

Improvement of water barrier properties of starch films by lipid nanolamination



Aníbal M. Slavutsky*, María A. Bertuzzi

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

ARTICLE INFO

Article history:

Received 19 October 2014
Received in revised form 5 October 2015
Accepted 19 January 2016
Available online xxx

Keywords:

Nanolaminated film
Starch matrix
Lipid nanolayer
Sorption isotherm
Water vapour permeability

ABSTRACT

A nanolaminate consists of two or more layers of material with nanometric dimensions that are physically or chemically bonded to each other. Starch based edible films present suitable characteristics for food protection, but their functional properties are affected by film water content. Nanolaminated films were formulated by coating the starch film with lipid nanolayers in order to improve their water resistance and barrier properties. Lipid nanolayer presence was confirmed by SEM images and contact angle measurements. Sorption isotherms of nanolaminated films showed an important reduction in film water adsorption through all the a_w range studied. The effect on permeability of the driving force (a_w difference) and the a_w values at each side of the film, were analysed. Water vapour transport was controlled by water diffusion through hydrophobic nanolayers. Nanolamination of edible films improved the water barrier properties of hydrophilic films by combining starch with lipids materials at nanometric scale.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, about 150 million tons of plastics are produced annually all over the world, and their production and consumption show a growing trend. Most of these plastics are petroleum based, and their production results in increasing use of non-renewable resource and serious environmental pollution problems (Parra, Tadini, Ponce, & Luga, 2004). Biopolymers produced from renewable resources are an innovating answer to replace conventional petroleum based products and fit with a real sustainable development approach. Biodegradable films based on starch, can be produced at low cost and large scale. However, the mechanical and barrier properties of this promising material have to be enhanced in order to be able to compete with conventional petroleum-based polymers (Averous, 2001; Vieira, Da Silva, Dos Santos, & Beppu, 2011). Starch is a hydrophilic material and their main functional properties depend on their water content. This is due to water vapour strongly interacts with polymer matrix affecting their structure (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Perdomo et al., 2009). Many attempts have been done in order to overcome this problem, such as the incorporation of nanofiller of organic or inorganic origin (Bodirlau, Teaca, &

Spiridon, 2013; Kampeerappun, Aht-ong, Pentrakoon, & Srikulkit, 2007), the introduction of lipids as microdroplets inside the film matrix (Debeaufort, Quezada Gallo, Delporte, & Voilley, 2000; Zahedi, Ghanbarzadeh, & Sedaghat, 2010), and the production of laminated films that consist in a lipid layer of micrometric dimensions on a polysaccharide or protein based film (Debeaufort et al., 2000; Phan The, Debeaufort, Luu, & Voilley, 2008).

Incorporation of nanofillers such as montmorillonite and cellulose nanocrystal has been used as an alternative to improve functional properties of starch based film (Chen, Liu, Chang, Cao, & Anderson, 2009; Svagan, Hedenqvist, & Berglund, 2009; Liu, Chaudhary, Yusa, & Tadé, 2011; Slavutsky, Armada, & Bertuzzi, 2012; Slavutsky & Bertuzzi, 2014). The decrease in gas or vapour permeability is due to the increase in tortuosity of the diffusion path of permeant molecules caused by nanoparticles (Slavutsky & Bertuzzi, 2014). Besides, nanoclay addition produces an increase in Young's module and tensile strength and a decrease in film elongation as a consequence of film structure reinforcement (Slavutsky, Bertuzzi, Armada, García & Ochoa, 2014).

Inclusion of lipids into the film can be made by two different methods: lamination or emulsion. Bi-layer films are obtained by lamination of a hydrophobic lipid layer over a preformed hydrophilic film, resulting in the lipid being a distinct layer, of micrometric thickness, atop the hydrophilic film. On the other hand, emulsion films are formed by dispersion of the lipid material throughout the hydrophilic film (Rhim and Shellhammer, 2005).

* Corresponding author. Fax: + 54 387 4251006.

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

Indeed, the association of lipids with a film forming compound, such as protein or carbohydrate (biopolymers), is required due to their non-polymeric nature, and thus, the poor mechanical resistance of solid fat. Mass transfer resistance of lipid compounds against gas and vapour migration is mainly due to their structure and hydrophobic character. The incorporation of lipid compounds in film forming solution, such as sunflower oil and essential lemon oil, could improve mechanical and barrier properties of hydrocolloids based films (Sánchez-González, Chiralt, González-Martínez, & Cháfer, 2011; Vargas, Albors, & Chiralt, 2011). Furthermore, essential oil compounds have a well-documented antimicrobial activity. Water vapour barrier efficiency of emulsion-based edible films depends on the nature of the lipids, the chain length of the fatty acids and the structure of the dried emulsion which constitutes the film. Several studies showed that bi-layer films are more effective barriers against water vapour transfer than emulsion films, due to the continuous hydrophobic phase in the film (Pérez-Gago and Krochta, 2005). Emulsion-based films reduce around 10 times the water vapour permeability of hydrocolloid based films, while bi-layer films have 10–1000 times better barrier efficiency against water transfer than emulsified film (Debeaufort et al., 2000). However, bi-layer films tend to delaminate and exhibit poor mechanical properties due to the fracture or cracking of the lipid layer. These problems are related to the low compatibility between the hydrophilic polymeric matrix and the lipid layer of non-polymeric characteristics.

A nanolaminated film consists of two or more layers of material with nanometric dimensions that are physically or chemically bonded to each other (Rubner, 2003). Multilayer films or coatings of nanometric thickness can be made by successive adsorption of oppositely charged polyelectrolytes on a solid support. They could be used for potential applications such as food preservation and coatings for implant devices (Rudra, Dave, & Hayne, 2006). Carneiro-da-Cunha et al., (2010) and De S. Medeiros, Pinheiro, Carneiro-da-Cunha, and (2012) Vicente studied the impact of hydrocolloid deposition, as nanolayers, over PET films. However, the only mention to a lipid nanolaminated hydrocolloid films was reported by our group in a previous work (Slavutsky and Bertuzzi, 2015). Nanolaminated films were formulated by coating starch film with a lipid nanolayer of sunflower oil, driven by favourable interfacial forces that interact between oil molecules and the starch film. The aims of this work were to formulate starch/oil nanolaminated films combining two different oil nanolayers and to investigate the improvements on water resistance and barrier properties of starch based films.

2. Materials and methods

2.1. Materials

Food grade corn starch (Unilever, Argentina) was used as polymeric matrix for film formulation. Essential lemon oil (ELO) was provided by CITROMAX S.A.C.I. (Argentina). Food grade sunflower oil (SO) was provided by Molinos Río de la Plata (Argentina). Glycerol (Mallinckrodt, USA) was added as plasticizer. Hexane was provided by Aldrich (USA). All salts used to obtain different relative humidity ambient (% RH) were provided by Aldrich (USA).

2.2. Film forming solution

Film forming dispersion was prepared by mixing 5 g of starch, 100 mL distilled water and glycerol in a concentration of 20% w/w of starch. The dispersion was gelatinized in a shaking water bath at 78–80 °C during 10 min. This procedure ensures the disintegration of starch granules to form a homogeneous solution. Starch

solution, while still hot, was cast over plastic dishes. Dishes were placed in an air-circulating oven at 45 °C until films were dry. After that, dishes were removed from the oven and the films were peeled off. Isotropic films were obtained.

2.3. Nanolaminated films

Nanolaminated films consist of oil nanolayers deposited over a starch film support. Starch/ELO/SO films were obtained according the following procedure. Starch films were stored at 53% RH for a week, before the lipid nanolayers were added. In order to form the oil nanolayer, starch films were dipped into ELO during 2 min and then, they were rinsed with hexane. Hexane was evaporated from the samples using an air flow at 25 °C for 24 h. A second layer of SO was deposited using the same procedure.

2.4. Characterization of nanolaminated starch/oil films

2.4.1. Scanning electron microscopy (SEM)

Cross-section and surface of film samples were examined by SEM using a JEOL JSM 6480 LV scanning microscope (Japan). Samples were previously stored in a relative humidity controlled ambient during a week (53% RH). Films were cryofractured by immersion in liquid nitrogen. Samples were stored at 25 °C under silica gel. Then film samples were mounted on aluminium stubs and coated with gold plasma. Samples were observed using an accelerating voltage of 15 kV.

2.4.2. Surface properties

Surface hydrophobicity was evaluated through static contact angle measurements. The contact angle was measured by the sessile drop method (Kwok and Neumann, 1999), using a goniometer (Standard Goniometer with DROP image standard, model 200-00, Ramé-Hart Instrument Co., Succasunna, USA). A small water droplet was released on the film surface, digital pictures were gathered and the image produced was used to calculate the contact angle. Contact angle measurements were taken at 5 s and 30 s for each type of film. Ten replicates were taken on each kind of film.

2.4.3. Moisture sorption isotherms

Constant relative humidity environments were established inside sorbostats (glass jars) using salt solutions. The salts used (LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, NaBr, NaCl, KCl) were the different salts recommended by the European project COST-90 (Spiess and Wolf, 1983), to cover a water activity (*a_w*) range from 0.10 to 0.90. Film samples (rectangular strips approximately 2 cm² area) were first freeze-dried (Thermovac Industries Corp, USA) and stored in a desiccator during a week. 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. Absorption tests were done in quadruplicate at each *a_w*. The moisture sorption determination was done at 25 °C.

The data obtained were fitted by GAB sorption model, as described by Eq. (1):

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

where w_e is the equilibrium moisture content (g water/100 g dry film), w_0 is the monolayer content (g water/100 g dry film), C is Guggenheim constant related to sorption heat monolayer, k is a correction factor related to sorption heat multilayer.

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

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

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 mean relative percentage error (%E) has been widely adopted throughout the literature to evaluate the goodness of fit of sorption models, with a %E value below 10% indicative of a good fit for practical applications. Test was performed in starch films and nanolaminated films at 25 °C.

2.4.4. Water vapour permeability

The apparatus and methodology described in ASTM E96 (ASTM, 2010) were used to measure film permeability. Film specimens were conditioned during 72 h in a chamber at 25 °C and 53% RH ($Mg(NO_3)_2$ saturated salt solution) before being analysed. Films were sealed on cups containing different saturated salt solution or distilled water. 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 desiccator cabin was lower than relative humidity inside the cups. Table 2 shows the range of a_w used in each assay. A fan 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 versus time and when steady state (straight line) was reached, 8 h more were registered. Thickness value was the mean of five measurements with an analogical thickness gauge (Digimess, 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. (3)) and measured water vapour permeability (P) was calculated according to Eq. (4):

$$WVTR = \frac{G}{A} \quad (3)$$

$$P = cte \times \frac{WVTR \times l}{(p_{w0} - p_{w2})} \quad (4)$$

Corrected values of water vapour permeability (P_c) were obtained according the equations proposed by Gennadios, Weller, and Gooding (1994):

$$P_c = cte \times \frac{WVTR \times l}{\Delta p_r} \quad (5)$$

$$\Delta p_r = p_{w1} - p_{w2} \quad (6)$$

$$p_{w1} = p_T - (p_T - p_{w0}) \exp^{(N_w \times h_i / c \times D)} \quad (7)$$

where l is the film thickness (cm); A is the area of exposed film (cm^2), p_{w1} is partial pressure of water vapour at underside of film (Pa), p_T is total atmospheric pressure (Pa), p_{w2} is partial pressure of water vapour at the film surface outside the cup (Pa), p_{w0} is partial pressure of water vapour in air at the surface of distilled water or

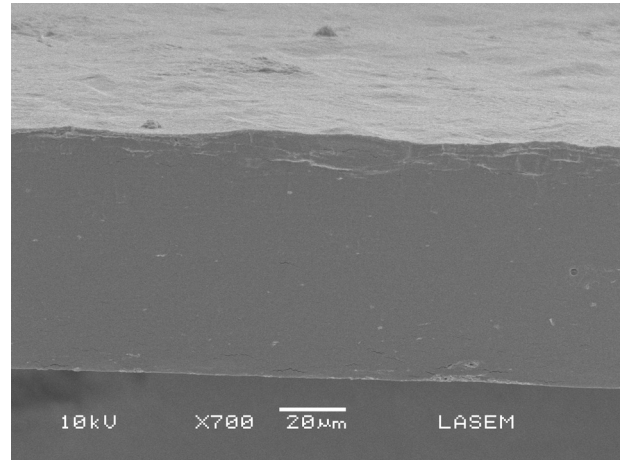


Fig. 1. SEM microphotograph of starch film (cross-section).

saturated solution, N_w is measured value of water vapour transmission rate ($g/mol\ cm^2\ s$) from surface of distilled water or saturated salt solution to the internal surface of the film (air gap resistance), h_i is air gap between film and surface of distilled water or saturated salt solution in the cup (cm), c is total molar concentration of air and water vapour ($g/mole.cm^3$), D is diffusivity of water vapour in air (cm^2/s) and cte is a constant to satisfy unit conversions. Test was carried out in triplicate for each film.

3. Results and discussion

3.1. Scanning electron microscopy

Fig. 1 shows the cross section and the surface of a starch film. Starch films exhibited a cross section of dense and homogeneous aspect and a flat and smooth surface. It is indicative that the starch granules were completely disrupted and the starch molecules were properly solubilized. Fig. 2 shows the cross section of a starch/ELO/SO nanolaminated film. This image points out the formation of oil nanolayers over the starch film surface. The nanolayer can be observed in the border of the upper side of the film due its separation from the starch matrix, Fig. 3 corresponds to the surface image of a nanolaminated film and it exhibits the strong attachment between the different layers on the starch matrix. The lipid layers show a wavy surface, which can be clearly seen in Figs. 2 and 3. This undulation of the surface is distinctly different

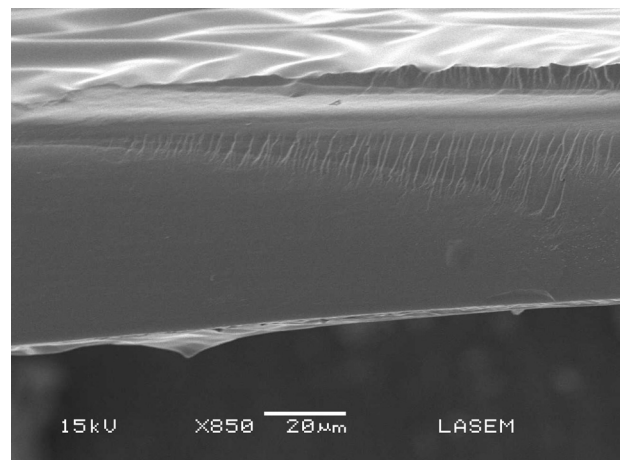


Fig. 2. SEM microphotograph of starch/ELO/SO film (cross-section).

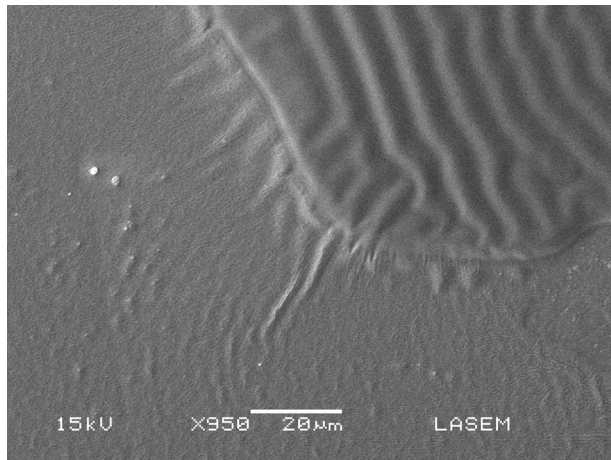


Fig. 3. SEM microphotograph of starch/ELO/SO film (surface).

Table 1

Contact angle measurements taken at different times.

Film	Contact angle	
	5 s	30 s
Starch	38.2° ± 1.2	35.3° ± 1.4
Starch/ELO	72.8° ± 2.5	71.8° ± 3.0
Starch/SO	52.4° ± 2.1	50.1° ± 1.9
Starch/ELO/SO	58.3° ± 1.7	55.9° ± 1.5

from that presented by starch films, which have a smooth, flat surface, confirming the presence of the nanolayers. Fig. 3 shows a zone with incomplete coverage of the lipid nanolayer. Starch is a hydrophilic material (polysaccharide), SO is a hydrophobic substance (fatty acids) and ELO has an intermediate behaviour (terpenes, alcohols, aldehydes, etc.) according to their composition. Therefore the compatibility between these materials is driven both, by composition and scale of work. As the size of systems goes down, surface effects become increasingly important. The control of intermolecular forces and interactions is fundamental for the achievement of the desired deposition.

3.2. Surface properties

The contact angle measurement is a useful tool to determine the hydrophobic or hydrophilic character of a film surface. The most wettable surfaces present low values ($\theta < 20^\circ$) and the hydrophobic surfaces, on the contrary, show high values ($\theta > 70^\circ$) of the contact angle. Table 1 shows contact angle measurements obtained at different times for nanolaminated film samples. Starch films presented the lower contact angle values at the different times tested. This indicates the hydrophilic character of starch film. Andrade and Sima (2005) reported similar values for maize starch films. Oil lamination over the film surface produced strong modifications. Starch/ELO films showed an important rise in the hydrophobic character of the film surface, and thus, a significant increase in contact angle due to the ELO presence. However, the addition of the second nanolayer of SO in starch/ELO/SO films resulted in a decrease in the contact angle. This contact angle value was close to that obtained for starch/SO films, according to results described by Slavutsky and Bertuzzi (2015). A similar behaviour was observed in heparin/chitosan multilayer films and pectin/chitosan films, where the last layer was dominant in surface behaviour (Fu, Ji, Yuan & Shen, 2005; De S. Medeiros et al., 2012). There are significant differences between contact angle values taken at different times in starch films due to their hydrophilicity and the high rate of the relaxation phenomena in this material. On the other hand, no significant differences were observed in contact angle of nanolaminated films.

The contact angle results showed the development of the alternated deposition of ELO and SO layers, which suggest that the layers are progressively built by deposition of the oils. According to Fu et al. (2005) the wettability of a surface depends on the nature of the outermost layer and not on the initial substrate film; however, interpenetration of layers may cause some influence on that property, especially at the nanoscale. Essential oils are very complex natural mixtures which may contain about 20–60 components at quite different concentrations. The components include two groups of distinct biosynthetic origin. The main group is composed of terpenes and terpenoids, and the other of aromatic and aliphatic constituents (Bakkali, Averdeck, Averdeck, & Idoamar, 2008). The methodology used in the formulations of starch/ELO films can be responsible of aromatic components elimination by evaporation coupled with hexane. Then, only terpenes and terpenoids remain deposited on the starch surface.

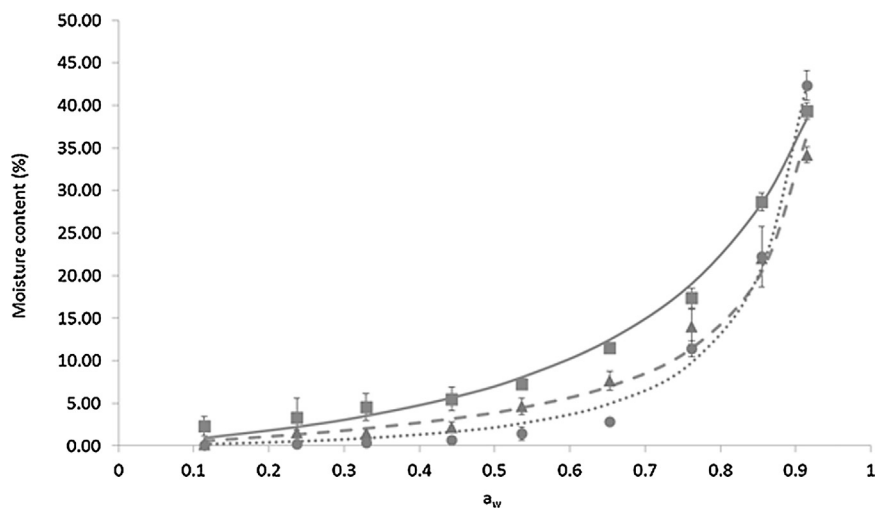


Fig. 4. Moisture sorption data of starch films (■), starch/ELO films (●) and starch/ELO/SO films (▲). GAB model fit (starch films —; starch/ELO films — — — —; starch/ELO/SO films — — — —). Bars indicate standard deviation.

Table 2
GAB model parameters of starch films and nanolaminated films.

	w_0	C	k	R^2	%E
Starch	11.352 ± 0.759	0.626 ± 0.085	0.869 ± 0.009	0.983	1.68
Starch/ELO	4.677 ± 0.569	0.112 ± 0.017	0.961 ± 0.008	0.954	4.13
Starch/ELO/SO	3.325 ± 0.416	0.285 ± 0.032	0.890 ± 0.008	0.975	2.43

Moreover, [Mayachiew, Devahastin, Mackey and Niranjana \(2010\)](#) reported that chitosan might interact with terpenes which are the major components of essential oils, mainly by weak interactions such as hydrogen bonding. The same type of interaction can be established between starch and ELO in the first nanolayer, ensuring the strong adhesion between those materials. In addition, the adhesion between ELO and SO nanolayers is due to hydrophobic bonds.

3.3. Moisture sorption isotherms

Moisture sorption experimental values of starch films and starch nanolaminated films, as well as their fitting curves using GAB model, are showed in [Fig. 4](#). These results indicate that the incorporation of lipid nanolayers produces an important decrease on water adsorption of starch films in all the range of a_w studied. The nanolaminated films display a low water uptake up to a_w values of 0.8, taking an exponential growth after this value. The increase in moisture content of films based on hydrophobic substances, at high a_w values, has been studied by several authors. [Morillon, Debeaufort, Blond, Capelle and Voilley \(2002\)](#) indicated that some hydrophobic substance containing hydrophilic groups, such as ester groups, carboxyl groups and hydroxyl groups, which can be hydrated at high values of a_w . [Donhowe and Fennema \(1992\)](#) reported that water content of beeswax film increases exponentially at a_w around 0.8. These results are according to those showed in [Fig. 4](#). The complex chemical composition of ELO and its amphiphilic characteristics, combined with SO hydrophobicity resulted in a material with improved water resistance, even at high water activity. In contrast to bi-layer films, nanolaminated films do not present fractures or delamination of the lipid layer.

GAB model parameters calculated for the different film samples are presented in [Table 2](#). Monolayer water content of Starch/ELO/SO films (3.325%) was substantially lower than that presented by starch films (11.352%). Starch/ELO films showed a value slightly higher than Starch/ELO/SO. The deposition of lipid nanolayers reduces the number of active sites of the film surface available for water molecule interaction. The C values are related to the

Table 3
Water vapour permeability of starch films and nanolaminated films under different driven forces.

$a_w^{ext} - a_w^{int}$	$ \Delta a_w $	$P_m \times 10^{10} \text{ g/m s Pa}$	$P_c \times 10^{10} \text{ g/m s Pa}$	Thickness (μm)
Starch				
0.329–0.536	0.207	3.73 ± 0.19	7.14	83 ± 7
0.536–0.762	0.226	4.59 ± 0.18	8.02	85 ± 6
0.762–1	0.238	6.93 ± 0.25	18.8	85 ± 4
Starch/ELO				
0.329–0.536	0.207	1.80 ± 0.11	2.44	82 ± 3
0.536–0.762	0.226	2.14 ± 0.09	3.11	85 ± 6
0.762–1	0.238	3.48 ± 0.26	7.03	86 ± 7
Starch/ELO/SO				
0.329–0.536	0.207	2.22 ± 0.21	3.32	88 ± 3
0.536–0.762	0.226	2.82 ± 0.12	4.82	83 ± 8
0.762–1	0.238	4.47 ± 0.34	9.01	84 ± 9

enthalpy of sorption, then indicates the affinity between water molecules and the film surface. The obtained values were according to the water content of each type of films and showed the same trend that the monolayer water content (w_0). All k values were below 1, showing that model selection was correct.

3.4. Water vapour permeability

Permeability of hydrophilic films depends both, on the relative humidity difference and on the absolute humidity values at both sides of the film ([Slavutsky & Bertuzzi, 2012](#)). Water vapour permeability was measured in three different intervals of the water activity range, in order to evaluate the effect of these parameters. [Table 3](#) shows permeability values obtained for a water activity difference (Δa_w) through the film of approximately 0.2, in three different ranges of a_w . Permeability increased with a_w values at each side of the film, when a similar driving force (Δa_w) was used. It is related to the increasing water solubility in the film with a_w showed by the sorption isotherms ([Fig. 4](#)). Water molecules plasticize starch films, even at low relative humidity gradient. Then, permeability increases with increasing film water content. The more plasticized the film, the higher water permeability values were obtained. Starch nanolaminated films presented similar behaviour than starch films, but their permeability values were reduced by half for all driving forces and ranges of a_w studied. Permeability of nanolaminated films also depended on Δa_w . These results indicate that nanolaminated films formulated using lipids are capable to repel water molecules. [Morillon et al. \(2002\)](#) reported a similar behaviour for several lipids compound. They observed that at the same relative humidity gradient, permeability increase with a_w range at each side of the films. Permeability values were consistent with the results of contact angle and sorption isotherms of the samples. Starch films exhibited a high hydrophilicity, followed by Starch/ELO/SO and finally Starch/ELO with the lowest water affinity. This can be due to water permeation phenomenon, in nanolaminated films, is controlled by the diffusion process through hydrophobic nanolayers. The study of the sorption isotherms indicates that water content of films plays a determinant role in the permeation process. At low a_w , water content of nanolaminated films is much lower than starch films, while at high a_w the moisture content has similar values. Deposited oil nanolayers form a barrier against water molecule transport due to their hydrophobic characteristic.

4. Conclusion

Nanolaminated films were formed by coating a starch films with lipid nanolayers. The nanolayer formation was proved by SEM images and surface properties. Images indicated that nanolayers were strongly attached to the starch surface and present a wavy aspect. Sorption isotherms evidenced a decrease in water adsorption of nanolaminated films in all the range of water activities. Permeation phenomenon was controlled by the water diffusion through the lipid nanolayers in starch/ELO/SO films. Then, the incorporation of lipid nanolayers improved the water vapour resistance and decreased by nearly half the water vapour permeability of starch films.

Acknowledgements

The financial support provided by Consejo de Investigación de la Universidad Nacional de Salta (CIUNSA) and by Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) are gratefully acknowledged. The authors thank technical assistance of LASEM (Laboratorio de Microscopia Electrónica de Barrido, ANPCyT, CONICET, UNSA).

References

- Andrade, C. T., & Sima, R. A. (2005). Surface modification of maize starch films by low-pressure glow 1-butene plasma. *Carbohydrate Polymers*, 61, 407–413.
- ASTM. (2010). Standards American Society for testing and materials. E96. Standard test methods for water vapour transmission of materials. Philadelphia.
- Averous, M. O. L. (2001). Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer*, 42, 6209–6219.
- Bakkali, F., Averbeck, S., Averbeck, D., & Idaomar, M. (2008). Biological effects of essential oils—a review. *Food and Chemical Toxicology*, 46(2), 446–475.
- Bertuzzi, M. A., Castro Vidaurre, E. F., Armada, M., & Gottifredi, J. C. (2007). Water vapor permeability of edible starch based films. *Journal of Food Engineering*, 80(3), 972–978.
- Bodirlau, R., Teaca, C. A., & Spiridon, J. (2013). Influence of natural fillers on the properties of starch-based biocomposite films. *Composites: Part B*, 44, 575–583.
- Carneiro-da-Cunha, M. G., Cerqueira, M. A., Souza, B. W. S., Carvalho, S., Quintas, M. A. C., Teixeira, J. A., et al. (2010). Physical and thermal properties of a chitosan/alginate nanolayered PET film. *Carbohydrate Polymers*, 82, 153–159.
- Chen, Y., Liu, C., Chang, P. R., Cao, X., & Anderson, D. P. (2009). Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: Effect of hydrolysis time. *Carbohydrate Polymers*, 76(4), 607–615.
- De S. Medeiros, B. G., Pinheiro, A. C., Carneiro-da-Cunha, M. G., & Vicente, A. A. (2012). Development and characterization of a nanomultilayer coating of pectin and chitosan—evaluation of its gas barrier properties and application on “Tommy Atkins” mangoes. *Journal of Food Engineering*, 110(3), 457–464.
- Debeaufort, F., Quezada-Gallo, J. A., Delporte, B., & Voilley, A. (2000). Lipid hydrophobicity and physical state effects on the properties of bilayer edible films. *Journal of Membrane Science*, 180, 47–55.
- Donhowe, I. G., & Fennema, O. (1992). The effect of relative humidity gradient on water vapour permeance of lipid and lipid-hydrocolloid bilayer films. *Journal American Oil Chemistry Society*, 69, 1081–1087.
- Fu, J., Ji, J., Yuan, W., & Shen, J. (2005). Construction of anti-adhesive and antibacterial multilayer assembly of heparin and chitosan. *Biomaterials*, 26, 6684–6692.
- Gennadios, A., Weller, C. L., & Gooding, C. H. (1994). Measurement errors in water vapour permeability of highly permeable, hydrophilic edible films. *Journal of Food Engineering*, 21(4), 395–409.
- Kampeerappun, P., Aht-ong, D., Pentrakoon, D., & Srikulkit, K. (2007). Preparation of cassava starch/montmorillonite composite film. *Carbohydrate Polymers*, 67, 155–163.
- Kwok, D. Y., & Neumann, A. W. (1999). Contact angle measurement and contact angle interpretation. *Advantage in Colloid and Interface Science*, 81, 167–249.
- Liu, H., Chaudhary, D., Yusa, S., & Tade, M. O. (2011). Glycerol/starch/Na⁺-montmorillonite nanocomposites: a XRD, FTIR, DSC and 1H NMR study. *Carbohydrate Polymers*, 83(4), 1591–1597.
- Mayachiew, P., Devahastin, S., Mackey, B. M., & Niranjana, K. (2010). Effects of drying methods and conditions on antimicrobial activity of edible chitosan films enriched with galangal extract. *Food Research International*, 43, 125–132.
- Morillon, V., Debeaufort, F., Blond, G., Capelle, M., & Voilley, A. (2002). Factors affecting the moisture permeability of lipid-based edible films: a review. *Critical Reviews in Food Science and Nutrition*, 42(1), 67–89.
- Parra, D. F., Tadini, C. C., Ponce, P., & Luga, A. B. (2004). Mechanical properties and water vapour transmission in some blends of cassava starch edible films. *Carbohydrate Polymers*, 58, 475–481.
- Perdomo, J., Cova, A., Sandoval, A. J., García, L., Laredo, E., & Müller, A. J. (2009). Glass transition temperatures and water sorption isotherms of cassava starch. *Carbohydrate Polymers*, 76(2), 305–313.
- Pérez-Gago, M. B., & Krochta, J. M. (2005). Emulsion and bi-layer edible films. In J. H. Han (Ed.), *Innovations in food packaging* (pp. 384–402). New York: Elsevier Academic.
- Phan The, D., Debeaufort, F., Luu, D., & Voilley, A. (2008). Moisture barrier, wetting and mechanical properties of shellac/agar or shellac/cassava starch bilayer bio-membrane for food applications. *Journal of Membrane Science*, 325(1), 277–283.
- Rhim, J. W., & Shellhammer, T. H. (2005). Lipid-based edible films and coatings. In J. H. Han (Ed.), *Innovations in Food Packaging* (pp. 362–383). London, U.K.: Academic Press.
- Rubner, M. F. (2003). pH-controlled fabrication of polyelectrolyte multilayers: assembly and applications. In G. Decher, & J. B. Schlenoff (Eds.), *Multilayer thin films: sequential assembly of nanocomposite materials* (pp. 133–154). New York: Weinheim & Wiley-VCH.
- Rudra, J. S., Dave, K., & Hayne, D. T. (2006). Antimicrobial polypeptide multilayer nanocoatings. *Journal of Biomaterial Science Polymer Edition*, 17(11), 1301–1315.
- Sánchez-González, L., Chiralt, A., González-Martínez, C., & 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(2), 246–253.
- Slavutsky, A. M., & Bertuzzi, M. A. (2012). A phenomenological and thermodynamic study of the water permeation process in corn starch/MMT films. *Carbohydrate Polymers*, 90(1), 551–557.
- Slavutsky, A. M., & Bertuzzi, M. A. (2014). Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. *Carbohydrate Polymers*, 110, 53–61.
- Slavutsky, A. M., & Bertuzzi, M. A. (2015). Formulation and characterization of nanolaminated starch based film. *LWT—Food Science and Technology*, 61(2), 407–413.
- Slavutsky, A. M., Armada, M., & Bertuzzi, M. A. (2012). Water barrier properties of starch-clay nanocomposite films. *Brazilian Journal of Food Technology*, 15(3), 208–218.
- 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 Hydrocolloids*, 35, 270–278.
- Spiess, W. E. L., & Wolf, W. F. (1983). The results of the COST 90 project on water activity. *Physical properties of foods*. London: Applied Science Publishers.
- Svagan, A. J., Hedenqvist, M. S., & Berglund, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Composites Science and Technology*, 69(3–4), 500–506.
- Vargas, M., Albors, A., & Chiralt, A. (2011). Application of chitosan-sunflower oil edible films to pork meat hamburgers. *Procedia Food Science*, 1(11), 39–43.
- Vieira, M. G. A., Da Silva, M. A., Dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: a review. *European Polymer Journal*, 47(3), 254–263.
- Zahedi, Y., Ghanbarzadeh, B., & Sedaghat, N. (2010). Physical properties of edible emulsified films based on pistachio globulin protein and fatty acids. *Journal of Food Engineering*, 100, 102–108.