



Research paper

# Thermodynamic study of water sorption and water barrier properties of nanocomposite films based on brea gum



Aníbal M. Slavutsky\*, María A. Bertuzzi

Instituto de Investigaciones para la Industria Química (CONICET), CIUNSA, Universidad Nacional de Salta, Av. Bolivia 5150, A4408TVY Salta, Argentina

## ARTICLE INFO

## Article history:

Received 2 October 2014

Received in revised form 4 February 2015

Accepted 5 February 2015

Available online 25 February 2015

## Keywords:

BG/Mt film

Sorption isotherms

Permeability

Thermodynamic parameters

## ABSTRACT

Water transport in edible films based on hydrophilic polymers is a complex phenomenon due to the strong interactions of sorbed water molecules with the polymeric structure. The effect of montmorillonite (Mt) nanoparticle incorporation into brea gum (BG) based films was studied through thermodynamic and phenomenological analyses. Moisture adsorption isotherms at three different temperatures of BG based films and BG/Mt nanocomposite films were obtained. Thermodynamic parameters showed an exothermic process that results less favourable when Mt is incorporated into the BG matrix, reducing the water uptake. Entropy change and net isosteric heat of adsorption showed a peak at monolayer water content, which is greater in composite films, indicating a more stable and ordered structure when Mt was added. Gibb's energy was indicative of process spontaneity and of the lower affinity to water composite films. Water vapour permeability depends on the tortuosity of the pathway formed by Mt nanoparticles and solubility of water molecules into the BG film matrix. Mt incorporation reduces the hydrophilic character of BG based films and thus their water vapour permeability.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In the past years the biodegradable films based on proteins and polysaccharides have attracted the attention of the general public and scientists due to their biodegradable properties and some functional characteristics. However, such hydrophilic materials tend to absorb surrounding humidity, resulting in plasticizing and swelling of the structure, thereby changing their functional properties.

Polysaccharide gums represent one of the most abundant raw materials. Researchers have mainly studied polysaccharide gums due to their sustainable, biodegradable and bio-safe characteristics. The term "gum" is used to describe a group of naturally occurring polysaccharides that come across widespread industrial applications due to their ability either to form gel or make viscous solution or stabilize emulsion systems. The considerably growing interest in plant gum exudates is due to their diverse structural properties and metabolic functions in food, pharmaceutical, cosmetic, textile and biomedical products (Mirhosseini and Amid, 2012).

Brea gum (BG) is the exudate obtained from the Brea tree (*Cercidium praecox*). The gum is harvested from wild trees throughout the north-west region of Argentina by native population (Chane, Wichis and

Churupies). BG is a complex hydrocolloid formed by L-arabinose, D-xylose, D-glucuronic acid, and 4-O-methyl-D-glucuronic acid and approximate 8% of protein. The major structural features of BG appear to be a  $\beta(1,4)$ -linked D-xylan backbone (possibly containing some 1,2-linkages) that is heavily 2-substituted by short branched-chains containing residues of D-xylose (and L-arabinose) and D-glucuronic acid, in which both types of residue may be terminal (Cerezo et al., 1969). Toxicological studies indicated that BG is not toxic for human ingest (Von Müller et al., 2009) and it was approved as food additive in Argentina. Physicochemical characteristics of BG are similar to Arabic gum (Bertuzzi et al., 2012), and then BG can be used as a replacement for Arabic gum in many applications. Bertuzzi and Slavutsky (2013) performed the formulation and characterization of BG films. According to this work, BG films are transparent with good mechanical properties and high water solubility and permeability. It was found that Mt nanoparticles' incorporation into the BG film matrix improved their barrier and mechanical properties (Slavutsky et al., 2014).

To further predict the physical properties and storage stability of these edible films, the thermodynamic properties of moisture sorption should be investigated. Generally, thermodynamic parameters are derived from sorption isotherms at different temperatures (Al-Muhtaseb et al., 2002).

The aims of this work were to study the nature of water adsorption process based on thermodynamic analysis and to investigate the effect of humidity gradient (driving force) on water vapour permeability of BG/Mt nanocomposite films.

\* Corresponding author at: Instituto de Investigaciones para la Industria Química (INIQUI-CONICET), Universidad Nacional de Salta, Av. Bolivia 5150, A4408TVY Salta, Argentina. Tel.: +54 387 4255410; fax: +54 387 4251006.

E-mail address: [amslavutsky@gmail.com](mailto:amslavutsky@gmail.com) (A.M. Slavutsky).

## 2. Materials and methods

### 2.1. Materials

BG was provided by a native community group who live in the area where the Brea tree grows (Tartagal, Salta, Argentine). The BG exudate from the plant is collected in the form of small drops or tears. The purification process included grinding, dissolution, decantation, filtration and drying in oven at temperatures below 50°. Then, the material is grinded to fine powder (mesh 80-ASTM). Characteristics of BG powder were described by Slavutsky et al. (2014). Natural sodium montmorillonite without purification and with quartz and albite present as accessory minerals, with a cation exchange capacity (CEC) of 89.8 meq/100 g clay, was supplied by Minarco S.A. (Buenos Aires, Argentine). Samples were homogenized by sieving in 200-mesh sieve (ASTM). P<sub>2</sub>O<sub>5</sub> (Mallinckrodt, USA) was used as a desiccant. Glycerol (Mallinckrodt, USA) was added as plasticizer. All salts used to obtain different relative humidity ambient (% RH) were provided by Aldrich (USA).

### 2.2. Preparation of Mt solution and film preparation

BG films and BG/Mt films were prepared according to Slavutsky et al (2014).

Mt dispersion was prepared by stirring nanoclay and water (1.5% w/v) during 3 h at 80 °C. The dispersion was centrifuged at 2500 rpm. Insoluble matter was rejected. Centrifugation was used as a selective method of size separation. Mt concentration in Mt solution was determined by drying to constant weight, 20 mL aliquot in an oven at 105 °C.

Film-forming solution was prepared by mixing BG (10% w/v), glycerol in a concentration of 25% w/w of BG, water and the addition of an appropriate amount of Mt solution to obtain a Mt concentrations of 5% w/w of BG. The resulting dispersion was kept 60 min in an ultrasonic bath. Film forming solution was poured onto polystyrene plates. Then, they were placed in an air-circulating oven at 35 °C and 53% RH for 15 h. After that, plates were removed from the oven and films peeled off. Films were stored at 25 °C and 53% RH before characterization.

### 2.3. Determination of moisture adsorption

Constant relative humidity environments were established inside sorbostats, glass jars, using salt solutions. The salts used (LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, NaBr, NaCl, KCl) were the different salts recommended by the European project COST-90 (Spiess and Wolf, 1983), to cover a water activity (a<sub>w</sub>) range from 0.10 to 0.90. Film samples (rectangular strips approximately 2 cm<sup>2</sup> area) were first freeze-dried (Thermovac Industries Corp, USA) and stored in a desiccator with P<sub>2</sub>O<sub>5</sub> during 72 h. Samples were weighed and placed on a plastic lattice by holding it on a tripod inside the sorbostats that contain the saturated salt solutions and then the sorbostats were sealed. The sorbostats were kept inside an environmental chamber maintained at constant temperature. Film samples were equilibrated in the sorbostats for 4 days before their weights were recorded. The weights of the samples were checked during 3 more days. Equilibrium was judged to have been attained when the difference between two consecutive sample weightings was less than 1 mg/g dry solid. Data were reported for each relative humidity as gram of water sorbed/100 g dry film. Adsorption tests were done in quadruplicate at each a<sub>w</sub>. The moisture adsorption determination was done at 5, 25 and 45 °C.

The data obtained were fitted by BET model (Eq. (1)):

$$w_e = \frac{w_0 \cdot C \cdot a_w}{(1-a_w) \cdot (1 + (C-1) \cdot a_w)} \quad (1)$$

where  $w_e$  is the equilibrium moisture content (g water/100 g dry film),  $w_0$  is the monolayer moisture content (g water/100 g dry film) and  $C$  is a temperature dependent adsorption constant.

The quality of the fitting was evaluated through the R<sup>2</sup> and through the mean relative percent error (%E) defined as:

$$\%E = \sum_{i=1}^n \left[ \left| \frac{w_{e,i} - w_{p,i}}{w_{e,i}} \right| \right] \times \frac{100}{n} \quad (2)$$

where  $n$  is the number of data points, ( $w_e$ ) and ( $w_p$ ) are experimentally observed and predicted by the model values of the equilibrium moisture content, respectively. The %E has been widely adopted throughout the literature to evaluate the goodness of fit of adsorption models, with a %E value below 10% being indicative of a good fit for practical applications (Al-Muhtaseb et al., 2002).

### 2.4. Thermodynamic parameters

The neat isosteric heat of adsorption ( $Q_{st}$ ) provides an indication of the binding energy of water molecules and has some bearing on the energy balance of drying operation (Iglesias and Chirife, 1982). It is defined as the difference between the actual enthalpy change of adsorption at constant moisture sorption,  $w_e$ , or isosteric heat of adsorption ( $\Delta H$ ), and the latent heat of water condensation ( $\lambda$ ):

$$Q_{st} = \Delta H - \lambda \quad (3)$$

These values can be deduced from the adsorption isotherm data, at a number of temperatures, by applying Clausius–Clapeyron equation:

$$\frac{\Delta H}{R} = \frac{\partial \ln p}{\partial (1/T)} \quad (4)$$

where  $p$  is the water vapour pressure ( $a_w$  multiplied by pure water vapour pressure at isotherm temperature),  $T$  is the absolute temperature and  $R$  is the universal gas constant. The relation is applied to the system and the pure water with the following assumptions: (1) the heat of vaporisation of pure water and excess heat of adsorption do not change with temperature, and (2) the moisture content of the system remains constant (Al-Muhtaseb et al., 2002).

Gibb's energy changes ( $\Delta G$ ) were calculated as follows:

$$\Delta G = R \cdot T \cdot \ln a_w \quad (5)$$

and entropy changes of adsorption process ( $\Delta S$ ) can be calculated from Gibb's equation as suggested by Gabas et al. (2000):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (6)$$

### 2.5. Water vapour permeability

The apparatus and methodology described in the ASTM E96 (ASTM, 2010) were used to measure film permeability. Film specimens were conditioned for 48 h in a chamber at 25 °C and 53% relative humidity (Mg(NO<sub>3</sub>)<sub>2</sub> saturated salt solution) before being analysed. Films were sealed on cups containing different saturated salt solutions or distilled water that provides higher relative humidity. Test cups were placed in a desiccator cabinet maintained at constant temperature. Saturated salt solutions were used to provide specific relative humidity. In all cases, relative humidity inside the desiccator cabin was lower than relative humidity inside the cups. Table 2 shows the range of  $a_w$  used in each assay. A ventilator was used to maintain uniform conditions at all test locations over the specimen. Weight loss measurements were taken by continuous weighing of the test cup to the nearest 0.001 g with an electronic scale (Ohaus PA313, USA). Data were transferred to a computer. Weight loss was plotted over time and when steady state (straight line) was reached, 8 h more was registered. Thickness value was the mean value of five measurements with an analogical thickness

gauge (Digimes, Argentine) and it was used for water vapour permeability calculations. The water vapour transmission rate (WVTR) was calculated from the slope (G) of a linear regression of weight loss versus time (Eq. (7)) and measured water vapour permeability (P) was calculated according to Eq. (8):

$$\text{WVTR} = \frac{G}{A} \quad (7)$$

$$P = \text{cte} \cdot \frac{\text{WVTR} \cdot l}{(p_{wi} - p_{wo})} \quad (8)$$

where  $l$  is the film thickness;  $A$  is the exposed film area,  $p_{wo}$  is the partial pressure of water vapour at the film surface outside the cup,  $p_{wi}$  is the partial pressure of water vapour of distilled water or saturated solution inside the cup, and  $\text{cte}$  is a constant that satisfies unit conversions. Corrected values of water vapour permeability ( $P_c$ ) were obtained according the equation proposed by Gennadios et al. (1994):

$$P_c = \text{cte} \cdot \frac{\text{WVTR} \cdot l}{\Delta p_r} \quad (9)$$

$\Delta p_r$  is the difference of water vapour partial pressure at each side of the film.

The test was carried out in triplicate for each film at constant temperature of 25 °C.

## 2.6. Statistical analysis

Statistics on a completely randomized design were performed with the analysis of variance (ANOVA) procedure in GraphPad Prism 5.01 software. Tukey's multiple range test ( $p \leq 0.05$ ) was used to detect differences among the mean values of film properties.

## 3. Results and discussions

A biodegradable film based on a nanocomposite formed with BG and Mt plasticized with glycerol, was elaborated. Due to the hydrophilic nature of both, BG and Mt, an enhanced nanodispersion state was expected.

### 3.1. Moisture adsorption isotherm

The effect of water vapour pressure on moisture content of BG films and BG/Mt films at different temperatures is shown in Fig. 1. The experimental data are presented as a function of water vapour pressure rather

than  $a_w$  for better readability of the figure. The BET model fits are also shown. Film water adsorption decreases as temperature increases in all samples. Curves present a relatively low slope at small values of water vapour pressure, but take an exponential course at high relative humidities. This behaviour indicates that the film structure is modified above a certain degree of freedom of water molecules. Under these conditions, polymeric chains swell altering its conformation.

Mt is capable to interact with hydrophilic group of BG. Experimental data obtained for BG/Mt film indicate that incorporation of nanoclay reduces the water adsorption. This effect notoriously increases at high  $a_w$ , demonstrating that water molecules have less affinity with the film matrix. These results indicated that the addition of Mt improves the water resistance of the BG matrix. According to Slavutsky et al. (2014), this effect increases at high  $a_w$ . It could be possible that the strong interactions between BG and the hydroxyl groups of the Mt layers, through hydrogen bonds, reduce the number of hydrophilic sites available for water molecules, resulting in a decrease of water solubility and diffusivity in the film matrix. As a result, the water sensitivity of a highly hydrophilic composite film is reduced. Water content data for  $a_w$  values exceeding 0.75 are not considered due to the high hydrophilicity of BG. Among the tested samples, the moisture content decreased with increasing temperature at constant  $a_w$ .

Table 1 shows the fitting model parameters to data (BET model). Water monolayer values decrease with temperature indicating an exothermic process. BG/Mt films presented monolayer values lower than BG film. This indicates that Mt reduce the number of sites where water molecules can interact with BG chains, decreasing the water adsorption of the film.

### 3.2. Thermodynamic parameters

The entropy change, Gibb's energy change and isosteric heat of adsorption were calculated using Eqs. (3), (4), (5) and (6). Fig. 2 represents the entropy changes for BG films and BG/Mt films. The entropy curve exhibits a well-defined minimum corresponding to the completion of the monolayer. The decrease in entropy is associated with the loss of mobility of water molecules followed by an increase in entropy as water recovers mobility by forming several layers (Bertuzzi et al., 2003; Al-Muhtaseb et al., 2004). BG/Mt films presented entropy change values smaller than BG films, indicating that the structure formed is more stable. At low moisture content a marked difference between both curves is observed suggesting that the interaction between water and BG/Mt films is stronger than between water and BG films. This trend could be attributed to the change of the number of available sorption sites of high energy level (Madamba et al., 1996). BG/Mt films

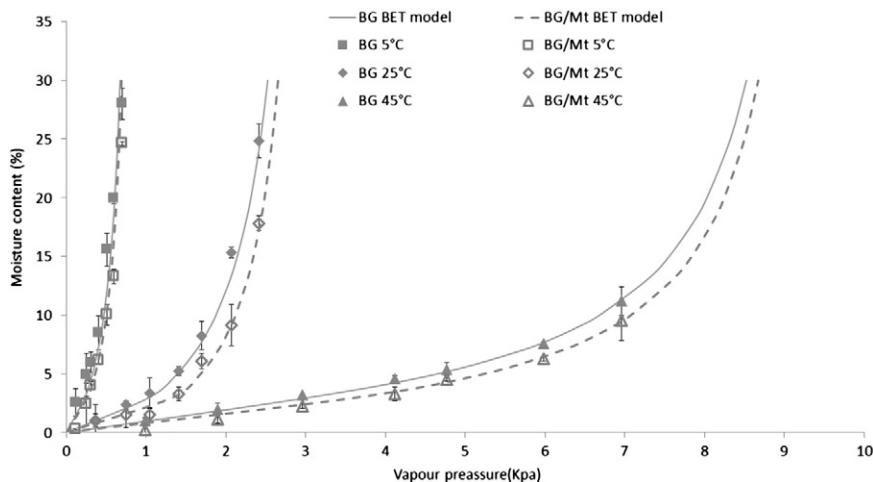


Fig. 1. Moisture sorption isotherm of BG films and BG/Mt films at different temperatures (BG: ■ 5°; ♦ 25°; ▲ 45°. BG/Mt: □ 5°; ◇ 25°; △ 45°) and BET model fit (BG: —; BG/Mt: - -). Bars indicate standard deviation.

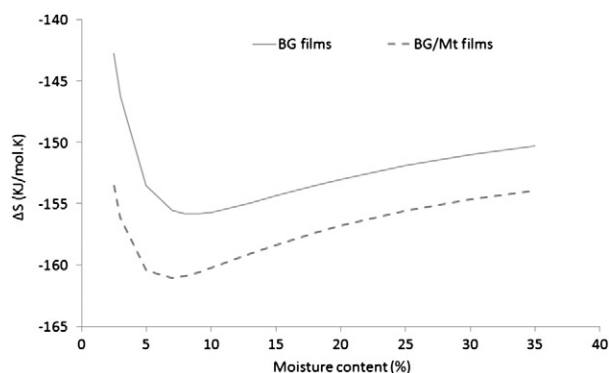
**Table 1**  
Estimated BET parameters of BG films and BG/Mt films.

Temperature (°C)	w <sub>0</sub>	C	R <sup>2</sup>	%E
<i>BG films</i>				
5	9.1580	0.8813	0.9815	2.37
25	8.6213	0.6202	0.9856	1.68
45	3.4513	3.1023	0.9876	2.53
<i>BG/Mt films</i>				
5	8.3837	0.7703	0.9835	0.97
25	6.9123	0.4488	0.9809	2.58
45	2.9531	2.7103	0.9889	1.63

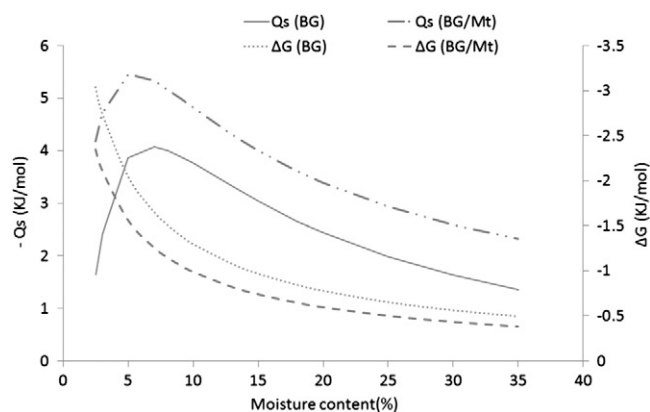
exhibited lowest  $\Delta S$  values than BG films in all moisture contents. These observations indicated that BG films were more hydrophilic, which is also consistent with the previous moisture adsorption isotherm results. The process of water adsorption is clearly irreversible because a net entropy production is observed along the whole process. Almost constant entropy can be observed at high moisture contents suggesting that adsorption is reversible until a critical moisture content is reached.

Fig. 3 shows the values obtained for Gibb's energy change and isosteric heat of adsorption. The values obtained for Gibb's energy change for both samples were negative as it was expected for a spontaneous process. In addition, BG film presented lower values (greater in absolute values) than BG/Mt films suggesting that the process occurs with more energy liberation, which indicates that adsorption is a more favourable process in BG films. The difference between curves decreases as moisture content increases. This thermodynamic behaviour was observed by several authors (Fasina et al., 1999; Sundaram and Durance, 2008; Xiao and Tong, 2013). According to Sundaram and Durance (2008) these curves also give the level of intermolecular force between the water vapour and the film surface. At low moisture content, water is adsorbed on the most accessible and polar locations at the external surface of the film. These are the sites with the highest intermolecular forces. When the film moisture increases, the intermolecular forces become weaker and the net isosteric heat of adsorption is reduced. As the moisture content increases, the sites available for the adsorption of water diminish, resulting in lower net isosteric heat.

The heat of adsorption is a measure of the energy released on sorption (the heat of adsorption is negative) (Al-Muhtaseb et al., 2002). Water adsorption process in BG based films is exothermic, within the range of water activities investigated. Values of net isosteric heat of adsorption have been deduced from water isotherm data, adopting the Clausius–Clapeyron equation. As water vapour is brought in contact with a heterogeneous surface, where active sites of different energy are present, the most active sites are those first sorbed by the water molecules followed by those less active until the first layer of water is completed (Bertuzzi et al., 2003). BG films and BG/Mt films present a peak at the monolayer values obtained by BET model. This indicates that the monolayer completion is accomplished with the release of



**Fig. 2.** Entropy change of BG films (—) and BG/Mt films (---).



**Fig. 3.** Gibb's energy change of BG films (.....) and BG/Mt films (---). Net isosteric heat of sorption of BG films (—) and BG/Mt films (---).

energy. In BG/Mt films this energy liberation is greater than in BG films, indicating a more stable final structure. After the monolayer is completed, net isosteric heat of adsorption decreases (absolute value) with moisture content at the same time as multilayer is formed. The formation of multilayer for BG/Mt films seems to be more pronounced with the increase of moisture content. That occurs because the water competes with Mt for OH-groups of BG, and at high moisture content this process is favoured, as it is observed in the curves of Gibb's energy change.

Slavutsky and Bertuzzi (2012) reported similar thermodynamic behaviour in starch/Mt films, but the difference between curves (starch films and starch/Mt films) decreases as the moisture content increases. In the present study, the curves corresponding to BG films and BG/Mt films maintain a constant difference in the moisture range studied. It is indicative that the addition of Mt does not affect the interaction between water and polymer and therefore has no effect on the mobility of water molecules in the multilayer. This may be due to the structural differences between starch and BG polymers. BG is an amorphous polymer with high water adsorption capacity, according the reported solubility values at  $a_w$  greater than 0.75.

### 3.3. Water vapour permeability

Table 2 shows the water vapour permeability of BG films and BG/Mt nanocomposite films measured with different driving forces ( $\Delta a_w$ ) and  $a_w$  ranges. The water vapour transmission rate (WVTR) indicates the flux of water molecules through the film. These values are lower for BG/Mt film than for BG films, in all conditions tested. According to the data, WVTR also depends on the driving force. WVTR increases with increasing  $\Delta a_w$ .

Table 2 also shows the measured and corrected values of water permeability (Pm and Pc), the last obtained according to Gennadios et al. (1994). Permeation process, developed in different ranges of  $a_w$  (below and above  $a_w = 0.6$ ), evidences some modifications of the polymer matrix (plasticization by water), showing a mild influence of the

**Table 2**  
Water vapour permeability of BG films and BG/Mt films.

Films samples	$\Delta a_w$	WVTR (g/m·s)	Pm (g/m·s·Pa)	Pc (g/m·s·Pa)	Thickness (m)
BG	0.33–0.54	0.0035	5.60E–10	1.10E–09	1.07E–04
BG/Mt	0.33–0.54	0.0027	4.14E–10	6.63E–10	1.03E–04
BG	0.54–0.76	0.0046	7.01E–10	1.74E–09	1.09E–04
BG/Mt	0.54–0.76	0.0031	4.50E–10	7.64E–10	1.07E–04
BG	0.33–0.76	0.0105	8.16E–10	2.82E–09	1.07E–04
BG/Mt	0.33–0.76	0.0081	6.19E–10	1.37E–09	1.05E–04
BG	0.00–1.00	0.0165	5.79E–10	1.12E–09	1.11E–04
BG/Mt	0.00–1.00	0.0110	3.64E–10	5.35E–10	1.05E–04

driving force and  $a_w$  range on permeability. The effect of the tortuous pathway generated by Mt incorporation is significant in all the ranges of  $a_w$  tested. In the same range of  $a_w$ , the interactions between BG and Mt were also observed. Incorporation of Mt produces a decrease on permeability in all the  $a_w$  ranges studied. Similar behaviour was reported by Slavutsky and Bertuzzi (2012) for starch/Mt films. The incorporation of nanostructures generates a tortuous pathway into the film that produces a decrease on diffusion rate of water molecules. The decrease on solubility produced by Mt incorporation is also important for water permeability reduction.

#### 4. Conclusion

Considering the complex mechanisms involved in water vapour transport through hydrophilic materials, the effect of Mt incorporation into BG films was studied through thermodynamic analysis. BG films and BG/Mt nanocomposite films were prepared, water adsorption data at different temperatures were collected and thermodynamic parameters of the water adsorption process were determined. Experimental data of water adsorption showed an exothermic process and they were adequately fitted by BET model. Results indicated that the incorporation of Mt produces a decrease on film water adsorption in all ranges of  $a_w$  studied. The water content of the monolayer, calculated with BET equation, reduces with Mt incorporation at all temperatures, indicating a lower affinity to water.

Entropy change and net isosteric heat of adsorption show a well-defined peak at monolayer water content, and in both cases, indicate a more stable and ordered structure when Mt was added. Gibb's energy changes show the process spontaneity and indicate that the final structure of BG/Mt films has less affinity to water than BG films. Permeability depends on the tortuosity of the pathway formed by Mt nanoparticles and solubility of water molecules. Mt incorporation reduces the hydrophilic character of BG based films.

#### Acknowledgements

The authors thank the financial support provided by Consejo de Investigaciones de la Universidad de Salta (CIUNSa Proyecto No. 1895/

2) and by Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT IP-RPH 2007).

#### References

- Al-Muhtaseb, A.H., McMinn, W.A.M., Magee, T.R.A., 2002. Moisture sorption isotherm characteristics of food products: a review. *Food Bioprod. Process.* 80 (C2), 118–128.
- Al-Muhtaseb, A.H., McMinn, W.A.M., Magee, T.R.A., 2004. Water sorption isotherms of starch powders. Part 2. Thermodynamic characteristics. *J. Food Eng.* 62, 135–142.
- ASTM, 2010. Standards American society for testing and materials. E96, Standard Test Methods for Water Vapour Transmission of Materials (Philadelphia).
- Bertuzzi, M.A., Slavutsky, A.M., 2013. Formulation and characterization of film based on gum. *J. Food Sci. Eng.* 3, 113–122.
- Bertuzzi, M.A., Armada, M., Gottifredi, J.C., 2003. Thermodynamic analysis of water vapour sorption of edible starch based films. *Food Sci. Technol. Int.* 9 (2), 115–121.
- Bertuzzi, M.A., Slavutsky, A.M., Armada, M., 2012. Physicochemical characterisation of the hydrocolloid from Brea tree (*Cercidium praecox*). *Int. J. Food Sci. Technol.* 47 (4), 768–775.
- Cerezo, A.S., Stacey, M., Webber, J.M., 1969. Some structural studies of brea gum (an exudate from *Cercidium australe* Jonhst.). *Carbohydr. Res.* 9 (4), 505–517.
- Fasina, O., Ajibola, O., Tyler, R., 1999. Thermodynamics of moisture sorption in winged bean seed and gari. *J. Food Process Eng.* 22, 405–418.
- Gabas, A.L., Menegalli, F.C., Telis-Romero, J., 2000. Water sorption enthalpy–entropy compensation based on isotherms of plum skin and pulp. *J. Food Sci.* 65 (4), 680–684.
- Gennadios, A., Weller, C.L., Gooding, C.H., 1994. Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films. *J. Food Eng.* 21 (4), 395–409.
- Iglesias, H.A., Chirife, J., 1982. Handbook of Food Isotherms: Water Sorption Parameters for Food and Food Components. Academic Press, New York.
- Madamba, P.S., Driscoll, R.H., Buckle, K.A., 1996. Enthalpy–entropy compensation models for sorption and browning of garlic. *J. Food Eng.* 28 (2), 109–119.
- Mirhosseini, H., Amid, B.T., 2012. A review study on chemical composition and molecular structure of newly plant gum exudates and seed gums. *Food Res. Int.* 46 (1), 387–398.
- Slavutsky, A.M., Bertuzzi, M.A., 2012. A phenomenological and thermodynamic study of the water permeation process in corn starch/MMT films. *Carbohydr. Polym.* 90 (1), 551–557.
- Slavutsky, A.M., Bertuzzi, M.A., Armada, M., García, M.G., Ochoa, N.A., 2014. Preparation and characterization of montmorillonite/brea gum nanocomposites films. *Food Hydrocoll.* 35, 270–278.
- Spies, W.E.L., Wolf, W.F., 1983. The results of the COST 90 project on water activity. *Physical Properties of Foods*. Appl. Sci. Publishers, London.
- Sundaram, J., Durance, T.D., 2008. Water sorption and physical properties of locust bean gum–pectin–starch composite gel dried using different drying methods. *Food Hydrocoll.* 22 (7), 1352–1361.
- Von Müller, A.R., López, C.B., Eynard, B., Aldo, R., Guzmán, C.A., 2009. Sub-chronic toxicological evaluation of brea gum (*Parkinsonia praecox*) as a food additive in BALB/c mice. *Drug Chem. Toxicol.* 32 (4), 307–311.
- Xiao, Q., Tong, Q., 2013. Thermodynamic properties of moisture sorption in pullulan–sodium alginate based edible films. *Food Res. Int.* 54 (2), 1605–1612.