Vol. 18, No. 2 (2019) 487-500
Ingeniería de alimentos
Revista Mexicana de Ingeniería Química

SORPTION BEHAVIOR OF CITRIC PECTIN FILMS WITH GLYCEROL AND OLIVE OIL

COMPORTAMIENTO DE SORCIÓN DE PELÍCULAS DE PECTINA CÍTRICA CON GLICEROL Y ACEITE DE OLIVA

J.G. Hernández-Carrillo[1], H. Mújica-Paz[2], J. Welti-Chanes[2], A. S. Spatafora-Salazar[2], A. Valdez-Fragoso[2]*

[1] *División Multidisciplinaria de la Universidad Autónoma de Ciudad Juárez, Ciudad Universitaria; C. José de Jesús Macías Delgado 18100, Ciudad Juárez, Chih., México.*

[2] *Escuela de Ingenieria y Ciencias, Tecnologico de Monterrey; Av. Eugenio Garza Sada 2501 Sur, Monterrey, N.L. 64849, México.*

Received: March 18, 2018; Accepted: June 15, 2018

Abstract

The effect of glycerol and olive oil on water sorption isotherms of orange (FOP) and grapefruit (FGP) peel pectin films was studied. Additives decreased the equilibrium moisture content (X) and the extent of the observed hysteresis. Abrupt changes in the adsorption isotherms of the films were noted, and were very well correlated to one of the maxima of the second derivative of X as function of a_w. Converted adsorption data for GAB regression (a_w/X) generated curves with a sharp peak, linked to the isotherms inflection points. a_w/X vs a_w diagrams were valuable to identify order-to-disorder transitions in pectin films. Glycerol concentration reduced the critical water activity in FGP. GAB model described adsorption isotherms above the transition ($R^2 > 0.932$), and Halsey model exhibited a better fit ($R^2 > 0.984$). Desorption phenomena was better described by Peleg model ($R^2 > 0.959$).

Keywords: Citric pectin, edible films, sorption isotherms, glass transition, second derivative.

Resumen

Se estudió el efecto del glycerol y aceite de oliva en las isotermas de sorción de películas de pectina de cáscara de naranja (FOP) y toronja (FGP). Los aditivos disminuyeron la humedad de equilibrio (X) y el nivel de histéresis observado. Se observaron cambios bruscos en las isotermas de adsorción de las películas, los que se correlacionaron bien con uno de los máximos de la segunda derivada de X en función de a_w. Los datos convertidos para la regresión de GAB (a_w/X) generó curvas con un pico agudo, ligado a los puntos de inflexión de la isoterma. Los diagramas a_w/X vs a_w fueron muy valiosos para identificar transiciones orden-desorden en las películas de pectina. El glicerol redujo la actividad de agua crítica en los FGP. El modelo de GAB describió las isotermas de adsorción por arriba de la transición ($R^2 > 0.932$) y el modelo de Halsey mostró un mejor ajuste ($R^2 > 0.984$). Los fenómenos de desorción se describieron mejor por el modelo de Peleg ($R^2 > 0.959$).

Palabras clave: Pectina cítrica, películas comestibles, isotermas de sorción, transición vítrea, segunda derivada.

1 Introduction

Orange and grapefruit peels are pectin-rich by products of citrus processing industries. Pectin is a polysaccharide with gelling properties that has been investigated for the development of edible films and coatings (Pérez *et al*., 2013; Hernández-Carrillo *et al*., 2015). However, the properties of pectin films are strongly influenced by their water content and hydrophilic nature (Bertuzzi *et al*., 2007). Knowledge and modeling of the hygroscopic properties of biodegradable films is useful to predict the behavior of the films under different environmental conditions.

The hygroscopicity of food materials can be determined by the adsorption and desorption isotherms, which relate their moisture content and water activity (a_w) at a constant temperature and pressure (Pascual-Pineda *et al*., 2017).

---

* *Corresponding author. E-mail*: `avfva@yahoo.com`

https://doi.org/10.24275/uam/izt/dcbi/revmexingquim/2019v18n2/Hernandez
issn-e: 2395-8472

Very few studies have been reported about desorption, compared to adsorption of moisture of polysaccharide-based films (Al-Hassan and Norziah, 2012; Jagadish and Raj, 2011; Cheng *et al.*, 2008).

Sorption properties could be affected by the incorporation of additives in film formulation. Plasticizers are needed to overcome film brittleness by decreasing intermolecular interactions and increasing the mobility of biopolymer chains (Srinivasa *et al.*, 2007). Among plasticizers, glycerol has been widely used in edible film development, it decreases the equilibrium water content at intermediate and low a_w values by reduction of available sites for water adsorption (Talja *et al.*, 2007).

The high water affinity of hygroscopic films can be reduced by dispersing lipids in the filmogenic solution, since lipids decrease the number of active sites for water adsorption (Pereda *et al.*, 2012; Fabra *et al.*, 2010). Liquid oils at room temperature are suitable for mixing with filmogenic solutions (Ghanbarzadeh and Almasi, 2011). Some essential oils and fatty acids have been added to biopolymer films (Sánchez-González *et al.*, 2011; Ghanbarzadeh and Almasi, 2011; Fabra *et al.*, 2010), as well as olive oil, which is rich in fatty acids, tocopherols and phenolic compounds (Ballus *et al.*, 2014; Pereda *et al.*, 2012; Ma *et al.*, 2012). Thus, besides modifying the water barrier properties, olive oil would impart an antioxidant activity to the films.

The objective of this work was to determine the effect of glycerol and olive oil concentration on water adsorption and desorption isotherms of edible films formulated with unpurified pectin extracts from orange and grapefruit peels.

2 Materials and methods

2.1 Raw material

Oranges (Citrus sinensis var. March) and grapefruits (Citrus paradisi var. Doble rojo) free of wax coatings or colorants were obtained from Distribuidora Mexicana de Cítricos, S. R. L de C. V (Montemorelos, N.L. México). Citrus fruits were washed with tap water, cut in half and squeezed. Then, the pulp was removed manually from citrus peels and the peels were stored in sealed plastic bags at -18 ºC for further use in the experiments.

Table 1. Additive concentrations in orange and grapefruit film samples.

Sample number	Glycerol (g/100 g)	Olive oil (μL/100g)
1	0	0
2	1.25	0
3	0	250
4	1.25	250
5	0.625	125

2.2 Films preparation

After thawing in the refrigerator, grapefruit or orange peels were blended (Osterizer, 450-10, Miami, FL, USA) in a peel to aqueous ethanol solution (15%, v/v) ratio of 1 to 10 (w/w). The pH of the obtained purees was adjusted to 1.5 with 1M HCl and immediately afterwards, the pectin extraction was performed during 30 min in a heating plate at 90 ºC under continuous stirring. The extracts were filtered, and the obtained filtrates were heated at 70 ºC until 12.5 °Brix were reached. Glycerol and olive oil were added to selected concentrated solutions, at 0.625 or 1.25% (w/w) and 125 or 250 μL of olive oil per 100 g, respectively (Table 1). Films without any additives are labeled as sample 1 and were taken as the controls. Ten milliliters of film forming solutions were casted on Petri dishes and were left to dry at room temperature (23.5 ± 1.25 ºC) for 36 h in order to obtain the films.

2.3 Sorption isotherms of films

The adsorption and desorption isotherms of the films were obtained in a vapor sorption analyzer (AquaLab VSA, Decagon Devices, USA) at 25 ºC by a dynamic dewpoint isotherm method. Disc-shaped samples (3 cm diameter) were placed in desiccators with silica gel at ambient temperature for at least two weeks to reduce a_w of the samples. Four discs of each sample (100-200 mg) were used for isotherms determinations in duplicate. The VSA was programmed to obtain the adsorption isotherm from a_w of 0.120 to 0.920, and then the desorption isotherm from 0.920 to 0.120, using an air flow rate of 100 mL/min. The equilibrium moisture content of samples was calculated by the VSA Downloader 1.0.967 software (Decagon Devices, USA) using the initial moisture content and the samples weight at the recorded a_w. The initial moisture content of the films was determined gravimetrically in triplicate (105 ºC, 24 h).

Table 2. Mathematic models used to describe moisture sorption isotherms^a.

Model	Equation	
GAB	$X = \frac{X_0 C K a_w}{(1-K z_w)(1-K a_w + C K a_w)}$	Eq. (1)
GAB as second order function	$\frac{a_w}{X} = \frac{1}{X_0 C K} + \frac{C-2}{(X_0 C)} a_w - \frac{K(C-1)}{X_0 C} a_w^2$	Eq. (2)
BET	$X = \frac{X_0 C a_w}{(1-a_w)(1-a_w + C \cdot a_w)}$	Eq. (3)
Linearized BET	$\frac{a_w}{X(1-a_w)} = \frac{1}{X_0 C} - \frac{C-1}{X_0 C} a_w$	Eq. (4)
Peleg	$X = k_1 a_w^{n_1} + K_2 a_w^{n_2}$	Eq (5)
Hasley	$X = \left(- \frac{C}{\ln a_w} \right)^{1/n}$	Eq (6)

X and X_0 are the equilibrium and monolayer moisture content (g H_2O/ 100 g dry solids) respectively; C and K are dimensionless parameters related to heat of sorption of the monolayer and multilayer region; k_1, k_2, n_1 and n_2 are dimensionless parameters; C and n in Halsey are dimensionless parameters.

2.4 *Mathematical modeling of water sorption isotherms*

Two theoretical and two empirical isotherm models were tested to model the experimental equilibrium sorption data (Table 2). GAB parameters were calculated from the constants of the second order polynomial regression of converted sorption data (a_w/X) using Eq. 2 (Table 2). BET parameters were determined from the linear form of Eq. 4 (Table 2). The determination coefficient (R^2) and the mean relative percentage deviation modulus (E) were used to evaluate the goodness of fit of each model (Pavón García *et al*., 2015),

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{|X_e - X_p|}{X_e} \qquad (1)$$

where X_e and X_p are the experimental and predicted moisture content (g H_2O/g dry solids), respectively, and N is the total number of experimental data. An E value below 10% is considered a good fit.

3 Results and discussion

The films obtained from orange and grapefruit peel were flexible, transparent, yellow colored, and with a characteristic aroma of citrus (Fig. 1).

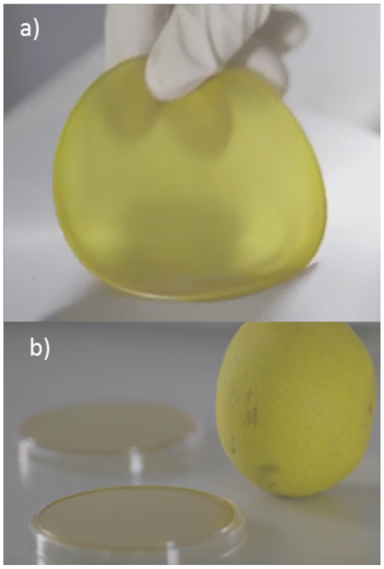

Fig. 1. Films from a) orange and b) grapefruit peel.

3.1 *Sorption isotherms*

The obtained moisture sorption isotherms of orange and grapefruit pectin films at 25 ºC are shown in Fig. 2 and Fig. 3, respectively. These isotherms follow an S-shaped behavior, corresponding to type II isotherms (Brunauer *et al*., 1940), which is characteristic of amorphous and soluble materials rich in hydrophilic compounds, such as pectin (Suppakul *et al*., 2013; Gorrasi and Bugatti, 2016).

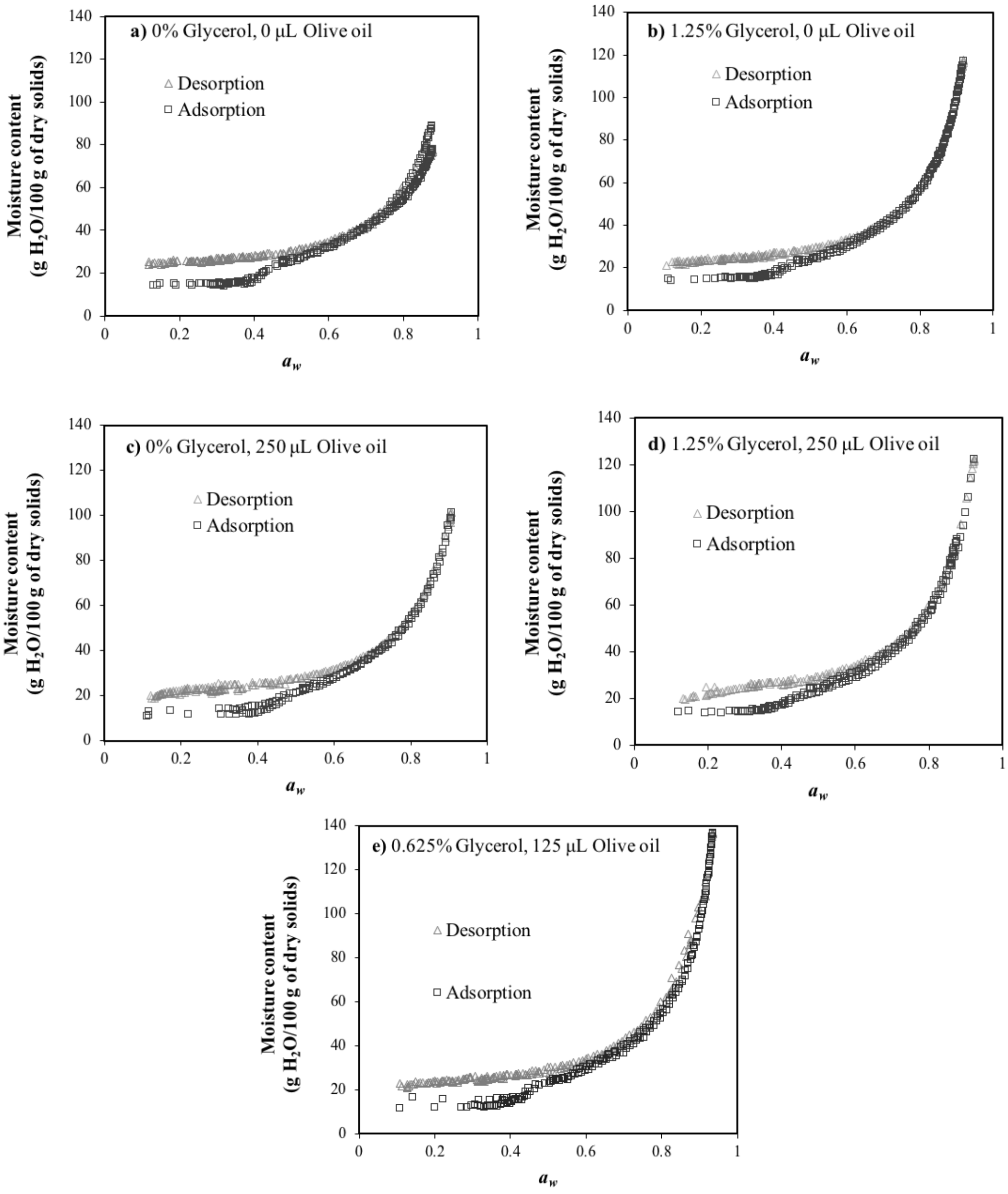

Fig. 2. Moisture adsorption () and desorption () isotherms at 25 ºC of orange pectin films (FOP) with different concentrations of glycerol and olive oil.

In general, pectin films from orange peel (FOP) had lower equilibrium moisture content (X) than films from grapefruit peel (FGP). It seems that the extracted compounds (pectin, sugars, phenolic, etc.) and the levels in each crude extract play an important role in the intensity of the molecular interactions. Differences in galacturonic acid content, molecular weight and monosaccharide composition of the pectin extracted from orange and grapefruit peel probably influence the sorption behavior (Kaya *et al*., 2014).

High equilibrium water contents are achieved in control FOP (~ 90 g H_2O/100 g dry solid) and FGP (~ 180 g H_2O/100 g dry solid) during adsorption (Fig. 2a and 3a). At this point, water present in the films would behave as bulk water (Al-Muhtaseb *et al*., 2002).

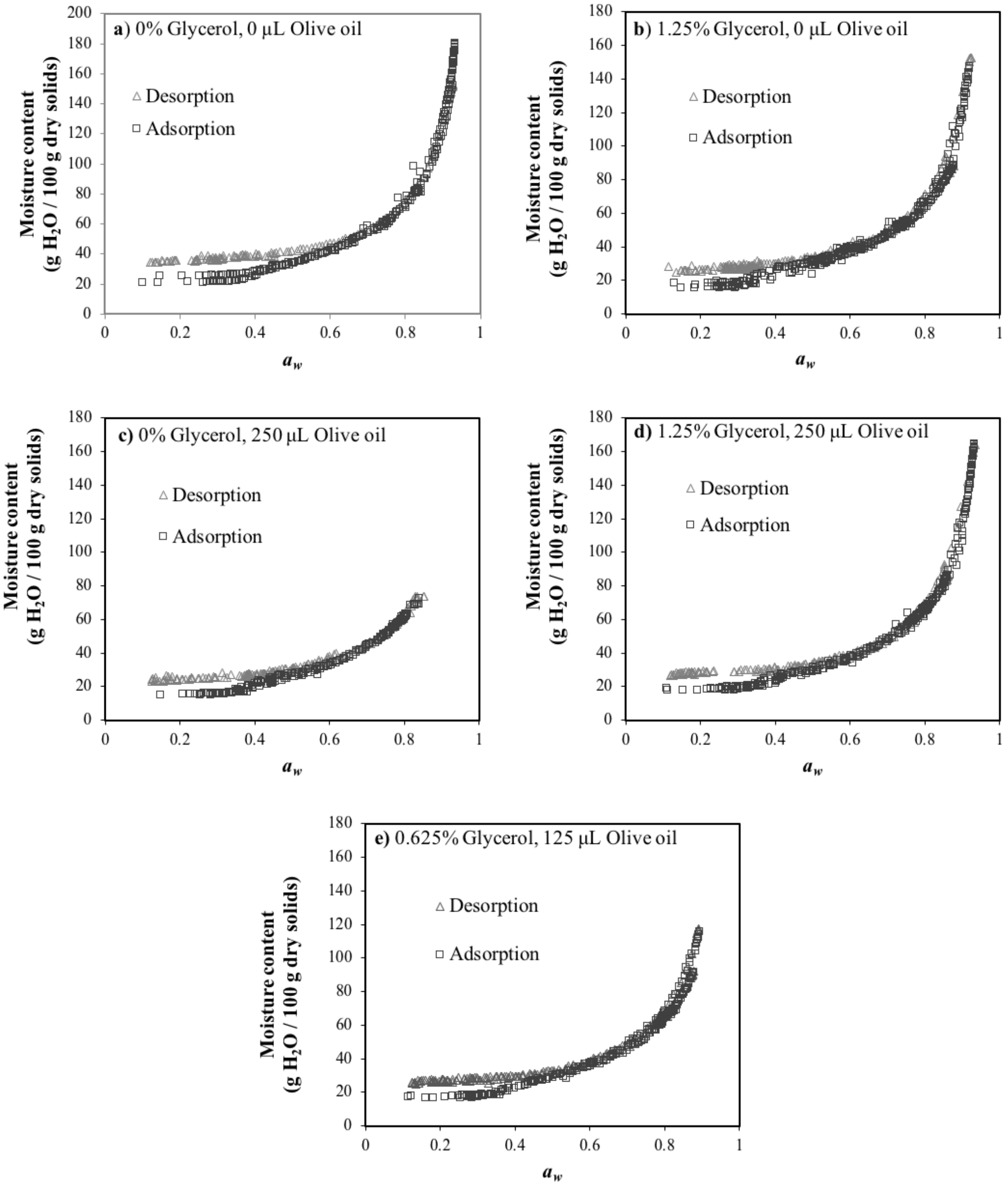

Fig. 3. Moisture adsorption () and desorption () isotherms at 25 ºC of grapefruit pectin films (FGP) with different concentrations of glycerol and olive oil.

On the other hand, the equilibrium moisture content of FOP and FGP decreased with the incorporation of additives during adsorption-desorption processes, compared to control films (Fig. 4 and Fig. 5). Films with high olive oil concentration (250 μl/100g) and without glycerol showed the lowest water content, specially at low and intermediate water activities. A more pronounced effect of glycerol and olive oil was observed in FGP than in FOP during both sorption processes, especially with 250 μL of olive oil. Besides the hydrophobic nature of the olive oil, the polar head of the fatty acids would form hydrogen bonds with pectin chains, reducing the availability of pectin polar sites and decreasing the amount of sorbed water in the films (Fabra *et al.*, 2010).

Compared to controls, glycerol-plasticized films would have less hydroxyl and carboxylic groups available for interaction with water in the film matrix, probably because part of the hydrogen bonds between pectin chains are replaced by hydrogen bonds between glycerol and pectin (Pasini Cabello *et al.*, 2015). The reduction of the equilibrium moisture content by the addition of plasticizer has also been observed in amylose and amylopectin films (Myllärinen *et al.*, 2002), and potato starch films (Talja *et al.*, 2007).

The obtained isotherms were similar to those of purified pectin from apple, sunflower and citrus (Panchev *et al.*, 2010), but showed lower X, mainly at $a_w > 0.5$. This different hygroscopic behavior could be partially attributed to the polar groups, polysaccharides structure, and low molecular weight carbohydrates (glucose, rhamnose, galactose, and arabinose) (Panchev *et al.*, 2010). FOP and FGP presented X values comparable to corn starch-carboxymethylcellulose/methylcellulose films (Arik Kibar and Us, 2013).

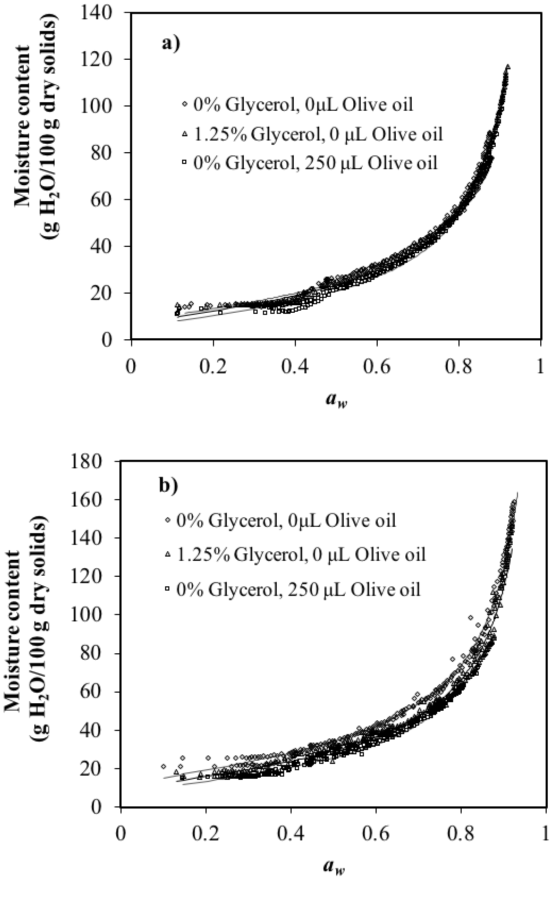

Fig. 4. Comparison of moisture adsorption isotherms of a) FOP and b) FGP at 25 °C with different additive concentrations. Experimental data (symbols) and Halsey fitted curves (lines).

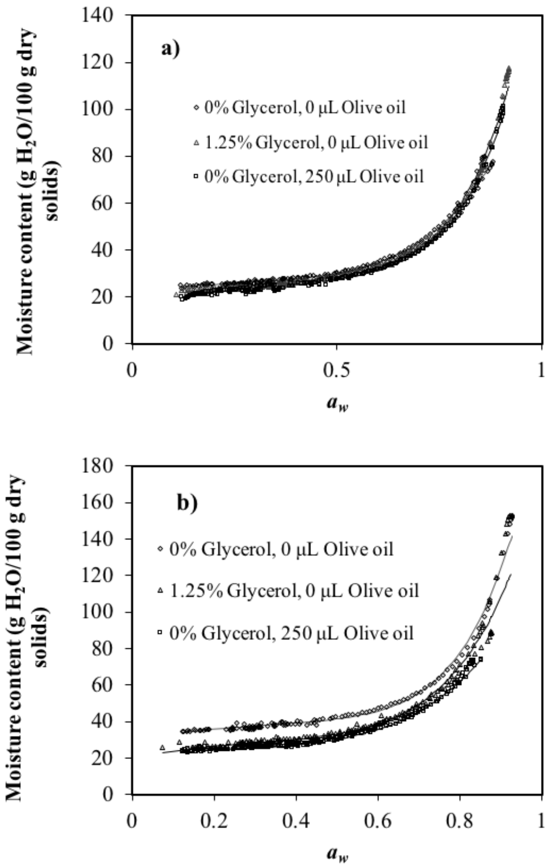

Fig. 5. Comparison of moisture desorption isotherms of a) FOP and b) FGP at 25 °C with different additive concentrations. Experimental data (symbols) and Peleg fitted curves (lines).

However, FOP and FGP showed higher X than other polysaccharide films, like glucomannan, guar gum and locust bean gum films (Kurt and Kahyaoglu, 2014), starch-gelatin films (Al-Hassan and Norziah, 2012), polyethylene oxide-starch films (Jagadish and Raj, 2011), glucomannan, carboxymethyl cellulose and palm olein films (Cheng *et al.*, 2008), and methyl and ethyl cellulose films (Velázquez de la Cruz *et al.*, 2001).

The different behavior of water adsorption and desorption processes lead to hysteresis phenomena observed in all the film samples at low water activities ($a_w < 0.6$) (Fig. 2 and 3), which is characteristic of materials with high pectin content (Al-Muhtaseb *et al.*, 2002). An equilibrium moisture difference as high as 11 g H_2O/100 g of dry solids was observed at low water activity (0.1-0.2).

Table 3. Adsorption isotherms BET, GAB and Halsey model constants for citrus peel pectin films at 25 °C.

			Sample number*				
Peel	Model	Parameter	1	2	3	4	5
Orange (FOP)	BET	X_0	9.36	9.5	7.73	10.12	8.46
		C	-22.25	-23.36	-23.38	-88.91	-31.84
		E	3.3	3.32	9.37	3.55	7.48
		R^2	0.972	0.971	0.913	0.966	0.896
	GAB	X_0	14.86	13.65	16.23	13.46	12.62
		C	16.68	10.77	2.49	12.55	41.38
		K	0.929	0.959	0.926	0.964	0.966
		E	3.18	1.55	2.04	2.69	2.57
		R^2	0.971	0.995	0.978	0.982	0.991
	Halsey	C	60.33	42.51	28.07	33.68	37.78
		n	1.4	1.3	1.22	1.24	1.29
		E	7	3.16	6.65	4.1	6.59
		R^2	0.984	0.999	0.994	0.996	0.997
Grapefruit (FGP)	BET	X_0	14.52	11.06	10.48	12.56	11.37
		C	-21.57	-21.14	-33.264	-30.905	-23.922
		E	9.28	6.1	2.86	3.22	2.34
		R^2	0.89	0.891	0.947	0.973	0.989
	GAB	X_0	18.27	17.3	16.17	15.22	16.59
		C	-148.63	-50.99	7.67	-56.59	14.09
		K	0.969	0.987	0.936	0.965	0.94
		E	9	16.53	3.09	3.48	6.53
		R^2	0.983	0.932	0.943	0.982	0.961
	Halsey	C	124.18	74.54	45.01	70.63	75.68
		n	1.47	1.39	1.29	1.37	1.37
		E	4.05	8.28	3.78	3.75	3.75
		R^2	0.994	0.986	0.995	0.995	0.995

*Composition of samples as in Table 1. X_0, monolayer moisture content (gH_2O/100 g of dry solids); E, mean relative error (%); R^2, determination coefficient. BET model was applied to data up to the critical water activity at the start of the glass transition of the films. GAB model was fitted to the data above the critical water activity at the end of the glass transition of the glass transition of the films.

In FOP, the difference in equilibrium moisture content was the highest in films containing intermediate concentrations of additives (0.625% glycerol and 125 μL olive oil, sample 5) and in control films (Fig. 2a and 2e). Regarding FGP, a higher difference was observed in control films (Fig. 3a), indicating that water was more strongly linked to the pectin matrix, making water more difficult to remove (Aguirre-Álvarez *et al*., 2010). These results indicate that olive oil and glycerol tend to reduce the hysteresis phenomenon in FGP.

All of the adsorption isotherms (Fig. 2 and Fig. 3) show an initial minimum slope where the films adsorb water in the available superficial hydrogen binding sites and in the interstitial spaces (Carter and Schmidt, 2012; Gorrasi and Bugatti, 2016). However, at approximately a_w of 0.40 in FOP and 0.35 in FGP, the films showed a slight increase in water uptake, leading to an inflection point that gives an isotherm shape not encompassed by Brunauer's classification (Burnett *et al*., 2004; Yuan *et al*., 2011). None of the desorption isotherms show such inflection points.

3.2 Mathematical modeling of sorption isotherms

The experimental data were fitted to the models (Table 2), and the fitted parameters are summarized in Tables 3 and 4 to describe adsorption and desorption behavior, respectively.

Table 4. Desorption isotherms GAB and Peleg model constants for citrus peel pectin films at 25 ºC.

			Sample number*				
	Model	Parameter	1	2	3	4	5
Orange (FOP)	GAB	X_0	15.44	14.23	13.79	14.4	14.24
		C	-16.73	-1680.93	-19.73	-17.22	-16.28
		K	0.907	0.942	0.937	0.942	0.946
		E	4.24	5.11	5.07	4.7	5.53
		R^2	0.972	0.969	0.971	0.959	0.966
	Peleg	C1	28.94	31.23	30.93	34.51	31.07
		C_2	94.5	144.66	135.27	133.63	152.72
		C_3	0.08	0.19	0.22	0.28	0.17
		C_4	5.12	7.15	7.12	7.12	7.17
		E	1.83	2.42	2.56	2.27	2.84
		R^2	0.989	0.995	0.997	0.992	0.993
Grapefruit (FGP)	GAB	X_0	21.16	16.38	16.62	16.27	16.24
		C	-15.01	-15.94	-21.41	-15.83	-17.42
		K	0.906	0.948	0.929	0.951	0.943
		E	6.22	4.54	2.8	5.27	4.67
		R^2	0.958	0.964	0.985	0.975	0.975
	Peleg	C1	43.58	34.14	28.12	33.45	31.67
		C_2	167.43	137.74	99.16	167.5	128.22
		C_3	0.12	0.16	0.09	0.1	0.1
		C_4	6.97	5.82	4.75	6.59	5.51
		E	2.48	3.66	2.08	3.39	2.88
		R^2	0.994	0.959	0.994	0.976	0.978

*Composition of samples as in Table 1. X_0, monolayer moisture content (g H_2O / 100 g of dry solids); E, mean relative error (%); R^2, determination coefficient.

In general, E values were lower than 10% and determination coefficients $R^2 \geq 0.890$, indicating that the models adequately predict X. The linear regression of the BET model fitted adsorption data at $a_w < 0.40$ ($E < 9.4$), as expected from its limited applicability to describe water sorption (Timmermann *et al.*, 2001).

Regression using the GAB equation as a second order polynomial was only able to fit the region after the inflection point (approximately $a_w > 0.40$-0.90) in both FOP and FGP adsorption isotherms (Fig. 6a and 6c), since a_w/X data did not formed typical parabolas, presenting sharp peaks near the a_w of the inflection point of the isotherms. In contrast, GAB regression fitted desorption data of every film in the entire range of a_w (Fig. 6b and 6d) because the converted desorption data formed parabolas without any sharp peaks.

The high concentration of olive oil in FOP gave the lowest C value for adsorption (Table 3). The magnitude of this parameter is a measure of the water binding forces to the primary sorption sites, weakened by the hydrophobicity of olive oil (Acosta Dominguez *et al.*, 2018). This effect has been observed in other hydrophilic films when oleic acid and beeswax were incorporated (Fabra, *et al.*, 2010).

Negative values of the C-constant were found for all FOP and FGP using the BET model (Table 3), for some cases of adsorption in FGP using GAB (Table 3), and for desorption in all FOP and FGP using GAB (Table 4). Negative values of C for GAB and BET have been reported for the moisture isotherms of high-methoxyl citric pectin (Panchev *et al.*, 2010), an arabian sweet (Ahmed *et al.*, 2004), freeze-dried garlic powder (Rahman and Al-Belushi, 2006), and pistachio nut paste (Maskan and Gögüs, 1997).

Even though the two models have R^2 values greater than 0.90 in most FOP and FGP, negative C values are thermodynamically unsound (Table 3).

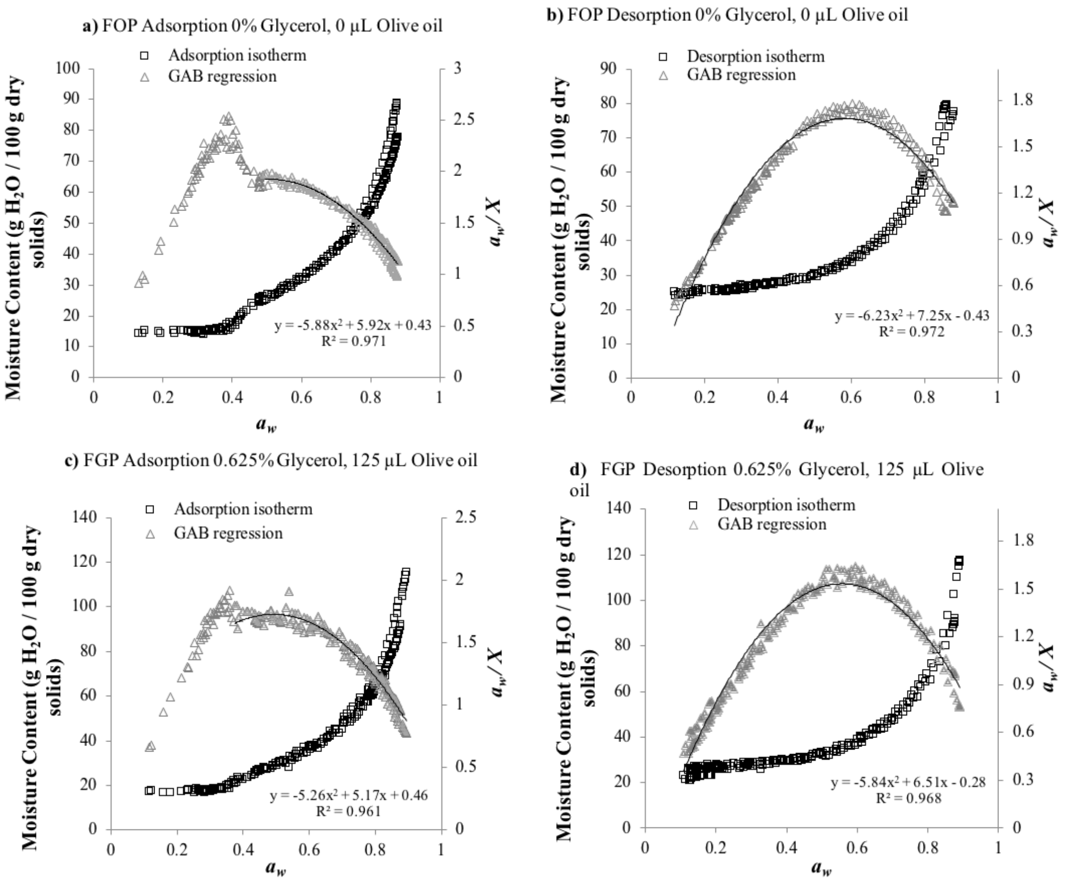

Fig. 6. a_w/X vs. a_w diagrams for GAB polynomial regression of a) FOP adsorption 0% glycerol, 0 μL olive oil b) FOP desorption 0% glycerol, 0 μL olive oil c) FGP adsorption 0.625% glycerol, 125 μL olive oil d) FGP desorption 0.625% glycerol, 125 μL olive oil.

Therefore, BET is not suitable to fit the adsorption isotherms of FOP and FGP, while GAB is not valid to describe water desorption in these FOP and both sorption processes in FGP (Table 4) (Maskan and Gögüs, 1997). It has been proposed that the physical meaning *C* in these models may not be valid in some cases, but this limited validity of the energy parameter does not restrict their application for the determination of monolayer moisture (Rahman *et al*., 2006).

The monolayer moisture content (X_0) obtained by GAB during adsorption was higher than the obtained with BET (Table 3), which is commonly reported in sorption isotherm modeling (Timmermann *et al*., 2001). FGP had X_0 values higher than those of FOP, which could be due to a different pectin extraction yield and galacturonic acid content. Other studies have obtained higher pectin extraction yield and galacturonic content, from grapefruit peels compared to orange peels (Kaya *et al*., 2014). The X_0 of the FOP and FGP is similar to those reported for other polysaccharides films, such as methylcellulose/carboxymethylcellulose-corn starch films (9.3 - 22 g H_2O/100 g dry solids) (Arik Kibar and Us, 2013), potato starch films (6.19 - 21.8 g H_2O/100 g dry solids) (Talja *et al*., 2007) and pea starch films (9.6 - 21.8 g H_2O/100 g dry solids) (Zhang and Han, 2008).

The GAB monolayer moisture in desorption isotherms was significantly affected by the composition of the films (Table 4). FOP and FGP without additives had X_0 values of 15.44 and 21.16 g H_2O/100 g dry solids, respectively, compared to the lower X_0 when olive oil was incorporated to the FOP (13.79 g H_2O/100 g dry solids) and FGP (15.62 g H_2O/100 g dry solids) (sample 3). These lower values of X_0 would most likely be ascribed to the hydrophobicity provided by olive oil (Shih *et al*., 2011). The monolayer moisture sorption was higher for desorption (Table 4) than for adsorption (Table 3), which gives a clear indication of hysteresis (Al-Muhtaseb *et al*., 2004).

The magnitude of the GAB constant K for desorption increased with glycerol and/or olive oil addition (Table 4), suggesting that behavior of water molecules in the multilayer of these films is more similar to bulk water than in control films (Quirijns *et al*., 2005). This behavior was not observed in the K constant of the GAB adsorption isotherms for the films with additives.

In regards to the fitted empirical models, the Halsey model reproduces the entire curves of both FOP and FGP adsorption isotherms with good accuracy ($E < 8.3\%$, $R^2 > 0.984$), except for the transition region (Table 3). It is well documented that the Halsey equation fits well adsorption data regarding type II isotherms (Andrade *et al*., 2011). For desorption, the Peleg model provided a better fit for the data ($E < 3.7$) compared to GAB ($E < 6.3$) due to lower E in most cases (Table 4). Even though the Peleg model described the experimental desorption data more adequately, the physical meaning of desorption processes cannot be obtained from its parameters.

3.3 Determination of the critical water activity

The shift in water sorption behavior observed on every adsorption isotherm of FOP and FGP indicates possible changes in the film structure associated to second-order phase transitions, crystallization events or dissolution of pectin or any other extracted components within the polymer matrix that occur during hydration (Burnett *et al*., 2004; Yuan *et al*., 2011). Fig. 7 presents an amplification of the a_w region in which the shift occurs in control FOP, deviating from conventional type II isotherms. The shifts appear as upward inflection points in every film. The resulting shape of the isotherm after the shift is characteristic of the glass transition of amorphous materials caused by the plasticizing effect of water during dynamic moisture uptake (Fabra *et al*., 2010; Carter and Schmidt, 2012; Yuan *et al*., 2011). In the rubbery state, increased molecular mobility makes the matrix more flexible, promoting greater availability of hydrogen binding sites in the bulk material. During this process, water absorption in the bulk occurs simultaneously with surface adsorption and thus, the films become more hygroscopic (Burnett *et al*., 2004).

Table 5. Critical water activity range of citrus peel pectin films at 25 ºC.

	Sample number	a_{w_c}	a_{w_d}
Orange (FOP)	1	0.4162	0.4939
	2	0.4113	0.4953
	3	0.3887	0.44
	4	0.4256	0.504
	5	0.4294	0.5506
Grapefruit (FGP)	1	0.351	0.3922
	2	0.2935	0.3482
	3	0.3652	0.3956
	4	0.3548	0.4008
	5	0.3447	0.3736

a_{w_c} is the critical water activity of the glass transition; a_{w_d} is the water activity at which film components start dissolving in sorbed water and the isotherm regains type II behavior.

The a_w value at which this transition occurs is known as the critical water activity (a_{w_c}). Fig. 8 shows a representative second derivative of the FOP and FGP, which were obtained using Moisture Analysis Toolkit software (Decagon Devices, USA). The second derivative of water content as a function of water activity is a useful mathematical tool able to confirm the existence of inflection points, at which film structure is modified, allowing the determination of a_{w_c} (Carter and Schmidt, 2012; Yuan *et al*., 2011). Since rubbery materials adsorb more water than in the glass phase, the inflection point of the transition is associated to a fast change in the slope of water adsorption capacity and therefore, appears as a maximum in the second derivative of the isotherm (Li, 2010; Yuan *et al*., 2011).

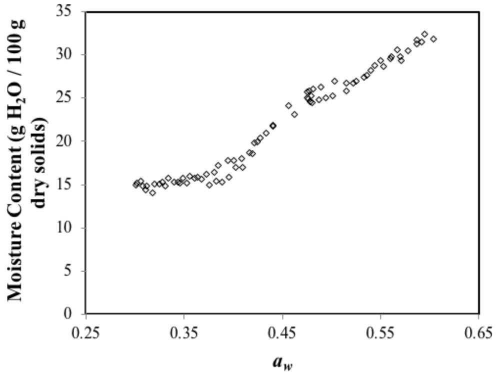

Fig. 7. Ampliation of the glass transition zone in the adsorption isotherm of FOP 0% glycerol, 0 μL Olive oil.

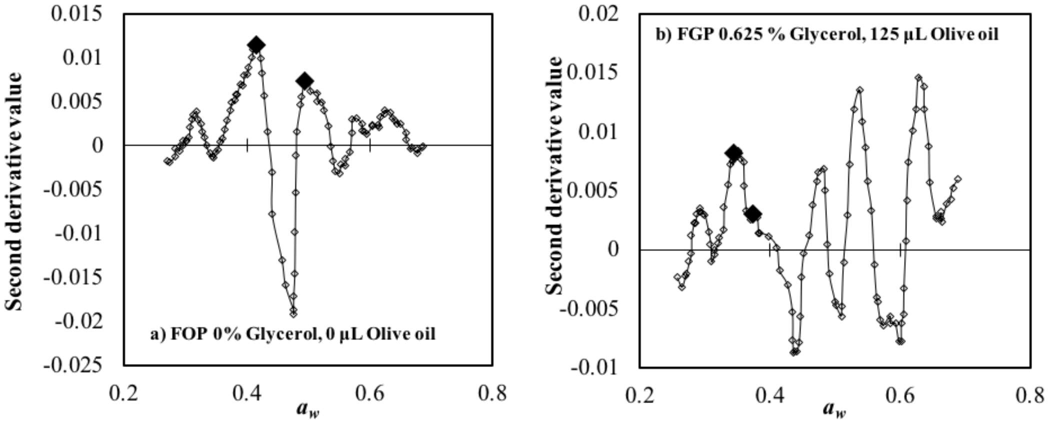

Fig. 8. Second derivative of X as a function of a_w for a) FOP adsorption 0% glycerol, 0 μL olive oil b) FGP adsorption 0.625% glycerol, 125 μL olive oil.

The second maximum point aligns to the inflection point of the isotherm at which all FOP and FGP become more hygroscopic. Table 5 lists the a_{w_c} of each film obtained from the second maximum of the respective second derivative. The high-resolution data obtained by the dynamic method made it possible to distinguish the transition points in the isotherms and to determine their corresponding maxima in the second derivative, which would have been difficult to observe by the static measuring method (Carter and Schmidt, 2012). In general, a_{w_c} in FGP is lower than in FOP (Table 5), maybe due to their higher water adsorption capacity. Moreover, the isotherms of FGP with the highest glycerol level (1.25%) presented the lowest a_{w_c}, 0.293. This behavior could be related to the plasticizing action of glycerol, requiring less water to increase molecular mobility and free volume within the film matrix. According to this, more flexible FOP and FGP could be obtained at higher a_w (> 0.5).

The third maximum of the second derivatives of the adsorption isotherms corresponds to the second inflection point (a_{w_d}) in Fig. 8. At the a_{w_d}, the films are in the rubbery state, but pectin and other extracted compounds would start to dissolve in the sorbed water (Burnett *et al.*, 2004; Yuan *et al.*, 2011). Therefore, adsorption capacity increases again, leading to a subsequent asymptotic behavior at high a_w, as described by conventional type II isotherms (Tsami *et al.*, 1992; Al-Muhtaseb *et al.*, 2004; Gorrasi and Bugatti, 2016).

No inflection points implying glass transitions were observed in any of the desorption isotherms. This suggests that these physical changes are not reversible by simply drying the film samples. Additionally, the irreversibility of the structural changes might be responsible for part of the high levels of hysteresis observed in the films, since the desorption process cannot return the samples to the less hygroscopic glass phase (Carter and Schmidt, 2012).

It is worth mentioning that the a_{w_c} values obtained from the second derivatives and the observed inflection in the isotherms approximately align to the a_w of the sharp peaks observed in converted adsorption data (a_w/X vs. a_w) used in GAB regression (Fig. 6a and 6c). Furthermore, the value of a_{w_d} corresponds to the water activity where the parabolic portion of the adsorption regression data starts.

Desorption isotherms show no glass transition inflection points and their converted data in GAB regression formed conventional parabolas with no sharp peaks.

Conclusions

Glycerol and olive oil decreased X and X_0 in FOP and FGP samples. The shape of the type II adsorption isotherms included inflection points related to a glassy to rubbery transition, demonstrated by the second derivative and the proposed tool of a_w/X vs. X diagrams used for fitting GAB as a second order polynomial function. It was observed that glycerol reduced the a_{w_c} of the glass transition. GAB adsorption isotherms indicate that the incorporation of olive oil weakened the binding forces, as indicated by C constant, between water in the monolayer and primary sorption sites in orange pectin films.

However, GAB as a second order polynomial function was only able to describe the isotherm above the glass transition. Hysteresis was observed between adsorption and desorption isotherms at $a_w < 0.60$, although the difference between the isotherms tends to decrease with the presence of additives.

Acknowledgements

The authors thank the financial support from CONACYT-México (Grant 223775) and Tecnologico de Monterrey. J.G. Hernández-Carrillo is grateful to CONACYT for the doctoral scholarship.

References

Acosta-Domínguez, L., Alamilla-Beltrán, L., Calderón-Domínguez, G., Jiménez-Aparicio, A. R., Gutiérrez-López, G.F. and Azuara-Nieto E. (2018). Determination of total and incipient solubilization point of fructans extracted of *A. tequilana* weber var. azul. *Revista Mexicana de Ingeniería Química 17*, 379-388.

Aguirre-Álvarez, G., Sandoval-Vergara, A., Pimentel-González, D.J., Campos-Montiel, R.G. and Hill, S.E. (2010). modelado de isotermas de adsorción/desorción de gelatina en polvo proveniente de diferentes orígenes. *XII Congreso Nacional de Ciencia y Tecnología de Alimentos*. Guanajuato, Guanajuato, México.

Ahmed, J., Khan, A.R. and Hanan, A.S. (2004). Moisture adsorption of an Arabian sweet (basbusa) at different temperatures. *Journal of Food Engineering 64*, 187-192.

Al-Hassan, A.A. and Norziah, M.H. (2012). Starch-gelatin edible films: Water vapor permeability and mechanical properties as affected by plasticizers. *Food Hydrocolloids 26*, 108-117.

Al-Muhtaseb, A.H., McMinn, W.A.M. and Magee, T.R.A. (2002). Moisture sorption isotherm characteristics of food products: A review. *Food and Bioproducts Processing 80*, 118-128.

Al-Muhtaseb, A.H., McMinn, W.A.M. and Magee, T.R.A. (2004). Water sorption isotherms of starch powders: Part 1: Mathematical description of experimental data. *Journal of Food Engineering 61*, 297-307.

Andrade, R.D., Lemus, R. and Pérez, C.E. (2011). Models of sorption isotherms for food: uses and limitations. *Vitae 18*, 325-334.

Arik Kibar, E.A. and Us, F. (2013). Thermal, mechanical and water adsorption properties of corn starch-carboxymethylcellulose/methylcellulose biodegradable films. *Journal of Food Engineering 114*, 123-131.

Ballus, C.A., Meinhart, A.D., de Souza Campos Jr, F.A., da Silva, L.F.d.O., de Oliveira, A.F. and Godoy, H.T. (2014). A quantitative study on the phenolic compound, tocopherol and fatty acid contents of monovarietal virgin olive oils produced in the southeast region of Brazil. *Food Research International 62*, 74-83.

Bertuzzi, M.A., Castro Vidaurre, E.F., Armada, M. and Gottifredi, J.C. (2007). Water vapor permeability of edible starch based films. *Journal of Food Engineering 80*, 972-978.

Brunauer, S., Deming, L.S., Deming, W.E. and Teller, E. (1940). On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society 62*, 1723-1732.

Burnett, D.J., Thielmann, F. and Booth, J. (2004). Determining the critical relative humidity for moisture-induced phase transitions. *International Journal of Pharmaceutics 287*, 123-133.

Carter, B.P. and Schmidt, S.J. (2012). Developments in glass transition determination in foods using moisture sorption isotherms. *Food Chemistry 132*, 1693-1698.

Cheng, L.H., Abd Karim, A. and Seow, C.C. (2008). Characterisation of composite films made of konjac glucomannan (KGM), carboxymethyl cellulose (CMC) and lipid. *Food Chemistry 107*, 411-418.

Fabra, M.J., Talens, P. and Chiralt, A. (2010). Water sorption isotherms and phase transitions of sodium caseinate-lipid based films as affected by lipid interactions. *Food Hydrocolloid 24*, 384-391.

Ghanbarzadeh, B. and Almasi, H. (2011). Physical properties of edible emulsified films based on carboxymethyl cellulose and oleic acid. *International Journal of Biological Macromolecules 48*, 44-49.

Gorrasi, G. and Bugatti, V. (2016). Edible bio-nano-hybrid coatings for food protection based on pectins and LDH-salicylate: Preparation and analysis of physical properties. *LWT - Food Science and Technology 69*, 139-145.

Hernández-Carrillo, J.G., Valdez-Fragoso, A., Welti-Chanes, J. and Mújica-Paz, H. (2015). Tracing phenolic compounds through manufacturing of edible films from orange and grapefruit peels. *Revista Mexicana de Ingeniería Química 14*, 567-578.

Jagadish, R.S. and Raj, B. (2011). Properties and sorption studies of polyethylene oxide-starch blended films. *Food Hydrocolloids 25*, 1572-1580.

Kaya, M., Sousa, A.G., Crépeau, M.J., Sørensen, S.O. and Ralet, M.C. (2014). Characterization of citrus pectin samples extracted under different conditions: influence of acid type and pH of extraction. *Annals of Botany 114*, 1319-1326.

Kurt, A. and Kahyaoglu, T. (2014). Characterization of a new biodegradable edible film made from salep glucomannan. *Carbohydrate Polymers 104*, 50-58.

Li, Q. (2010). *Investigating the glassy to rubbery transition of polydextrose and corn flakes using automatic water vapor sorption instruments, DSC, and texture analysis*. M.S. Thesis, University of Illinois at Urbana-Champaign. 167 p.

Ma, W., Tang, C.-H., Yin, S.-W., Yang, X.-Q., Wang, Q., Liu, F. and Wei, Z.-H. (2012). Characterization of gelatin-based edible films incorporated with olive oil. *Food Research International 49*, 572-579.

Maskan, M. and Gögüs, F. (1997). The fitting of various models to water sorption isotherms of pistachio nut paste. *Journal of Food Engineering 33*, 227-237.

Myllärinen, P., Partanen, R., Seppälä, J. and Forssell, P. (2002). Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers 50*, 355-361.

Panchev, I.N., Slavov, A., Nikolova, K. and Kovacheva, D. (2010). On the water-sorption properties of pectin. *Food Hydrocolloids 24*, 763-769.

Pascual-Pineda, L.A., Alamilla-Beltrán, L., Gutiérrez-López, G.F, Azuara, E. and Flores-Andrade E. (2017). Predicción de condiciones de almacenamiento de alimentos deshidratados a partir de una isoterma de adsorción de vapor de agua. *Revista Mexicana de Ingeniería Química 16*, 207-220.

Pasini Cabello, S.D., Takara, E.A., Marchese, J. and Ochoa, N.A. (2015). Influence of plasticizers in pectin films: Microstructural changes. *Materials Chemistry and Physics 162*, 491-497.

Pavón-García, L.M.A., Gallardo-Rivera, R., Román-Guerrero, A., Carrillo-Navas, H., Rodríguez-Huezo, M.E., Guadarrama-Lezama, A.Y. and Pérez-Alonso, C. (2015). Moisture sorption properties and storage stability conditions of a nutraceutical system microencapsulated by spray drying. *Revista Mexicana de Ingeniería Química 14*, 601-613.

Pereda, M., Amica, G. and Marcovich, N.E. (2012). Development and characterization of edible chitosan/olive oil emulsion films. *Carbohydrate Polymers 87*, 1318-1325.

Pérez, C.D., De'Nobili, M.D., Rizzo, S.A., Gerschenson, L.N., Descalzo, A.M. and Rojas, A.M. (2013). High methoxyl pectin-methyl cellulose films with antioxidant activity at a functional food interface. *Journal of Food Engineering 116*, 162-169.

Quirijns, E.J., van Boxtel, A.J., van Loon, W.K. and van Straten, G. (2005). Sorption isotherms, GAB parameters and isosteric heat of sorption. *Journal of the Science of Food and Agriculture 85*, 1805-1814.

Rahman, M.S. and Al-Belushi, R.H. (2006). Dynamic isopiestic method (DIM): Measuring moisture sorption isotherm of freeze-dried garlic powder and other potential uses of DIM. *International Journal of Food Properties 9*, 421-437.

Sánchez-González, L., Chiralt, A., González-Martínez, C. and Cháfer, M. (2011). Effect of essential oils on properties of film forming emulsions and films based on hydroxypropylmethylcellulose and chitosan. *Journal of Food Engineering 105*, 246-253.

Shih, F.F., Daigle, K.W. and Champagne, E.T. (2011). Effect of rice wax on water vapor permeability and sorption properties of edible pullulan films. *Food Chemistry 127*, 118-121.

Srinivasa, P.C., Ramesh, M.N. and Tharanathan, R.N. (2007). Effect of plasticizers and fatty acids on mechanical and permeability characteristics of chitosan films. *Food Hydrocolloids 21*, 1113-1122.

Suppakul, P., Chalernsook, B., Ratisuthawat, B., Prapasitthi, S. and Munchukangwan, N. (2013). Empirical modeling of moisture sorption characteristics and mechanical and barrier properties of cassava flour film and their relation to plasticizing-antiplasticizing effects. *LWT - Food Science and Technology 50*, 290-297.

Talja, R.A., Helén, H., Roos, Y.H. and Jouppila, K. (2007). Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. *Carbohydrate Polymer 67*, 288-295.

Timmermann, E.O., Chirife, J. and Iglesias, H.A. (2001). Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? *Journal of Food Engineering 48*, 19-31.

Tsami, E., Vagenas, G.K. and Marinos-Kouris, D. (1992). Moisture sorption isotherms of pectins. *Journal of Food Processing and Preservation 16*, 151-161.

Velázquez de la Cruz, G.V., Torres, J.A., and Martín-Polo, M.O. (2001). Temperature effect on the moisture sorption isotherms for methylcellulose and ethylcellulose films. *Journal of Food Engineering 48*, 91-94.

Yuan, X., Carter, B. P. and Schmidt, S. J. (2011). Determining the critical relative humidity at which the glassy to rubbery transition occurs in polydextrose using an automatic water vapor sorption instrument. *Journal of Food Science 76*, E78-E89.

Zhang, Y. and Han, J.H. (2008). Sorption isotherm and plasticization effect of moisture and plasticizers in pea starch film. *Journal of Food Science 73*, E313-E324.