Food and Bioproducts Processing 110 (2018) 16–25

Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Water adsorption and rheological properties of full-fat and low-fat cocoa-based confectionery coatings

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ARTICLE INFO

Article history:
Received 9 August 2017
Received in revised form 17 April 2018
Accepted 23 April 2018
Available online 30 April 2018

Key-words:
Fat replacer
Edible films
Adsorption isotherms
Rheology
Sensory analysis
Film thickness

ABSTRACT

Growth in consumer demand for healthier and/or reduced calorie foods often brings with it the requirement to match the performance of existing products. Cocoa-based coatings are widely used in food manufacturing and low-fat formulations need to meet performance targets in terms of water adsorption (for storage), rheology (for coating), and taste. Low-fat coatings containing 3, 6 or 9% w/w vegetable oil or microparticulate whey protein as fat replacer were studied alongside a full-fat fluid as control. Equilibrium moisture contents of dried films were measured at 25 °C and gave similar adsorption behaviour which could be modelled using the Guggenheim–Anderson–de Boer model. The fat replacer increased the viscosity of the coating fluids and all the formulations exhibited Quemada model behaviour, so that the thickness of layers obtained by dip coating could be predicted by a previously reported mechanistic mathematical model. The model gave good agreement with measured layer thicknesses, indicating that the model could be used to optimise a coating film. One full-fat and one low-fat formulation with identical coating capacities were subjected to sensory analysis testing by untrained consumers and the low-fat product was found to be acceptable.

1. Introduction

Cocoa beans are regularly processed into chocolate and cocoa products. The separation of cocoa butter from cocoa solids results in a defatted cocoa powder that can be dissolved easily in water and other liquids. Cocoa powder is used for flavouring biscuits, cakes, snacks, ice-creams, dairy products, and beverages and in the manufacture of coatings for frozen desserts and confectionery products (Afoakwa, 2014). Cocoa-based confectionery coatings enhance the food aspect, giving texture, gloss, and cocoa (or chocolate-like) flavour (Stauffer, 1996). The formulations usually include other ingredients such as sweetening agents (sucrose, corn syrup, etc.) and a lipid phase, with cocoa butter, shortenings, and fluid vegetable oils being the most popular. Non-tempering vegetable fats and oils offer several advantages in comparison to cocoa butter, such as simpler and lower cost manufacturing, good heat stability, and gloss retention (Mohos, 2017).

Although vegetable-origin lipids have several nutritional benefits in the human diet (non-cholesterol and essential fatty acid contents), they increase the energy content of foods. The calorific content of fats (9 kcal g^{-1}) is greater than other food components, such as carbohydrates and proteins (4 kcal g^{-1}). In addition, fat-rich or full-fat foods are associated with pleasant sensations and they are highly regarded organoleptically, promoting their consumption (Tan, 2014). The intake of large amounts of full-fat foods is associated with weight and obesity problems and their negative health consequences (FAO, 2003). This has prompted the production of foods with reduced energy content and high quality. The manufacture of low-fat products using fat replacers is one strategy for this (Sandrou and Arvanitoyannis, 2000). A large variety

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https://doi.org/10.1016/j.fbp.2018.04.005
0960-3085/

Nomenclature

$a_{i,exp}$	experimental value (Eq. (6))
$a_{i,theor}$	theoretical value (Eq. (6))
A	total area available for coating (Eq. (3)) [m^2]
C	constant of Eq. (1) [–]
EPP	mean percentage error (Eq. (6))
$F_1(\alpha; \beta, \gamma; \delta; z_1, z_2)$	Appell hypergeometric function of the first kind of Eq. (4)
g	gravity acceleration (Eq. (5)) [$m\,s^{-2}$]
h	film thickness at the x position of the plate (Eq. (4)) [m]
$\langle h \rangle$	theoretical average film thickness of Eq. (4) [m]
$\langle h \rangle_{exp}$	experimental average film thickness (Eq. (3)) [m]
K	constant of Eq. (1) [–]
N	total number of samples (Eq. (6))
p	constant of Eq. (2) [–]
t	draining time [s]
w	film weight (Eq. (3)) [kg]
x	film length on the plate (Eq. (5)) [m]
X	equilibrium moisture content of Eq. (1) [$kg\,kg^{-1}$]
X_m	monolayer moisture content of Eq. (1) [$kg\,kg^{-1}$]
Z	function represented by $Z = (x/\dot{\gamma}_c h t)^p / \left[1 + (x/\dot{\gamma}_c h t)^p\right]$ (Eq. (4)) [–]

Greek symbols

$\dot{\gamma}$	shear rate of Eq. (2) [–]
$\dot{\gamma}_c$	characteristic shear rate of Eq. (2) [s^{-1}]
η	steady shear viscosity of Eq. (2) [Pa s]
η_c	constant defined by $\eta_c = 1 - (\eta_\infty/\eta_0)^{-1/2}$ (Eq. (4)) [–]
η_∞	limiting steady shear viscosity when $\dot{\gamma}/\dot{\gamma}_c \to \infty$ of Eq. (2) [Pa s]
η_0	limiting steady shear viscosity when $\dot{\gamma}/\dot{\gamma}_c \to 0$ of Eq. (2) [Pa s]
ρ	density [$kg\,m^{-3}$]

of fat replacers has been developed, such as products based on modified proteins or carbohydrates that mimic some of the organoleptic and physical properties of conventional fats (O'Connor and O'Brien, 2011). Low-fat confectionery glaze materials, elaborated with microparticulated whey proteins as a fat replacer, were recently studied by Meza et al. (2016).

Several technological problems are associated with the reduction or replacement of fat in confectionery coatings. The response of coated confectionery foods to storage conditions (temperature and humidity) determines their quality and shelf-life. Coatings have the potential to protect the core food, but variations in temperature and humidity will influence the moisture content and/or water activity of the coating (Ghosh et al., 2005; Galus and Kadzinska, 2015). For example, at water activities higher than 0.6 or 0.7, bacterial, yeast and/or mould growth are expected (Rizvi, 2014). In addition, texture, colour, and gloss capacity can be altered by water adsorption or condensation over the confectionery film (Mohos, 2017). The presence of fats will influence the food water adsorption capacity, due to their hydrophobic or non-polar nature. Fat mimetics are generally polar water-soluble compounds that facilitate water binding and can alter the hygroscopicity and water adsorption properties of the product (O'Connor and O'Brien, 2011).

Sorption isotherms represent the relationship between the equilibrium moisture content and the water activity of a material at a constant temperature (Rizvi, 2014). Coated confectionery products, like sweet biscuits, usually take the form of dried products. For this reason, the study of adsorption isotherms of full-fat and low-fat coatings is important for establishing suitable preserving methods and optimal storage conditions.

The film thickness obtained by coating techniques is strongly affected by the rheological behaviour of the fluid (Sullivan and Middleman, 1986; Andersson et al., 1996; Snoeijer et al., 2008). Since the rheological properties influence the coating deposition characteristics (such as film thickness, levelling capacity, and homogeneity), measurement and evaluation of these properties is necessary for optimal operation and processing design. The rheological behaviour of a film-forming fluid will be influenced by changes in its fat content and nature. For example, Ghorbel et al. (2011) reported that a reduction in fat content produced an increase in the apparent viscosity and the Casson yield stress of chocolate-based formulations used for ice-cream coating. Similarly, Meza et al. (2016) found that replacement of fat by a fat replacer affected the rheological properties of sugar-based confectionery coatings. They showed that the values of dynamic yield stress and consistency index (obtained by fitting the Herschel-Bulkley equation) were higher in formulations with microparticulated whey protein used as a fat replacer compared to samples with sunflower vegetable oil.

The type and content of fat used for confectionery coating will determine organoleptic aspects, such as the lubrication and palate-clearing properties of coated baked products (Gomez, 2008). Some fat replacers cannot imitate the flavour-carrying capacity of fat (O'Connor and O'Brien, 2011). As result, the use of fat replacers in the development of new low-fat products can lead to less favourable sensory evaluation results (Gomez, 2008). Sensory analysis involves quantifying, interpreting, and analysing the human response to food during ingestion, which is a complex process involving all five senses (Lawless and Heymann, 2010). It is not currently possible to predict the outcome of the sensory analysis directly from coating's physical properties, so sensory evaluation needs to be included as part of a development programme.

Although cocoa-based coatings are extensively used in the bakery and confectionery industries, studies of sorption properties of the dried films and the rheological behaviour of the cocoa-based coating formulations containing fat replacers have not been reported in the literature. This information can be used to control and predict the film thickness during an industrial confectionery coating process and the shelf life at different conditions (temperature and humidity). The main objective of this work was to study the water adsorption and rheological behaviour of full-fat and low-fat cocoa-based confectionery coating formulations. Samples were prepared with vegetable oil or a whey protein-based fat replacer. Rheological data were obtained and the average film thickness at different conditions estimated using an analytical mathematical model presented by Peralta and Meza (2016). The predictions were compared with experimental measurements of films obtained by dip coating. In addition, two selected formulations with identical coating capacity but different composition (one full-fat and the other low-fat) were tested by untrained panellists in order to evaluate the consumer acceptability thought sensory analysis.

2. Materials and methods

2.1. Materials

The main ingredient used to formulate the confectionery coatings was defatted cocoa powder (Joaquin Cutchet e Hijos S.R.L., Santa Fe, Argentina). The composition supplied by the manufacturer was: 11.7% w/w fat and 2.1% w/w moisture. Protein content was calculated from the total nitrogen content determined by the Kjeldahl method (2 replicates), using a Buchi 430 automatic digester, a distillation unit (Buchi 322, Flawil, Switzerland), and an automatic titrator (Mettler DL40RC, Mettler Instrumente AG, Greifensee, Switzerland). The total protein content, calculated using 6.25 as correction, was 25.4 ± 0.6% w/w. The ash content (8.9 ± 2.0% w/w) was determined in duplicate by burning in a muffle oven at 560 °C for 12 h. The total carbohydrate content, determined by difference, was 52.0% w/w. The mean particle size (±standard deviation) of the cocoa powder was 7.6 ± 4.2 μm, which agrees with values in the literature for similar materials (Mongia and Ziegler, 2000). Mean particle size was estimated using optical microscopy (Allen, 1997). A transmitted polarized light microscope was used (Olympus BH-2, Tokyo, Japan), equipped with a digital camera and capturing software Olympus Studio 2 Version 2.11 (Olympus Imaging Corp., Tokyo, Japan). A few drops of a suspension of 20% cocoa powder in distilled water were placed onto glass slides and covered with a slip. Photomicrographs were obtained at 40× magnification and analysed using the image analysis software ImageJ 1.51w (National Institute of Health, USA).

Skimmed milk powder (SanCor Coop. Unidas Ltda., Santa Fe, Argentina) was used, with composition supplied by the manufacturer as: 50% w/w carbohydrate, 35.0% w/w protein, 1.5% w/w fat, and 4.0% w/w moisture. Glazing sugar (Borgato y Pirola S.R.L., Santa Fe, Argentina) and sunflower oil (Aceitera General Deheza S.A., Córdoba, Argentina) were obtained from local markets.

Microparticulated whey protein powder (MWP) (Simplesse Dry100, CPKelco US Inc., Atlanta, GA) was used as a fat replacer. The composition provided by the manufacturer was: 52.9% w/w protein, 4.8% w/w fat, and 2.9% w/w moisture. The ash content (8.7 ± 0.9% w/w) was determined in duplicate by burning in a muffle oven at 560 °C for 12 h. The total carbohydrate content, determined by difference, was 30.7% w/w. The mean particle size (±standard deviation) of the MWP supplied by the manufacturer was 1.2 ± 0.3 μm.

Soy lecithin in the liquid state (Yeruti S.R.L., Santa Fe, Argentina) was used as vegetable oil emulsifier, food-grade glycerin (Cirse S.R.L., Buenos Aires, Argentina) was used as plasticizer, and potassium sorbate (Cicarelli, Reagents S.A., Santa Fe, Argentina) was included in each formulation (0.1% w/w) as a preservative.

2.2. Cocoa-based confectionery coatings

Cocoa-based confectionery coatings were prepared as shown in Table 1, employing the methodology published by Meza et al. (2016) with modifications, taking into account the local legislation (CAA, 2010).

Table 1 – Full-fat and low-fat cocoa-based confectionery coating formulations recipe.

Code	Ingredient [% w/w]						
	Cocoa[a]	Milk[b]	Sugar[c]	Fat[d]	Whey[e]	Glycerin	Water
Control	20	15	10	0	0	1	54
Full-fat 3%	20	15	10	3	0	1	51
Full-fat 6%	20	15	10	6	0	1	48
Full-fat 9%	20	15	10	9	0	1	45
Low-fat 3%	20	15	10	0	3	1	51
Low-fat 6%	20	15	10	0	6	1	48
Low-fat 9%	20	15	10	0	9	1	45

[a] Cocoa: defatted cocoa powder.
[b] Milk: skimmed milk powder.
[c] Sugar: icing sugar.
[d] Fat = sunflower oil (2, 5, 8%) and soy lecithin (1%).
[e] Whey: microparticulated whey protein powder (fat replacer).

Samples with different fat contents were prepared by mixing the dry ingredients (cocoa, skimmed milk, icing sugar, and potassium sorbate) and wet ingredients (distilled water and glycerin) in a glass bowl (10 cm diameter) using a manual stainless steel blender (2 cm diameter) for 3 min. Samples were mixed manually to minimise the breaking of the microstructure and the incorporation of air bubbles. After that, liquid soy lecithin was dissolved in the vegetable oil and both ingredients were then incorporated into the mixture by hand using the same manual stainless steel blender for 3 min to give full-fat cocoa-based confectionery formulations with fat contents of 3, 6, and 9% w/w. The vegetable oil droplet sizes ranged from 0.1 to 47 μm. The mean value (±standard deviation) was 1.5 ± 4.1 μm, which agrees with values reported by Drapala et al. (2015). The fat content had negligible effect on the oil droplet sizes.

Low-fat formulations with different fat replacer loadings were prepared as above, but replacing the lipid-phase (vegetable oil and soy lecithin) by the appropriate amount of MWP (3, 6, and 9% w/w). Formulations without vegetable oil and MWP were prepared and used as control samples.

Each cocoa-based confectionery formulation was degassed at room temperature (~25 °C) for 15 min under vacuum (0.3 atm abs) to remove bubbles. Degassed samples were then placed in hermetic plastic containers with a plastic film over the surface to avoid crust formation and stored at 7 °C overnight before further analysis. The coating capacity of the fluid was confirmed by dip coating (see Section 2.6.2) (Fig. 1a). Samples were prepared in duplicate. They were stable, over the experimental time (24 h), judged by the absence of visual phase separation (sedimentation or creaming).

2.3. Dry cocoa-based confectionery films

A sample (10 g) of each cocoa-based confectionery formulation (Table 1) was placed on glass plates (10 cm diameter) and heated in a natural convection oven (60 °C and 20% humidity) for 20 h. This gave dry films with uniform thick-

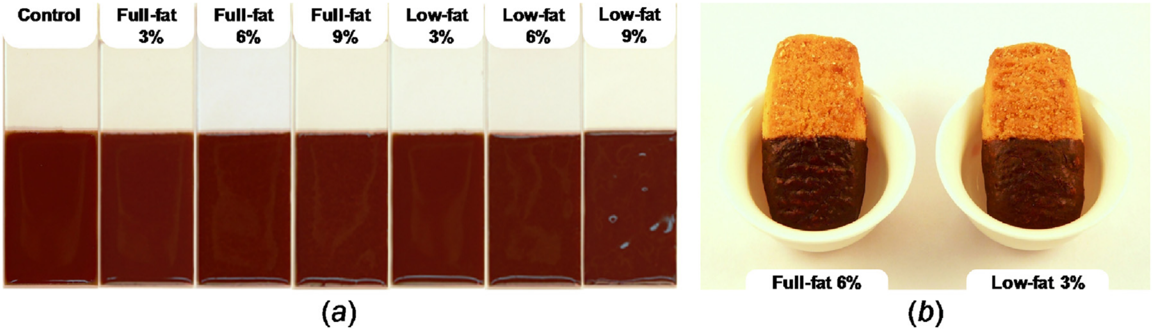

Fig. 1 – Full-fat and low-fat cocoa-based confectionery coatings obtained by dip-coating technique using (a) glass plates as substrate and (b) commercial sweet biscuits.

Table 2 – Water activity (a_w) at 25 °C of selected saturated salt solutions.

Salt	a_w	Source
Potassium acetate ($KC_2H_3O_2$)	0.225	Greenspan (1977)
Magnesium chloride ($MgCl_2$)	0.330	Pollio et al. (1996)
Potassium carbonate (K_2CO_3)	0.432	Greenspan (1977)
Magnesium nitrate (MgN_2O_6)	0.529	Greenspan (1977)
Cobalt chloride ($CoCl_2$)	0.633	Pollio et al. (1996)
Sodium chloride (NaCl)	0.751	Pollio et al. (1996)
Potassium chloride (KCl)	0.842	Pollio et al. (1996)
Potassium nitrate (KNO_3)	0.927	Pollio et al. (1996)

nesses (1.0–1.5 mm) which were then cut into small pieces (50 × 50 mm) and stored in hermetic plastic containers at room temperature (~25 °C) for 24 h before further analysis.

2.4. Water adsorption isotherms

The adsorption isotherms at 25 °C were determined using the static-gravimetric method widely reported in the literature (Bradley, 2010; Rizvi, 2014). Pairs of representative samples (1.5 g) of each dry cocoa-based confectionery film were picked randomly and placed in sealed glass jars containing eight selected saturated salt solutions with water activities (a_w) ranging from 0.225 to 0.927 (Table 2). Potassium acetate and magnesium nitrate (both analytical grade) were obtained from Anedra (Research Ag S.A., Buenos Aires, Argentina). Magnesium chloride, potassium carbonate, cobalt chloride, sodium chloride, potassium chloride, and potassium nitrate were all obtained as analytical grade from Cicarelli (Reagents S.A, Santa Fe, Argentina). Pairs of glass jars were placed in a controlled temperature cabinet (25.0 ± 0.7 °C) for 5 weeks to ensure the samples reached equilibrium (expressed as constant weight gain). After that, the equilibrium moisture content, calculated on a dry basis (kg water/kg dry solids), was determined gravimetrically in quadruplicate by drying samples in an oven at 100 ± 2 °C for 3 h (Marth, 1978; Bradley, 2010). The initial moisture content of the cocoa-based confectionery films was $0.056 \pm 0.012\,\mathrm{kg\,kg^{-1}}$.

The experimental data were fitted to the multilayer adsorption isotherm model proposed by Guggenheim–Anderson–de Boer (GAB) (van den Berg, 1981):

$$X = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{1}$$

where X is the equilibrium moisture content of the sample expressed on a dry basis. X_m is the monolayer value, which is a measure of the availability of active sites for water sorption by the material, C is the Guggenheim constant, which quantifies the strength of water binding to the primary binding sites, and K is the corrective constant that accounts for properties of multilayer molecules with respect to the bulk liquid (van den Berg, 1981).

The GAB model was selected due to its versatility. It is considered a further refinement of the Langmuir and BET theories of physical adsorption (Langmuir, 1918; Brunauer et al., 1938) that introduces a second sorption stage of sorbate molecules. The GAB model simplifies to the BET equation when K is equal to 1 (Rizvi, 2014). It is widely used to fit experimental data for food materials (van den Berg, 1981; Lewicki, 1997; Timmermann et al., 2001; Horta de Oliveira et al., 2011) and edible films (Kim and Ustunol, 2001; Srinivasa et al., 2007; Shih et al., 2011).

2.5. Rheological behaviour

Rheological measurements were made at 25.0 ± 0.5 °C using a Brookfield DV3TLVCP rheometer with cone and plate geometry CPA-52Z (3° angle and 24 mm diameter) at set rotational speeds (Brookfield Engineering Laboratories Inc., MA). The temperature was maintained constant by a thermostated bath with recirculation (LKB 2219 Multitemp II, Bromme, Sweden). Rotational rheometry was carried out at shear rates ranging from 0.1 to 50.0 $\mathrm{s^{-1}}$. Some samples exhibited flow problems at high shear rates and non-reproducible data could be obtained. Values of steady state apparent viscosity as function of shear rate were determined for each formulation in quadruplicate. Differences of less than 5% among four replicates were obtained for all formulations.

The data were fitted to the four-parameter rheological model proposed by Quemada (1998):

$$\eta = \eta_\infty \left[\frac{1 + (\dot{\gamma}/\dot{\gamma}_c)^p}{(\eta_\infty/\eta_0)^{1/2} + (\dot{\gamma}/\dot{\gamma}_c)^p} \right]^2 \tag{2}$$

Here η is the steady shear viscosity, $\dot{\gamma}$ is the shear rate, $\dot{\gamma}_c$ is the characteristic shear rate, η_∞ is the limiting steady state viscosity when $\dot{\gamma}/\dot{\gamma}_c \to \infty$, η_0 is the limiting steady state viscosity when $\dot{\gamma}/\dot{\gamma}_c \to 0$, and p is a dimensionless coefficient. Quemada (1998) developed this model according to a structural approach for mono-dispersed suspensions, where dispersions of structural units are based on the concept of the effective volume fraction that depends on flow conditions. This model was selected because coating formulations and other fluids used for industrial applications (paints, foods, and cosmetics) have rheological properties under steady and unsteady conditions that can be described approximately as concentrated dispersions of structural units (Quemada, 1998).

2.6. Film thickness

2.6.1. Density measurements

The density of the cocoa-based confectionery coatings was determined at 25 °C gravimetrically (5 replicates) by weighing a plastic container with known volume (2.31 $\mathrm{cm^3}$) containing an aliquot of each sample (Meza et al., 2015). The mean values and standard deviations are shown in Table 3.

2.6.2. Experimental film thickness

Experimental average film thickness values were determined by quintuplicate using the dip-coating technique described by Meza et al. (2015). Glass plates (75 mm height, 25 mm width, and 1 mm thick) stored at room temperature (~25 °C) were used as substrates. They were submerged to 20 or 40 mm depth for 10 s by hand in a plastic vessel containing the coating for-

Table 3 – Density (mean values and standard deviation of five replicates) of full-fat and low-fat cocoa-based confectionery coatings.

Sample	ρ [$\mathrm{kg\,m^{-3}}$]
Control	1153 ± 9
Full-fat 3%	1125 ± 23
Full-fat 6%	1072 ± 10
Full-fat 9%	1043 ± 20
Low-fat 3%	1055 ± 31
Low-fat 6%	1061 ± 28
Low-fat 9%	1115 ± 12

mulation at 25 °C. Each substrate was then withdrawn quickly, held upright over the vessel to drain for 30 s, and placed in hermetically sealed containers to prevent water vaporization. The experimental average film thickness ($\langle h\rangle_{\text{exp}}$) was determined from (Bhattacharya and Patel, 2007):

$$\langle h\rangle_{\text{exp}} = \frac{w}{\rho A} \tag{3}$$

where w is the film weight, ρ is the film density (Table 3), and A is the total area available for coating (in this study, 10.4 and 20.8 cm^2). Values of w were determined by difference between the substrate weight before and after dipping.

2.6.3. *Theoretical film thickness*

The theoretical average film thickness values were calculated using the model proposed by Peralta and Meza (2016) for a dip-coating draining stage of a vertical plate using a fluid that can be described by the Quemada model (Eq. (2)):

$$\frac{\langle h\rangle}{h} = 1 - \frac{(1-\eta_c Z)^4}{3(1-Z)^{-3/p}}\left[\frac{6\eta_c p Z}{(3+p)} F_1\left(\tfrac{3}{p}+1;\tfrac{3}{p},5;\tfrac{3}{p}+2;Z,\eta_c Z\right)\right.$$
$$\left. + F_1\left(\tfrac{3}{p};\tfrac{3}{p}+1,4;\tfrac{3}{p}+1;Z,\eta_c Z\right)\right] \tag{4}$$

$$h^{p+1} - \left(\frac{\eta_0}{\rho g}\frac{x}{t}\right)^{1/2} h^p + \frac{1}{\dot{\gamma}_c^p}\left(\frac{\eta_0}{\eta_\infty}\right)^{1/2}\left(\frac{x}{t}\right)^p h$$
$$- \frac{1}{\dot{\gamma}_c^p}\left(\frac{\eta_0}{\rho g}\frac{x}{t}\right)^{1/2}\left(\frac{x}{t}\right)^p = 0 \tag{5}$$

where $\langle h\rangle$ is the theoretical average film thickness, x is the film length on the plate, h is the local film thickness at x, g is the gravity acceleration, $F_1(\alpha;\beta,\gamma;\delta;z_1,z_2)$ is the Appell hypergeometric function of the first kind, η_c is defined by $\eta_c = 1-(\eta_\infty/\eta_0)^{-1/2}$, Z is a function represented by $Z = (x/\dot{\gamma}_c ht)^p/\left[1+(x/\dot{\gamma}_c ht)^p\right]$, and t is the draining time. Values of $\langle h\rangle$ were calculated using the fitted parameters of the Quemada model (Eq. (2)) presented in Table 5 and the values of ρ, presented in Table 3.

2.7. *Sensory analysis*

Two cocoa-based confectionery formulations (Full-fat 6% and Low-fat 3%) were selected to perform an acceptability test based on their similar coating capacity (Section 3.3). They were prepared as shown in Table 1, but using tap water and without potassium sorbate. Commercial sweet biscuits (Tía Maruca S.A., Buenos Aires, Argentina) were used as the substrate. The composition supplied by the manufacturer was: 65.0% w/w carbohydrate, 6.9% w/w proteins, and 22.0% w/w fat.

Biscuits (220 units) were selected with fewer imperfections and rectangular-like shape (60 mm height, 30 mm width, and 5 mm middle thick). Full-fat 6% (250 g) and Low-fat 3% (250 g) formulations were placed in plastic containers and kept at room temperature (~25 °C) for 2 h. Each biscuit was coated using a dip-coating technique consisting of immersing half of the biscuit height (30 mm) for 10 s into the fluid and then withdrawing it, draining the excess off the coating fluid for 30 s. Each biscuit picked up approximately 2 g (1.9–2.1 g) of cocoa-based fluid after dipping.

Coated biscuits were placed horizontally on a plate previously covered with a plastic film. They were dried using a hot air dryer for 5 min (GA.MA, Arimex S.A., Buenos Aires, Argentina) and then, stored overnight at 5–7 °C in hermetically sealed containers for further analysis.

Acceptability testing (Kemp et al., 2009) was carried out at room temperature (~25 °C) by 105 inexperienced panellists without any training (*i.e.* consumers). The coated biscuits were offered to the panellists in randomly coded containers (Fig. 1b) and they were invited to taste samples without any restriction (it is usual to expect that some consumers will taste the full biscuit and other ones only the coated part). Each panellist was asked to rate the samples for acceptance and to indicate which sample was the most preferred (paired-preference test). A 9-point hedonic scale was used, with 1 = dislike extremely, 2 = dislike very much, 3 = dislike moderately, 4 = dislike slightly, 5 = neither like nor dislike, 6 = like slightly, 7 = like moderately, 8 = like very much, and 9 = like extremely (Lawless and Heymann, 2010).

2.8. *Statistical analysis*

One way analysis of variance (ANOVA) was used in the statistical analysis of the mean values of $\langle h\rangle_{\text{exp}}$. When the effect of the factors was significant ($p < 0.05$), the Tukey's honestly significant difference multiple rank test was applied with a confidence level of 95%. A non-parametric test (Kruskal–Wallis) was used for statistical analysis of the median values of consumer acceptance levels (9-point hedonic scale). In addition, a paired-preference test was used for sensory analysis, applying the Chi-square test with a confidence level of 95% and one degree of freedom.

Non-linear regression was used to obtain the parameters of GAB and Quemada models (Eqs. (1) and (2), respectively). The goodness of fit of the GAB model to the equilibrium moisture contents as function of water activity was evaluated based on the mean percentage error (*EPP*):

$$EPP = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{a_{i,\exp} - a_{i,theor}}{a_{i,\exp}}\right| \tag{6}$$

where N is the number of samples, $a_{i,exp}$ is the experimental value, and $a_{i,theor}$ is the value predicted by the model. The goodness of fit of the rheological data to the Quemada model (Eq. (2)) and the prediction error of Eq. (4) compared to the $\langle h\rangle_{\text{exp}}$ were evaluated using *EPP*. Statistical analysis was performed using Minitab 13.20 software package (Minitab Inc., State College, PA, USA).

3. Results and discussion

3.1. *Water adsorption isotherms*

Adsorption isotherms obtained for full-fat and low-fat cocoa-based confectionery coatings are shown in Fig. 2. The shape of each isotherm corresponds to a type II behaviour, according to the five-types of adsorption isotherms or BET classification (Khalfaoui et al., 2003). A type II isotherm that usually represents the sorption phenomena in biological materials, is sigmoidal in shape (Al-Muhtaseb et al., 2002; Yanniotis and Blahovec, 2009).

The values of the estimated GAB parameters and fitting errors are shown in Table 4. According to the literature, for a type II isotherm, C and K values are constrained to the range $0 < K \le 1$ and $C > 2$ (Blahovec, 2004). Information about mechanisms of sorption can be deduced from the combination of K

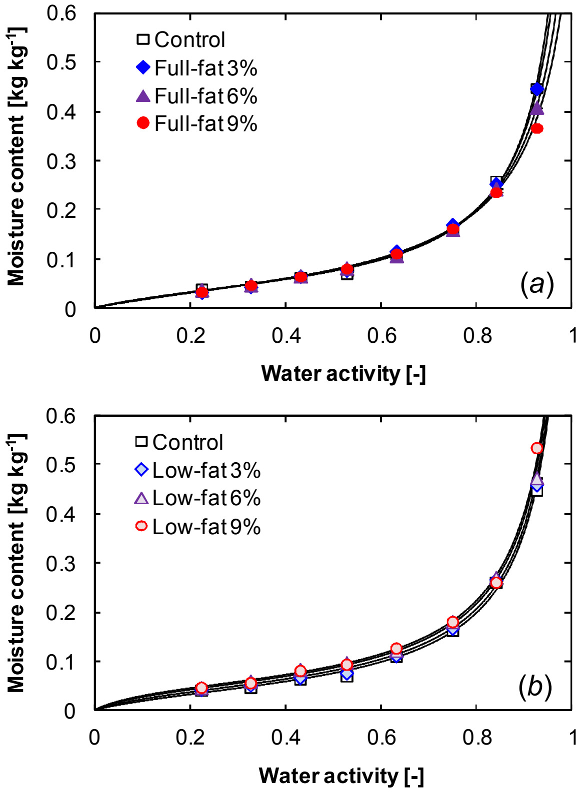

Fig. 2 – Adsorption isotherms at 25 °C of full-fat and low-fat cocoa-based confectionery coatings. Symbols and vertical bars are mean values and standard deviation of four replicates. Lines represent the GAB model (Eq. (1)).

Table 4 – Estimated GAB parameters (Eq. (1)) for full-fat and low-fat cocoa-based confectionery coatings.

Sample	X_m [kg kg^{-1}]	C [–]	K [–]	EPP [%]
Control	0.046	5.027	0.972	5.85
Full-fat 3%	0.049	4.507	0.962	4.60
Full-fat 6%	0.052	4.101	0.947	2.28
Full-fat 9%	0.054	3.624	0.933	1.49
Low-fat 3%	0.048	6.455	0.972	4.39
Low-fat 6%	0.050	8.316	0.972	3.63
Low-fat 9%	0.051	9.560	0.972	3.98

and C values (Quirijns et al., 2005). In this work, high values of C are accompanied by values of K approaching 1 (Table 4), indicating that multilayer molecules have properties comparable with those of bulk liquid molecules. Following the framework proposed by Quirijns et al. (2005), the sorption of both full-fat and low-fat formulations studied here is apparently characterized by a monolayer of water molecules, which are strongly bound to the material. The subsequent water molecules are not or slightly structured in a multilayer, but they have characteristics comparable with the molecules of the bulk liquid.

The values of C for low-fat formulations were higher than values obtained for full-fat and control samples (Table 4). In addition, the C values increase as the fat substitute content increases in low-fat formulations and decrease as the fat content increases in full-fat samples. As explained above, the numerical value of parameter C can be considered as a measure of the strength of water binding to the primary binding sites in the material. The larger C is, the stronger water is bound in the monolayer (van den Berg, 1981; Quirijns et al., 2005). It could be assumed that the lipid phase present in formulations with film-forming capacity reduces the hygroscopicity and increase moisture barrier properties of coatings (Bourlieu et al., 2006). In addition, it is known that water molecules are strongly bound to hydrophilic biopolymers like proteins and polysaccharides (Yanniotis and Blahovec, 2009). The use of protein-based fat replacers, like microparticulated whey proteins that are polar water-soluble compounds, could facilitate water binding and the tendency to increase sorption ability (O'Connor and O'Brien, 2011).

The values of X_m for all the full-fat and low-fat cocoa-based formulations lie in the narrow range of 0.046–0.054 kg kg^{-1}, indicating that the availability of active sites for water absorption by the formulations is not noticeably affected by fat or fat substitute content. Those values are of similar magnitudes to X_m obtained by the GAB model for sorption isotherms at 25 °C of cocoa-based and chocolate-based products (Sandoval and Barreiro, 2002; Medeiros et al., 2006). The monolayer value is often reported to represent the moisture content at which water attached to each polar and ionic group starts to behave as a liquid-like phase, corresponding with the optimal moisture content to ensure physical and chemical stability of dehydrated and low moisture foods (Rizvi, 2014).

The relatively low *EPP* obtained values (<6%) indicate good accuracy, suggesting that GAB model is a suitable and useful model for predicting the equilibrium moisture content of the full-fat and low-fat formulations in a wide range of water activities (Fig. 2). Coatings have the potential to protect the core food, but variations in temperature and humidity will influence the moisture content or water activity of the coating (Ghosh et al., 2005; Galus and Kadzinska, 2015). For this reason, the results obtained in this work related to the adsorption isotherms modelling can be useful for establishing suitable preserving methods and optimal storage conditions at room temperature for full-fat cocoa-based coated products (like sweet biscuits) and alternative low-fat formulations.

3.2. *Rheological behaviour*

Examples of steady state viscosity as a function of shear rate for full-fat and low-fat cocoa-based confectionery coatings are shown in Fig. 3. Shear-thinning behaviour is observed over the experimental range of shear rate in all samples, indicating a disruption of the sample structure by the shear field (Rao, 2014).

The estimated Quemada parameters and fitting errors are summarised in Table 5. For simplicity, the p parameter was set at 0.43 for all samples. This value, in the range of 0.5, provides a Casson-type behaviour to Eq. (2) near the zone where $\dot{\gamma} \to \dot{\gamma}_c$ (i.e. $\eta_\infty \ll \eta_0$) (Peralta and Meza, 2016), consistent with the modelling of cocoa suspensions viscosity (De Graef et al., 2011).

η_0 values ranged from 0.41 Pa s for the control to 1130 Pa s for the Low-fat 9% sample. In general, as the concentration of

Table 5 – Estimated Quemada parameters (Eq. (2)) for full-fat and low-fat cocoa-based confectionery coatings.

Sample	η_0 [Pa s]	η_∞ [Pa s]	$\dot{\gamma}_c$ [s^{-1}]	p [–]	EPP [%]
Control	0.41	0.06	96.1	0.43	6.31
Full-fat 3%	7.71	0.06	227	0.43	10.80
Full-fat 6%	15.0	0.09	454	0.43	5.32
Full-fat 9%	21.3	0.12	535	0.43	1.78
Low-fat 3%	21.5	0.41	40.0	0.43	0.85
Low-fat 6%	144	3.12	2.76	0.43	3.75
Low-fat 9%	1130	5.29	1.15	0.43	4.59

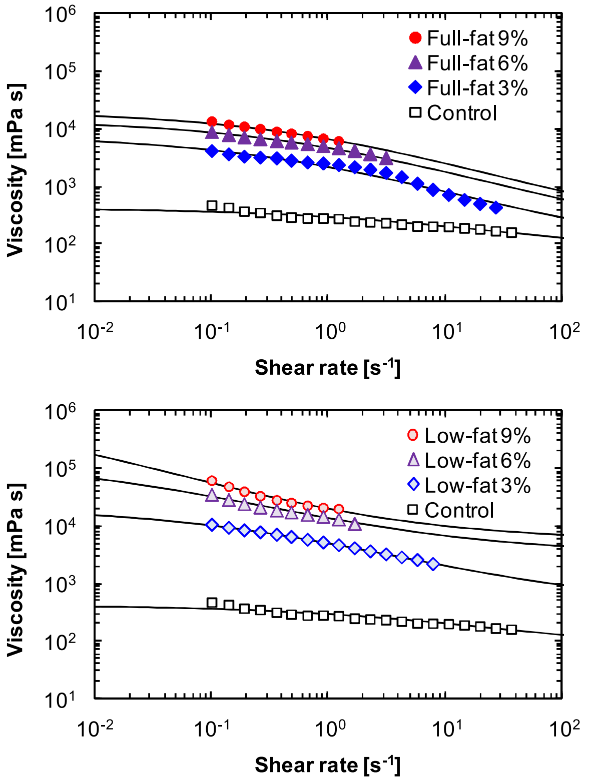

Fig. 3 – Steady shear viscosity as function of shear rate at 25 °C of full-fat and low-fat cocoa-based confectionery coatings. Symbols are experimental values (one of four replicates) and lines represent the Quemada model (Eq. (2)).

fat and fat replacer increased, the suspensions became more viscous at low values of shear rate. This enhancement was more pronounced in the samples with fat replacer. An addition of fat replaces water from the suspension (*i.e.* addition of a more viscous component), resulting in an increase in overall viscosity (Fang et al., 1995). Also, an addition of MWP introduces an agent that produces inter-particle interactions, resulting in an increase in viscosity (Zhang et al., 2016). The relative value of η_0 in non-Newtonian liquid formulations with film-forming capacity can be considered as a feature, especially when is high enough to help preventing gravity defects during coating (*i.e.* sagging), but is sufficiently low to allow film levelling (Kheshgi, 1997; Peressini et al., 2003).

The values of η_∞ ranged from 0.06 Pa s for the control to 5.29 Pa s for the Low-fat 9% sample. Addition of fat or fat replacer increased the viscosity of the suspensions at high shear rate. The comments on η_0 apply to η_∞ (Fang et al., 1995; Chung et al., 2014; Zhang et al., 2016).

Finally, the parameter $\dot{\gamma}_c$ was found to lie in the range of 1.15 s^{-1} (for Low-fat 9%) to 535 s^{-1} (for Full-fat 9%). On one hand, an increment in the fat content produced an $\dot{\gamma}_c$ increment. This could be explained taking into account that $\dot{\gamma}_c \propto a^{-3}$, where a is the mean particle size of the suspension (Peralta and Meza, 2016). The value of a may be lowered by the addition of smaller particles into the suspension (oil droplets) compared to the cocoa powder particles. On the other hand, an addition of MWP would produce an aggregation effect that increases the value of a in low-fat formulations, giving a decrease in $\dot{\gamma}_c$ (Zhang et al., 2016). This aggregation effect was not observed among oil droplets in full-fat formulations.

The relatively low *EPP* obtained values (<11%) indicate acceptable accuracy, suggesting that the Quemada model can be used to estimate the steady state viscosity data of full-fat and low-fat formulations in wide range of shear rates (Fig. 3).

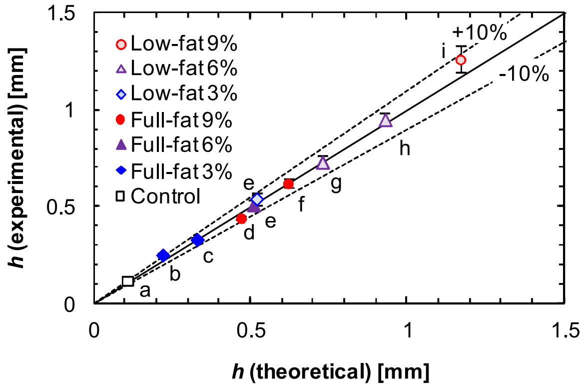

Fig. 4 – Experimental and theoretical average film thickness values at 25 °C for full-fat and low-fat cocoa-based confectionery coatings. Bars are standard deviations and dashed lines represent ±10% error. Means with different letter are significantly different (p<0.05).

3.3. *Average film thickness*

The experimental and theoretical average film thickness values are compared in Fig. 4. Significant differences are evident between the experimental values ($p < 0.05$); the film thickness increases as the fat and fat replacer contents increase. However, there is not a significant difference between $\langle h \rangle_{\text{exp}}$ values for Full-fat 6% and Low-fat 3% samples ($p > 0.05$), suggesting that both formulations have the same coating capacity.

There is a satisfactory agreement between the experimental data and the theoretical predictions with errors lower than 10%. Similarly, good agreement was reported by Peralta and Meza (2016) using the same analytical model. Based on these results, Eqs. (4) and (5) can be used to predict average film thickness values of cocoa-based confectionery coating formulations with good accuracy, decreasing the requirement to perform experimental assays for this purpose.

3.4. *Sensory analysis*

A histogram showing the consumer preference distribution of sweet biscuits coated with two selected cocoa-based confectionery formulations is presented in Fig. 5. Both samples were evaluated with a prevalence of positive preference scores.

The quantification of consumer acceptability was analysed using the 9-point hedonic scale and no significant differences were obtained in the acceptance level of both sweet biscuits coated with Full-fat 6% and Low-fat 3% formulations ($p > 0.05$). In addition, the paired preference test was used to evaluate which sample was the most preferred. No significant differences were observed in the preference level of both sweet biscuits coated with Full-fat 6% and Low-fat 3% formulations ($p > 0.05$). These results are in agreement with other sensory analysis results obtained for sweet desserts (ice-creams) containing whey proteins as a fat replacer (Prindiville et al., 2000). Chung et al. (2014) evaluated the effect of microparticulated whey protein as a fat replacer on the sensory characteristics of mayonnaise. They showed that, although a reduction in fat content had a negative influence on some sensory attributes of low-fat mayonnaise, the use of MWP as fat replacer did not affect the consumer preference.

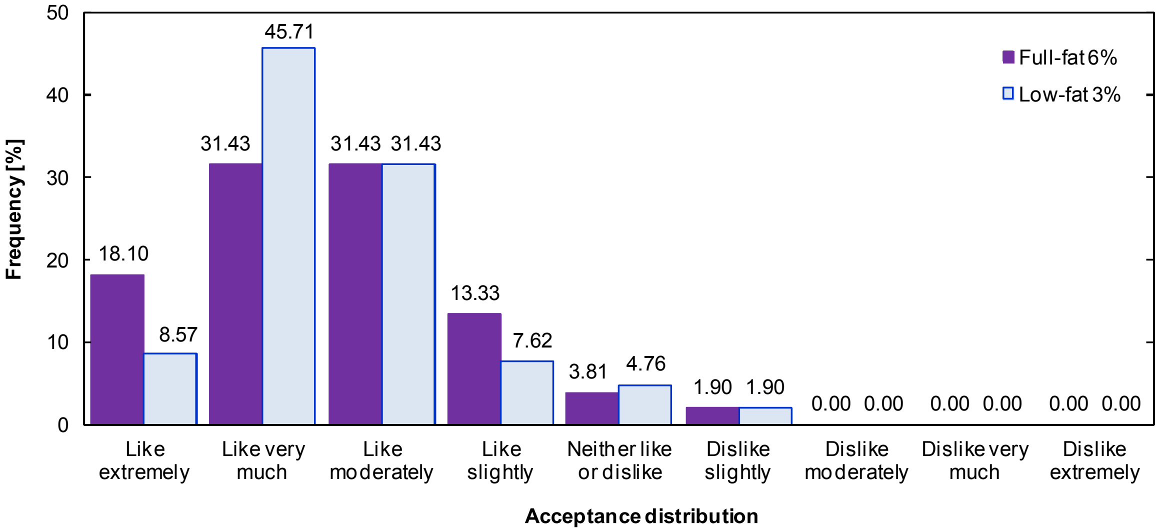

Fig. 5 – Histogram of consumer acceptance distribution (9-point hedonic scale) of sweet biscuits coated with Full-fat 6% and Low-fat 3% cocoa-based confectionery formulations. Numbers over each bar indicate mean values.

Full-fat 6% and Low-fat 3% formulations used to coat sweet commercial biscuits were accepted with high positive scores by a significant portion of the population of untrained panellists. In addition, the same acceptance level was obtained for both samples. These results indicate that alternative low-fat cocoa-based confectionery formulations could be used as substitutes of their full-fat counterparts, opening opportunities for further marketing studies.

4. Conclusions

A characterisation of full-fat and low-fat cocoa-based formulations used for confectionery coating was performed. The water adsorption behaviour of the formulations was studied through adsorption isotherms at 25 °C which showed a type II behaviour. The equilibrium moisture contents were described well by the GAB model. In practice, this model can be used to predict the equilibrium moisture content of the full-fat and low-fat formulations in a wide range of water activities. These results may help with the shelf-life control of the coatings in storing conditions at room temperature. The rheology of the samples was studied and the Quemada model was used to fit the experimental data. A good fit over an extended range of shear rates was obtained. In addition, the film capacity of the formulations was studied through experimental and theoretical film thickness values. The model predicted average film thicknesses that agreed well with the experimental data. Finally, a sensory analysis was performed using commercial sweet biscuits and two formulations with identical coating capacities (Full-fat 6% and Low-fat 3%). Tasting by untrained panellists indicated good consumer acceptability. This study showed that alternative low-fat cocoa-based confectionery coatings, prepared with a whey protein-based fat replacer, can provide attractive options for new products in the food coating industry.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This research was supported partially by Consejo Nacional de Investigaciones Científicas y Técnicas (Project PIP 2015-2017 11220150100185) (CONICET, Argentina), Universidad Nacional del Litoral (Projects CAI + D 501 201101 00031 LI, 501 201101 00088 LI, and 504 201501 00002 LI; Beca de Iniciación a la Investigación para estudiantes de las carreras de grado, Res. CS 570/15) (Santa Fe, Argentina), and Agencia Nacional de Promoción Científica y Tecnológica (Projects PICT 2011-182, 2012-1413 and 2015-365) (Argentina). This work is part of the Trabajo Final de Licenciatura en Nutrición of Angela D. Carboni (Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral, Santa Fe, Argentina).

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