro software for image analysis.

Moisture migration experiments. Samples of SC with or without formed-in-place film were punched out (∅ = 2.5 cm and height = 2.5 cm) and placed in a close-fitting plastic tube. The SC cylinders with formed-in-place films were placed in direct contact with an AG compartment in a hermetically sealed glass diffusion cell (5). For the noncoated SC, precut

self-supporting films were placed between the SC and AG before introducing the SC into the diffusion cell. The diffusion cells were kept in a constant-temperature chamber (20 ± 0.1°C). Experimental humidity profiles were obtained at given times (1, 6, 22, and 30 d) by using an adapted microtome (Sercom, Montpellier, France) to slice the cylindrical components (the AG and the SC) into disks 2 mm thick and then by determining the moisture content of each slice (weighing before and after complete desiccation 24 h in a 103°C oven). The average of three replications of all experimental profiles at a 95% confidence interval represented experimental error. One set of profiles was carried out at 1, 6, 22, and 30 d for each film-forming technique and for each self-supporting film thickness with AG at an initial a_w of 0.999. One set of profiles was also carried out with AG at an initial a_w of 0.950 for AMG sprayed onto the SC. Since the film layers could not be sliced with our microtome, moisture profiles in the films were not determined.

Simulations. Moisture transfer simulations were performed using the model previously developed and validated using MATLAB® software (The Mathworks Inc., Natick, MA) for a three-compartment food system (5). Model parameters were identified for each compartment: thickness, initial a_w, initial moisture content, water sorption, diffusivity values, or diffusivity law as a function of moisture content and density. Initial parameters for the simulations were given previously for each food compartment (5).

Parameters were identified from the experimental moisture profile data by minimizing the sum of the squared error between the experimentally measured and predicted moisture content values using the Gauss–Newton algorithm (17). The root mean square error (RMSE) was used to estimate the quality of model fitting and was calculated as follows :

$$\text{RMSE} = \sqrt{\frac{(\hat{y} - y)^2}{(N - p)}} \qquad [1]$$

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

RESULTS AND DISCUSSION

Influence of film thickness on moisture barrier properties. The moisture barrier performance of AMG films of thicknesses ranging from 200 to 1500 μm in realistic commercial conditions were compared by measuring their moisture distribution profiles in a three-compartment system of AG/AMG/SC (Fig. 1). Because the formed-in-placed film thicknesses could not be rigorously controlled, the influence of film thickness on moisture barrier properties was investigated only for self-supporting films. As shown in Figure 1, for storage times longer than 6 d, the AMG film had an important effect in delaying moistening of the SC compared with the moisture content of
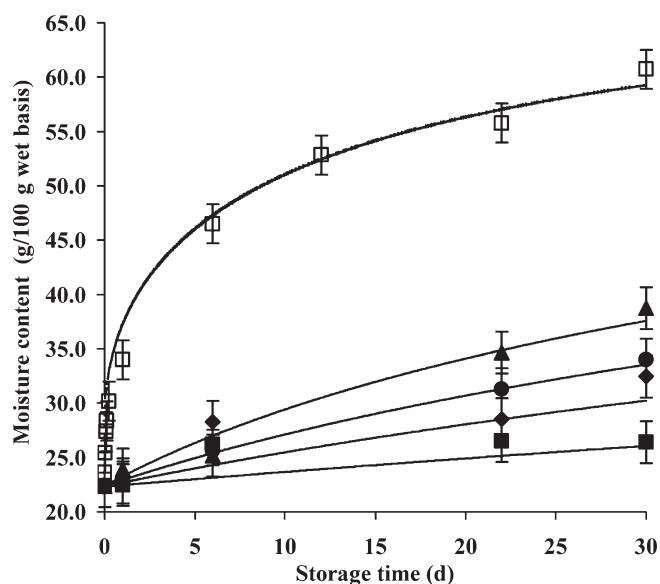
FIG. 1. Experimental (symbols) and predicted (curves) moisture content evolution with time at 20°C of sponge cake in direct contact with agar gel of initial water activity (a_w) of 0.999 (□); (from Ref. 5) or sponge cake separated from the same agar gel by a self-supporting film of 1544.0 μm (■), 797.8 μm (◆), 557.1 μm (●), or 200.0 μm (▲) thickness. Vertical bars represent experimental error.

the SC placed in direct contact with AG.

Moisture transfer in the AG/AMG/SC composite food was then modeled for each film thickness to assess the influence of film thickness on moisture barrier properties. The resulting evolution of predicted moisture content with time in the SC is shown in Figure 1 and is compared with the experimental results. The model successfully predicted the experimental data, with RMSE values varying from ±1.80 to ±2.31 g/100 g w.b. (Table 1), consistent with experimental error (±1.93 g/100 g for all the experiments). No major deviations in model accuracy were attributable to film thickness, indicating that barrier performance of the AMG self-supporting films was not influenced by variations in thickness. This is an important observation and one that was expected. Indeed, unlike the hydrocolloids, whose structure varies with moisture content, there is no reason for the barrier performance of lipid film to change with moisture content since their structure is not influenced by moisture.

Many investigators have described a reduction in moisture barrier performance with an increase in film thickness, such as in chocolate layers (9,16), in cellulose–paraffin wax films (15), and in acetostearin films (18). But in all these studies, moisture barrier performance was studied through permeability measurements. The dependence of permeability on film thickness has mainly been related to either a positive interaction between water and film material that is not taken into account in Fick's and Henry's laws (9,16,18), or to discontinuities in the film, which would be more important for thin films (15). In our study, by using the predictive model, deviations in barrier permeability with changes in film thickness could not have occurred since nonlinear evolutions of both solubil-

TABLE 1
Application Type, Measured and Identified Thickness and Diffusivity with Corresponding RMSE Values for Acetylated MG (AMG) Films in an Agar Gel (AG)/AMG/Sponge Cake (SC) System[a]

| Application type	Measured thickness (μm)	RMSE with measured thickness (g/100g w.b.)	Effective thickness (μm)	RMSE with effective thickness (g/100g w.b.)	Apparent diffusivity (m²/s)	RMSE with apparent diffusivity (g/100g w.b.)
Self-supporting film						
Exp. 1	200.0 (± 10.0)	1.90	212.6	1.80	2.1×10^{-11}	1.90
Exp. 2	557.1 (± 33.6)	1.88	532.5	1.87	2.1×10^{-11}	1.88
Exp. 3	797.8 (± 24.2)	2.31	575.3	1.45	2.1×10^{-11}	2.31
Exp. 4	1544.0 (± 50.0)	1.80	1688.1	1.76	2.1×10^{-11}	1.80
Sprayed film						
Exp. 1	500.0 (± 50.0)	18.80	24.9	1.90	46.1×10^{-11}	1.86
Exp. 2 (AG of 0.95 a_w)	500.0 (± 50.0)	12.30	24.9	2.80	46.1×10^{-11}	2.65
Cast film	500.0 (± 80.0)	20.00	12.5	2.96	47.5×10^{-11}	3.60

[a]Initial water activity (a_w) of the AG was 0.999. RMSE, root mean square error; w.b., wet basis; Exp., experiment.

ity and diffusivity with moisture content were taken into account to characterize moisture transfer through the film. Our result also indicated that the integrity of self-supporting films was not disturbed by a significant increase in film thickness, probably because of the low m.p. of the AMG studied (30°C), which conferred a high plasticity to the AMG film. The practical significance of this fact appears to be that control of moisture transfer between two compartments separated by an AMG film could be significantly retarded by a moderate increase in the thickness of the coating.

Influence of the film-forming technique on moisture barrier properties. The influence of the film-forming technique on moisture barrier properties was studied by measuring and modeling the moisture distribution profiles in an AG/AMG/SC system for sprayed, cast, and self-supporting films. The typical experimental moisture distribution profiles are given in Figure 2A for a 200-μm self-supporting film and

in Figure 2B for a 500-μm sprayed film. Unexpectedly, moisture transfer through the sprayed film was significantly higher than through the self-supporting film. Model predictions (black lines) are compared with experimental results in Figures 2A and 2B. For the sprayed film, a large deviation between the experimental and modeled curves was observed with high RMSE values (Table 1). The same large underprediction of the moisture contents in SC by the model was also noticed with the 500-μm cast film (Table 1). The tendency of the model to underpredict the moisture content in SC with formed-in-place films, one not observed with self-supporting films, could be directly correlated to film integrity.

The influence of film integrity on the moisture barrier performance of the AMG film was studied by evaluating its effect either on film thickness or on apparent diffusivity. An "effective" thickness and apparent diffusivity were successively identified by using the model and an optimization pro-
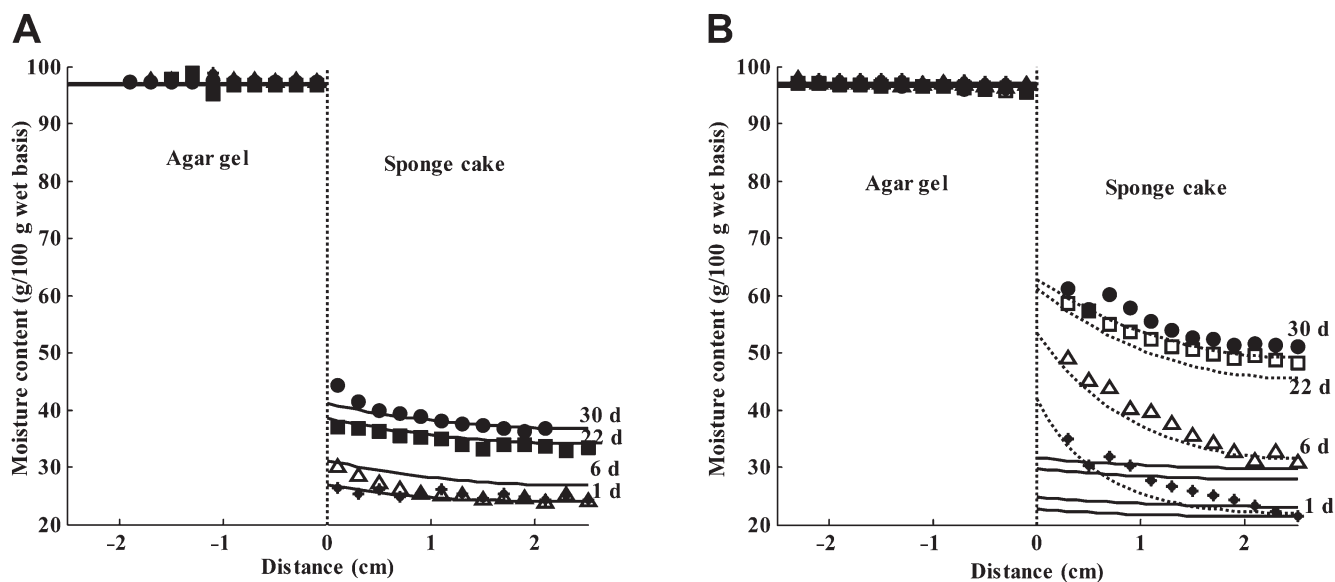
FIG. 2. Experimental (symbols) and predicted (curves) moisture distribution profiles at 20°C in a three-compartment food system (agar gel/acetylated MG/sponge cake) at 1, 6, 22, and 30 d of storage for (A) a 200-μm self-supporting film and (B) a 500-μm sprayed film. The dotted lines in panel 2B represent simulations that took into account a corrective factor for film integrity.
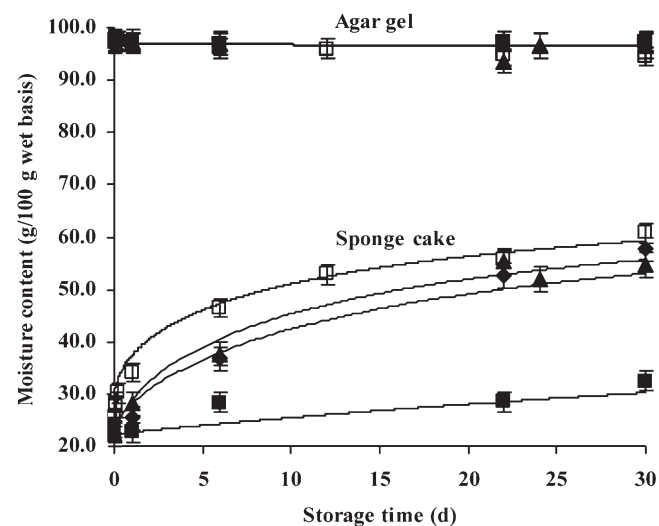
cedure. By this means, good fits of the experimental data for both sprayed (Fig. 2B, dotted lines) and cast films were obtained with RMSE lower than ±3.60 g/100 g w.b. (Table 1). Indirect estimations of film integrity were thus achieved. The thickness and diffusivity identified for sprayed films were then successfully validated in an independent experiment with AG of lower initial a_w (0.95). With RMSE for this validation of ± 2.65 (Table 1), the model proved to be a relevant tool for characterizing the reduction in moisture barrier performance of sprayed films in variable initial conditions.

The film-forming technique strongly influenced film integrity, as evaluated through an effective thickness and apparent diffusivity, respectively, that were largely lower and higher than the initial values. Whatever the thickness of the self-supporting films, no significant modifications of effective thickness and apparent diffusivity were observed after the identification procedure, confirming the previous result that film integrity was not disrupted by an increase in thickness.

As shown in Figure 3, the barrier performance of films of the same thickness formed by different techniques were compared by observing the predicted and experimental evolution of SC moisture content with time. For formed-in-place films, the SC moisture contents could not be significantly distinguished by the film-forming technique used and were very close to the SC moisture content obtained without any coatings. This result confirms the close similarity in very low barrier properties of sprayed and cast films of same thickness. At 30 d of storage, the barrier performance of sprayed and cast films in an AG/AMG/SC system were respectively 41 and 44% lower than the performance of self-supporting films of the same thickness as determined by SC moisture content (Fig. 3). The magnitude of this difference vividly demonstrated how much more difficult it was to achieve excellent barrier properties in a film formed on an irregular food surface than it was in a self-supporting film formed on a hard, smooth surface. The AMG may partially solidify into small particles during atomization before being laid on the rough SC surface, yielding a discontinuous association of fat crystal agglomerates. This may enhance moisture transfer through the film in spite of the substantial thickness of the fatty material (500.0 μm). Similar results were encountered by Greener and Fennema (13,14), who noticed that the permeability properties of a formed-in-place beeswax–methylcellulose film, sprayed onto brownies, were about fourfold greater than those of the same type of film applied on a smooth, flat surface.

In commercial practice, where spraying would be the best means of applying a fatty layer on cereal products, the barrier performance of formed-in-place films would probably be better than that indicated in this study. The poor performance we experienced may have been caused (i) by the high a_w (0.999) imposed on the film at the AG–AMG film interface, which would probably not be encountered in a commercial filling, and (ii) by the particularly high porosity of the SC. We should also note that industrial spraying was applied in the extreme conditions of the laboratory testing scale, and the film-forming techniques would probably be better controlled on an industrial or semi-industrial scale. This study also highlights the importance of predictive models for characterizing barrier performance of both formed-in-place and self-supporting films in real conditions. This was the only valuable approach, since the affinity of the films to water was taken into account in the model. The relatively low barrier efficiency of the sprayed film suggests the need to pretreat porous food surfaces on which fatty material is applied. Pretreatments such as toasting, surface chemical modifications, or depositing a smooth, thin layer of film on the food surface might improve the integrity of the sprayed film.

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FIG. 3. Experimental (symbols) and predicted (curves) moisture content evolution with time at 20°C of both sponge cake and agar gel with an initial a_w of 0.999, either in direct contact (□, from Ref. 5) or separated by a 557.1-μm self-supporting film (■), a 500.0 μm sprayed film (▲), or a 500.0-μm cast film (◆). Vertical bars represent experimental error.

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