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Effect of drying temperature and beeswax content on moisture isotherms of whey protein emulsion film

M. Soazo[a], A.C. Rubiolo[a], R.A.Verdini[b]*

a Instituto de Desarrollo Tecnológico para la Industria Química (INTEC, UNL- CONICET), Universidad Nacional del Litoral, Güemes 3450, (3000) Santa Fe, Argentina.
b Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario (UNR) & Instituto de Química Rosario (IQUIR, UNR-CONICET), Suipacha 531, (2000) Rosario, Argentina.

Abstract

The objective of this investigation was to study the effect of drying temperature and beeswax (BW) content on moisture sorption behavior of whey proteins emulsion films. For this purpose, films were obtained by the casting method and dried at two selected temperatures (5 and 25 ºC) and constant relative humidity (RH) (58%). After drying, films were removed from the casting plates and were conditioned in the environmental chamber set at 25 °C and 58% RH for 3 days. Subsequently, portions of 400 mg of film were placed in glass bottles and pre-dried in desiccators containing drierite (a_w=0) during 10 days. Then, the bottles were placed in hermetically sealed glass jars containing 10 different desiccants to achieve a_w ranging from 0.11 to 0.90, and allowed to reach equilibrium. The analyses were made in quintuplicate at 25 ºC. The equilibrium moisture content (EMC) was determined by drying samples in an oven and the experimental data were fitted by the Brunauer-Emmett-Teller (BET) and the Guggenheim-Anderson-De Boer (GAB) models. The results showed that both models were effective to describe the moisture sorption behavior of the films. The GAB model gave better fit than the BET model. The increase of the drying temperature of 5 to 25 ºC and the incorporation of lipids reduced the EMC of whey protein emulsion films. Finally, data from experimental sorption isotherms are a useful tool to predict the effect of the environmental conditions that surround the film on its properties; particularly considering that the stability of an edible film is function of its mechanical and moisture barrier properties and both are strongly influenced by the presence of water, film formulation and drying and storage conditions.

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Keywords: Whey protein emulsion films; drying temperature; sorption behavior

* Corresponding author. Tel.: +54-341-4372704; fax: +54-341-4372704.
E-mail address: verdini@iquir-conicet.gov.ar

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1. Introduction

Edible films and coatings have received great interest in recent years because they can extend the shelf life and improve the food quality by providing a barrier to mass transfer, carrying food ingredients and/or improving the mechanical integrity or handling characteristics of the food [1]. An edible film prevents texture decay particularly in fruits and vegetables, since water is essential for preservation of cell turgor [2].

Whey proteins have excellent nutritional and functional properties and the ability to form films; therefore they are a good constituent for the manufacture of edible coatings [3]. However, because of their hydrophilic nature, these coatings will absorb water from the surrounding media or from the food product. Several authors reported that physical and barrier properties of hydrophilic protein films can be significantly influenced by the moisture concentration in the film [4, 5]. Consequently, data from experimental sorption isotherms are a useful tool to predict the effect of the environmental conditions that surround the film on its properties; particularly considering that the stability of an edible film is function of its mechanical and moisture barrier properties and both are strongly influenced by the presence of water, which is related to film formulation and both drying and storage conditions. Accordingly, the objective of this investigation was to study the effect of drying temperature and beeswax (BW) content on moisture sorption behavior of whey proteins emulsion films.

2. Materials & Methods

2.1. Materials

Whey protein concentrate (WPC) 80% (Arla Food Ingredients S.A., Buenos Aires, Argentina), Beeswax (BW) (yellow, refined, Sigma-Aldrich), glycerol (Gly) (Cicarelli, Argentina), potassium sorbate (Anedra, Argentina) and Tween 80 (Anedra, Argentina).

2.2. Film formation

Aqueous solutions of 8% (w/w) WPC were plasticized with Gly and added with 0, 20 and 40% of BW [6]. Then, films were obtained by pipetting 8 g of the degassed solutions on 90 mm diameter disposable polyethylene Petri dishes. Films were dried on a leveled surface in an environmental chamber Tabai Comstar PR 4GM (Tabai Espec. Corp., Osaka, Japan) at two selected temperatures (5 and 25 °C) and constant relative humidity (RH) (58%). After drying, films were removed from the casting plates and were conditioned in the environmental chamber set at 25 °C and 58% RH for 3 days.

2.3. Moisture sorption isotherm

Film portions of 400 mg were placed in glass bottles previously weighted and were pre-dried in desiccators containing drierite (a_w=0) during 10 days. Then, the bottles were placed in hermetically sealed glass jars containing desiccants. Ten different humidity conditions were obtained using saturated salt solutions of LiCl, $KC_2H_3O_2$, $MgCl_2 \cdot 6H_2O$, K_2CO_3, $Mg(NO3)_2 \cdot 6H_2O$, NaBr, $SrCl \cdot 6H_2O$, NaCl, KCl and $BaCl_2 \cdot 2H_2O$ with an RH of 0.11, 0.22, 0.33, 0.43, 0.53, 0.58, 0.71, 0.75, 0.84, 0.90, respectively [7]. The film portions were allowed to reach equilibrium at 25 ºC in the relative humidity corresponding to each salt solution during 10 days. After that, glass bottles were weighted to obtain the sample weight at equilibrium and then they were dried at 105 ºC during 4 hours to obtain the weight of the dry sample. The analyses were made in quintuplicate. The equilibrium moisture content (EMC) was determined and the experimental data were fitted by the Brunauer-Emmett-Teller (BET) and the Guggenheim-Anderson-De Boer (GAB) models as followed:

BET model**:**

$$EMC=k_0k_1a_w/((1-a_w)(1-a_w+k_1a_w)) \quad (1)$$

where k_0 is the monolayer moisture content and k_1 is the surface heat constant .

GAB model:

$$EMC=m_0C\,ka_w/((1-ka_w)(1-ka_w+Cka_w)) \quad (2)$$

where m_0 is the monolayer moisture content, C is the surface heat of sorption of the first layer and k is a factor related to the total heat of sorption of the multilayer that improves the fit of the GAB model to a wider range of moisture contents than the BET model.

The parameters were calculated minimizing the error function using an algorithm written in Matlab [8].

2.4. Statistical analysis

A full factorial design was performed. Two factors were chosen as variables (drying temperature and BW content) and were tested at two (5 and 25 ºC) and three levels (0, 20 and 40% BW), respectively. Analysis of variance was used and when the effect of the factors was significant ($p < 0.05$), the test of multiple ranks honestly significant difference (HSD) of Tukey was applied (95% of confidence level) in each value of a_w. The statistical analysis was performed using Minitab 13.20 (Minitab Inc., State College, PA).

3. Results & Discussion

Experimental data and moisture sorption isotherm predicted by the BET and GAB models are shown in Figure 1. The increase in EMC with a_w was slow at low values of a_w for all the films. However, at $a_w \geq 0.58$ values of EMC of films rapidly increased. Such sigmoidal water sorption isotherms are characteristic of materials rich in hydrophilic polymers [9]. This behaviour of whey protein films was also observed by Fabra *et al.* [10].

Analyzing EMC values for each film formulation and drying condition at each a_w, we observed that the behaviour of the films with drying temperature was dependant on the BW content. In the case of films with 0 and 40% of BW, EMC at 5 °C was lower than at 25 °C; while in films with 20% of BW the effect was opposite. This behaviour shows an interaction between film formulation and drying temperature that result in different moisture sorption characteristics of whey protein edible films as film formulation and film forming conditions change. On the other hand, the addition of BW significantly decreased the EMC of the films. Interestingly, when drying was carried out at 5 ºC the lowest value of EMC obtained at all values of a_w corresponded to the formulation with 20% of BW. In films obtained at 25 ºC, for $0.11<a_w<0.58$ only a 40% of BW significantly decreased the EMC of the films, while for $a_w >0.58$, a decreasing tendency of EMC with the increase in the BW content was observed. The effect of the addition of BW on the EMC could be explained taking into account that the incorporation of lipids into the hydrocolloidal matrix of the films, in order to promote water vapor barrier, modifies the equilibrium water content-relative humidity relationships. A change in the overall hydrophobicity of the matrix as a consequence of the presence of more hydrophobic tails and the potential interactions among components can affect the total active points for water sorption [10].

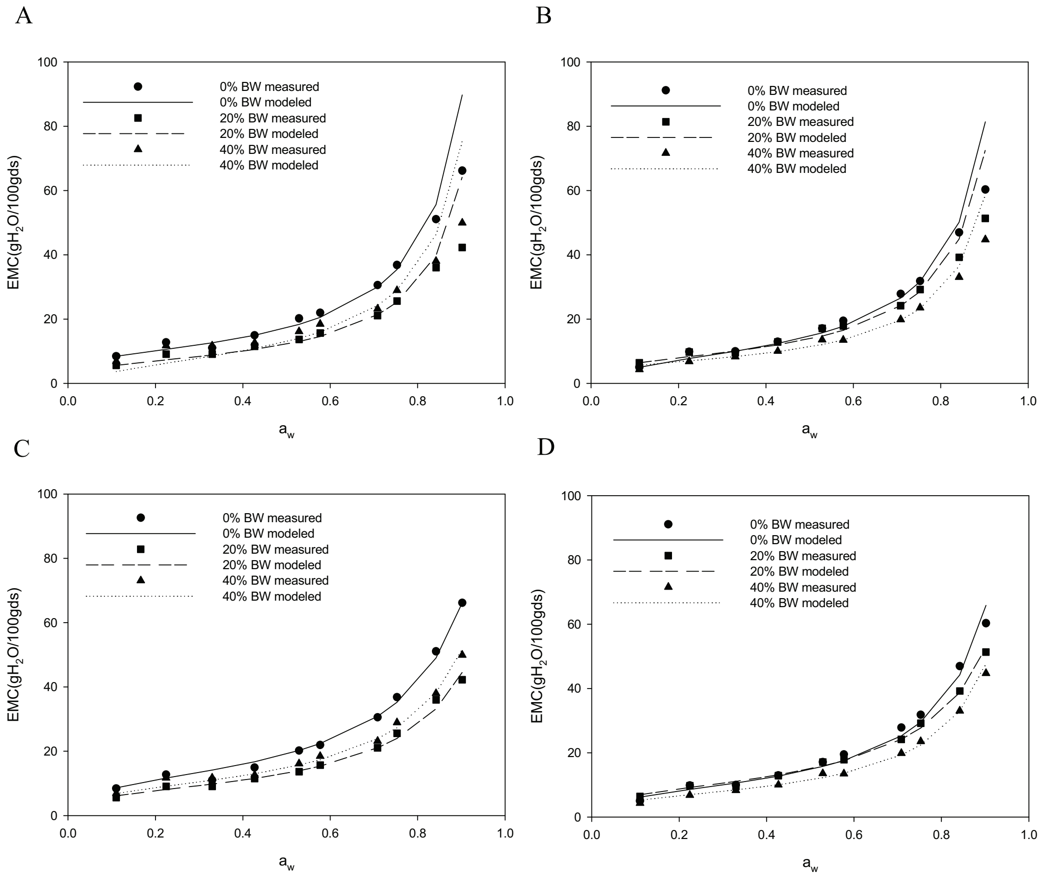

Fig.1. Measured and modeled values of EMC. A and B: EMC values of films dried at 5 ºC and 25 ºC, respectively, measured and predicted through fitting to BET model. C and D: EMC values of films dried at 5 ºC and 25 ºC, respectively, measured and predicted through fitting to GAB model.

Kim and Ustunol reported that the incorporation of lipids reduced the EMC of whey protein films plasticized with sorbitol and glycerol [11]. However, Zinoviadou et al. found that the addition of low concentrations of oregano oil to WPI films did not markedly affect the water content of the films [9].

Water sorption isotherms of edible films provide information of the driving potential for moisture migration from the food surface coated with edible films. Many models have been reported in the literature for estimating water activity through water sorption isotherms. In this investigation we fitted the experimental data of EMC to BET and GAB models because they are generally adequate for food systems. Table 1 shows the parameters obtained by fitting of the experimental data of EMC to BET and GAB models. As seen in table 1 and figure 1 both models were successful to describe the moisture sorption behaviour of the films (fitting error <0.1292). However, the GAB model gave better fit than the BET model especially at high values of aw. The GAB model usually gives better fit than BET but this is probably more due to the additional fitting parameter than any improved physical understanding of sorption [8].

In reference to the parameters calculated, the four parameters k0 and k1 in BET model and m0 and C in GAB model were dependent on drying temperature and film composition while k, in GAB model, was independent on both factors. The parameter k0 in BET model showed the same general trend that m0 in GAB model. This result was expected taking into account the similarity in the physical interpretation of these parameters. This result was in accordance with Coupland et al. [8]. The increase in drying temperature from 5 to 25 ºC decreased k0 and m0 parameters of films with 0 and 40% of BW and increased the k0 and m0 values of films with 20% of BW. In the case of k1, the effect of the increase in the drying temperature was a decrease in films with 0% of BW and an increase in those with 20 and 40% of BW. C parameter decreased in films with 0 and 40% of BW and increased in those with 20% of BW when drying temperature was increased from 5 to 25 ºC. In reference to the addition of BW, a tendency of decrease in k0 and m0 at both drying temperatures was observed. The parameters k1 and C showed an increasing tendency with the addition of BW at 25 ºC while at 5 ºC k1 decreased and C increased with de addition of BW.

Table 1. Parameters, coefficient of determination and error obtained by fitting of the experimental data of EMC of whey protein emulsion films to BET and GAB models.

	Film sample					
	5 ºC			25 ºC		
	0% BW	20% BW	40% BW	0% BW	20% BW	40% BW
BET model						
k_o	8.8254	6.3118	7.5294	8.0733	7.1316	5.7784
k_1	45.3268	29.9369	6.2285	9.9761	32.5994	53.3607
R^2	0.9649	0.9385	0.9698	0.9779	0.9591	0.9766
error[a]	0.0904	0.1060	0.1292	0.0719	0.1139	0.0598
GAB model						
m_0	10.7813	7.3951	8.2737	8.0160	8.3333	6.2270
C	22.3652	25.5188	25.6141	18.3299	25.6033	25.2034
k	0.9297	0.9261	0.9329	0.9748	0.9348	0.9651
R^2	0.9958	0.9869	0.9931	0.9910	0.9935	0.9949
error[a]	0.0516	0.0554	0.0543	0.0750	0.0580	0.0361

[a] It was calculated according to Coupland *et al.* [8].

4. Conclusion

Whey protein films showed to be sensitive to the environment humidity, particularly at high aw values. Accordingly, whey protein films in an environment of high humidity would absorb water and this fact could modify their properties. The increase in the drying temperature and the addition of BW could reduce this effect, which would be especially important considering the application of the films to protect fruits with high moisture content.

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