



Hydration and water vapour transport properties in yeast biomass based films: A study of plasticizer content and thickness effects



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ABSTRACT

Research on biodegradable films is a topic of strategical interest in the field of food science and technology. These films are membranes conformed by biopolymers that interact strongly with water and they generally require the addition of plasticizer in order to improve its integrity and mechanical properties. The study of the hydration and water transfer properties through these films, as well as understanding in what way the thickness and the addition of the plasticizer affect these properties, is essential for a better knowledge and optimization of the required protective function of these membranes. In this work the hydration kinetics and water transport through biodegradable films obtained from yeast biomass were studied, in order to know the performance against changes in thickness and glycerol content. Hydration kinetics experiments allowed obtaining solubility of water in the matrix film, and the diffusion coefficient. Results demonstrated that when glycerol content was increased, the solubility of water increased while diffusion remained constant. Moreover, when the film thickness was grown, the solubility of water decreased but the diffusion increased. Experimental water vapour permeability obtained through traditional cup method was compared to the theoretical permeability calculated by multiplying diffusion coefficient and water solubility. The good agreement observed between both values allowed the analysis of how solubility and diffusion contributed to permeability. As a result this study revealed that the increment of permeability with the plasticizer content was due to the increase in solubility, while the effect of the thickness increasing permeability was dominated by diffusion.

1. Introduction

Research and development of new methods to extend shelf-life and make a better use of available resources are very active areas in the field of food science and technology. In this regard, the study of biodegradable coatings and films based on biopolymers has taken great interest in recent years [1–5]. These films are a thin matrices preformed from a solution or dispersion of biopolymers. To form the film matrix it is necessary to remove the solvent by an appropriate method in order to decrease the distance between polymers and favouring their interaction [5]. This interaction promotes an interleaving of polymers chains that increase the viscosity of the system, allowing the formation of a polymer network that will be ended with a film conformation [5].

For food applications, these films should present certain flexibility and they must offer a good protection acting as a permselective membrane [6,7]. Plasticizers increase film flexibility due to their ability to reduce internal forces between polymer chains while increasing molecular space [8]. The best plasticizers will generally resemble most closely the structure of the polymer that they plasticize, thus polyols

such as glycerol are commonly used in biopolymers based films [9].

The analysis of interactions between these films and water molecules has a great importance in the area of packaging, in order to know if films can be applied as an efficient barrier to avoid hydration or dehydration of the food. Depending on the type of food where the coating or film will be applied, in some cases they may require low water vapour permeability [7]. For other products, it may act as sacrificing agent losing in first place its own humidity and preserves the humidity of the food product, extending the shelf-life [10].

Polysaccharides and proteins interact strongly with water; therefore films made from these biopolymers are hydrophilic films. Films based on yeast biomass represent a good model for the study of hydrophilic films and their interaction with water because they are formed basically by polysaccharides and proteins [11].

In general, hydrophilic films made from biopolymers show water sorption isotherms with a slight increase in hydration water content for low values of water activity (a_w), and a significant increase for $a_w > 0.6$ [5,11]. This shape of sorption isotherms suggests that the hydration is presented in a multilayer form, with a small amount of water strongly

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bounded to the polymeric matrix forming the monolayer and then, most of the hydration water forming multilayers [5,11], which are indirectly bounded to the polymer matrix [12]. As follows, hydration water in these materials is susceptible to be moved by diffusion mechanism.

The study of the water transport properties through films is essential for a better understanding and optimization of the required protective function of these membranes [13,14]. Hydration water affects the main structural and functional properties of hydrophilic films [15], because water acts as plasticizer by embedding itself between the polymers chains, spacing them, lowering the glass transition temperature (T_g), and affecting flexibility [16].

The water transport through polymeric films does not occur through pores, but can be understood through a simple model that proposes that process occurs in four steps: (i) absorption of water vapour on to the polymer matrix surface; (ii) solution of water vapour into the polymer matrix; (iii) diffusion of water vapour through the matrix; and (iv) desorption of water vapour from the other surface of the film [17,18]. Therefore water vapour permeability in these materials depends on the hydration or solubility of water in the film, as well as the water mobility within the matrix [18,19]. Thus, the chemical structure, polarity, degree of crystallinity, density, crosslinking degree, molecular weight and polymerization, as well as the presence of other plasticizers, are factors affecting permeability, because they influence hydration properties, degree of molecular mobility and diffusion through the material [13,20,21].

The mechanism in which water molecules are transported through hydrophilic polymeric films is a complex phenomenon not well understood. It was reported some anomalies that occur in biopolymeric films strongly interacting with the species that permeates, especially the strong dependence of permeability coefficient with film thickness [22–25] and plasticizer content [26–29]. Therefore, understanding in what way the thickness and the addition of the plasticizer affect the permeation process, is essential for a better knowledge and optimization of the required protective function of these membranes. The aim of this work is contribute to the explanation of these aspects, not completely lightened up to now [30].

In this work, the hydration kinetics and water transport through biodegradable films obtained from yeast biomass were studied against changes in film thickness and glycerol content. Through kinetics experiments, the solubility of water in the matrix film and the diffusion coefficient of water were obtained. Taking into consideration that the theoretical permeability coefficient is expressed as the contribution of solubility of water in the film and the diffusion of the permeant in the matrix [17–20], this theoretical quantity was compared with experimental permeability obtained by the traditional cup method [31]. The agreement between theoretical and experimental permeability allowed studying the effect of thickness and plasticizer on the water vapour permeability, in a more comprehensive manner analysing the contribution of solubility and diffusion.

2. Materials and methods

2.1. Materials

Saccharomyces cerevisiae yeast cells were obtained from commercial pressed cells from Calsa, AB Mauri (Tucumán, Argentina). Glycerol, silica gel, and all salts used were purchased from Biopack (Buenos Aires, Argentina).

2.2. Preparation of films

Films were prepared by using *Saccharomyces cerevisiae* yeast cells that were previously cleaned with distilled water and centrifuging at 750g. The supernatant was discarded and replaced by distilled water to reach 10% w/vol (dry matter of yeast/volume). As described in a previous work [11], the standardized dispersion was submitted to high

pressure homogenization (H) at 125 MPa in a continuous flow during 9 min, followed by a thermal treatment (T) in a water bath at 90 °C for a time lapse of 20 min. A second high pressure homogenization step was applied at the same conditions of the first homogenization process to obtain the sample named HTH [11]. The final pH of the prepared dispersions was 6. Glycerol was added to dispersion at levels of 0, 10, 20, and 30% w/w with respect to dry matter (d.m.). Volumes of 5, 10, and 20 mL of HTH dispersions were placed in 8.6×10^{-2} m diameter Petri dishes, in order to obtain films of thicknesses close to 7, 15, and 30×10^{-5} m respectively. Evaporation of water was done at 40 °C in a ventilated oven, until the remaining water content of the films was between 10 and 15%. Next, films were stored at 24 °C and 43% r.h. generated by a saturated solution of K_2CO_3 .

2.3. Density and thickness measurements

For density determination of dried films, samples with $5.8 \times 10^{-3} \text{ m}^2$ of circular area were dried at 0% r.h. into desiccators containing silica gel until a constant weight was achieved; this process lasted around 7 days. Films were weighed using analytical balance ($\pm 10^{-4}$ g). Thickness was measured by a digital calliper ($\pm 10^{-6}$ m) at ten different places of the film, obtaining for each specimen an average value with an error lower than 5%. The values measured were close to 7, 15, and 30×10^{-5} m, as expected according to the volumes of 5, 10, and 20 mL of dispersion placed in the Petri dishes. Film density was calculated through Eq. (1)

$$\rho_{d.f.} = \frac{m}{AL} \quad (1)$$

where $\rho_{d.f.}$ is the density of dried film (g m^{-3}), m the dry mass (g), A the area (m^2), and L the thickness (m).

2.4. Microstructural characterization by scanning electron microscopy (SEM)

The equipment used was a scanning electron microscope SEM LEO EVO 40-XVP (Carl Zeiss AG, Germany). For best viewing under a microscope, the samples were coated with a gold layer. Magnifications used were $500\times$ with a potential difference of 5kV. The absolute pressure during the study was 80 Pa (High vacuum conditions).

2.5. Kinetics of water sorption experiments

Dried films with different content of glycerol and thickness, were placed in Petri dishes and located into a sorption container at 90% r.h. generated by a saturated solution of $BaCl_2$. A fan was used to maintain uniform conditions inside the desiccators following the recommendations of previous authors [22]. Samples were removed at specific intervals of time and weighted for data collection. Weighing of samples was made using analytical balance ($\pm 10^{-4}$ g). The water content h , given in units of g of water per g of dried mass was evaluated as function of time t , taking the difference between the mass of the hydrated film and that of the dried film. Three replicates of each film were tested. Experiments were carried out at 24 °C.

Water content as function of time, $h(t)$, was fitted with Fick's mass transport differential law solution in Fourier series, for one-dimensional diffusion of water in a plane infinite sheet as was described by Crank [32], and done by Eq. (2)

$$h(t) = h_{\infty} \left\{ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[-D_w^{\text{eff}} (2n+1)^2 \frac{\pi^2 t}{4L^2} \right] \right\} \quad (2)$$

where h_{∞} is the water content at equilibrium, L is the film thickness, and D_w^{eff} is the apparent diffusion coefficient in units of $\text{m}^2 \text{ s}^{-1}$. Hydration experiments were performed with one surface of the film exposed to the wet atmosphere, where water molecules penetrated in

direction to the other face, in contact with the Petri dish. Because of this, the characteristic length in Eq. (2) is the film thickness L .

In kinetic experiments, h_∞ corresponds to the water content of the film in equilibrium at 90% r.h. This value was used to obtain the water solubility coefficient $\beta = (h_\infty p_s^{-1})$ [33], at the vapour saturation pressure $p_s = 2687.3$ Pa corresponding to the atmosphere of 90% r.h. at 24 °C. According to the Henry's law, the solubility of water S_w in the film at 90% r.h., is given by Eq. (3)

$$S_w = \beta \rho_{d.f.} = \frac{h_\infty}{p_s} \rho_{d.f.} \quad (3)$$

where S_w is given in units of g of water per m³ of dried mass per Pa, and $\rho_{d.f.}$ is the dry matter density of the film.

2.5.1. Short time lapse (STL) model

In the initial period of sorption, the water uptake as function of time $h(t)$ can be expressed as displayed in Eq. (4) [34].

$$h(t) = 2h_\infty \left(\frac{D_w^i t}{\pi L^2} \right)^{1/2} \quad (4)$$

Eq. (4) was proposed to fit sorption data when $h(t)/h_\infty < 2/3$ [34]. This equation gives a value of initial diffusion coefficient D_w^i that take into account the diffusion of water in the film during the initial period of sorption (first twelve hours in the present study). As was used in previous equations, L is the film thickness.

2.5.2. Type of transport through the film

Korsmeyer & Peppas (KP) model [35] was used to evaluate the type of transport, fitting the kinetics data by the Eq. (5)

$$h(t) = h_\infty k t^n \quad (5)$$

where k is a constant that depends on characteristics of the matrix, and n is the diffusional exponent. Eq. (5) is valid for $h(t)/h_\infty \leq 2/3$. The Korsmeyer & Peppas equation is based on Eq. (4), when n is equal to 0.5 both equations are essentially the same and the transport is purely fickian. In this way, n is an indicator of how the process is deviated from the ideal transport and determines the type of diffusion of water through the film [36,37]:

- $0 < n \leq 0.5$: quasi-fickian or fickian diffusion
- $0.5 < n \leq 1$: non-fickian or anomalous diffusion, where diffusion of water is very rapid as compared with the relaxation process of polymer chains, and the latter controls the sorption process.

2.6. Water vapour permeability

2.6.1. Indirect determination of permeability from diffusion and solubility coefficients

Water transport through polymeric films depends on the hydration or solubility of water in the film, as well as the water mobility within the same [18,19]. When there are no pores, faults or film punctures, permeability P can be expressed by multiplying the diffusion coefficient D and the solubility coefficient S [18,19,24]. Therefore, water vapour permeability P_w is defined as displayed in Eq. (6)

$$P_w = D_w S_w \quad (6)$$

where P_w is given in units of g s⁻¹ m⁻¹ Pa⁻¹, and S_w and D_w can be obtained by Eq. (3) and Eq. (4), respectively. In the ideal case, permeability is only an intrinsic property of film when D and S are not influenced by permeant content. In practice, for most biodegradable films the permeant interacts with the matrix film, though D and S are dependent on differential partial pressures between the film faces.

2.6.2. Experimental determination of water vapour permeability

The apparatus and methodology described in ASTM-E96 (2016)

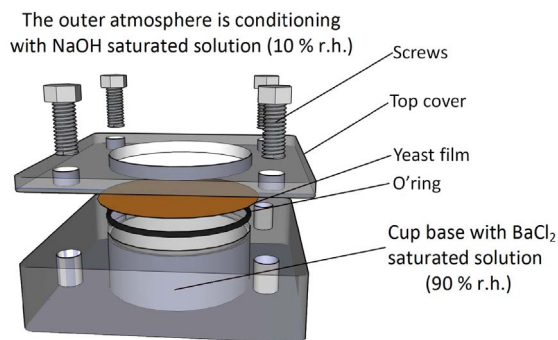


Fig. 1. Scheme of the cell used to measure the experimental water vapour permeability of yeast film.

were used to measure the experimental water vapour permeability P_w^{exp} of the films [31]. Films were conditioned during ten days at 24 °C and 43% r.h. Afterwards, films were sealed on top of the cups which contained a saturated solution of BaCl₂ that provides the highest r.h. of 90% (see Fig. 1). Test cups were placed in desiccators cabinets at 10% r.h. provided by a saturated solution of NaOH. A fan was placed over the films to maintain uniform conditions inside the desiccators, according to the recommendations of previous authors [22,23]. Experiments were performed at 24 °C.

Weight loss measurements were carried out by weighing the test cup using an analytical balance ($\pm 10^{-3}$ g). Weight loss versus time was plotted and when steady state (straight line) was reached 10 h further were registered. The water vapour flux through the film J_w was calculated from the slope of a linear regression of weight loss versus time ($\Delta m/\Delta t$) by Eq. (7)

$$J_w = \frac{1}{A} \left(\frac{\Delta m}{\Delta t} \right) \quad (7)$$

where A is the effective area of exposed film (2.2×10^{-3} m²). The experimental water vapour permeability P_w^{exp} was calculated according to Eq. (8)

$$P_w^{\text{exp}} = \frac{J_w L}{\Delta p_w} \quad (8)$$

where L is the film thickness, and $\Delta p_w = (p_{w2} - p_{w1})$ is the differential water vapour partial pressure across the film, p_{w1} and p_{w2} are the partial pressures (Pa) of water vapour at the film surface outside and inside the cup, respectively, corrected by air gap distance (5×10^{-3} m in the present study) between saturated solution of BaCl₂ level and the film position [23]. The experiment was carried out with films of different content of glycerol and thickness, and repeated three times for each type of film.

Eq. (8) is derived from a combination of Fick's and Henry's laws for vapour or gas diffusion through films and assumes that there is no interaction between the matrix film and the diffusing gas or vapour molecules [13,19,38]. Ideally, when no interaction occurs between a polymer film and the permeating water vapour, permeability is independent of Δp_w . However, permeation of water vapour through hydrophilic films deviates substantially from the ideal behaviour and depend on Δp_w [13,19,38]. Thus, the value of the permeability obtained through Eq. (8) is named as experimental water vapour permeability P_w^{exp} [38].

2.7. Statistical analysis

Statistical analyses were performed using OriginPro 8 (OriginLab Corporation). The data were subjected to the analysis of variance, and the means were compared using Student's t -test. Differences were considered to be significant at $P < .05$.

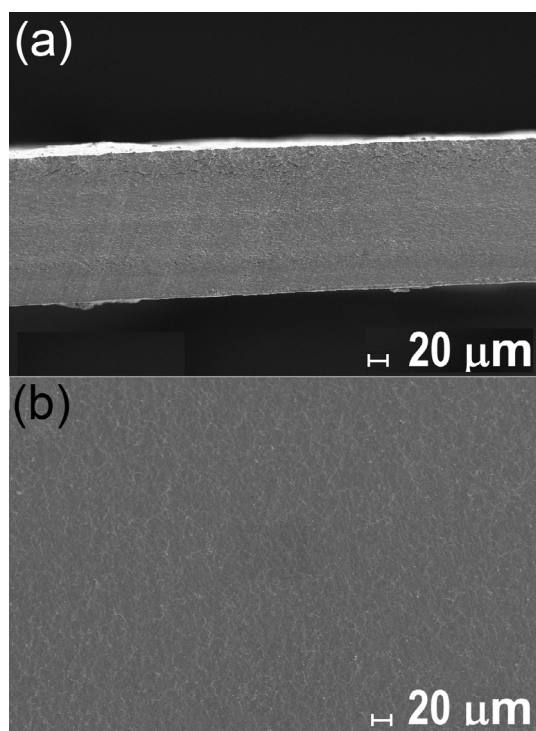


Fig. 2. SEM observations of cross-sections (a) and of the face (b) of unplasticized film. Magnification used was $500\times$.

3. Results and discussion

3.1. Microstructural characterization of films

The micrographs displayed in Fig. 2 allowed to know how the biopolymers are organized in the matrix film. Images obtained of unplasticized and plasticized films were practically indistinguishable.

Fig. 2(a) shows the obtained cross section image of the unplasticized film and a continuous and homogenous matrix was exhibited, without agglomerates, pores, faults, or film punctures. The image of the face of the film (Fig. 2(b)) demonstrated that no cell particles were distinguished and yeast cell wall structures were lost. These studies indicated that water transport in yeast biomass based films did not occur through pores but by means of the mechanism of sorption-diffusion-desorption [17,18].

3.2. Kinetics of water sorption

A key role of packaging materials including edible films is to reduce the exchange of water between the food and the environment, in particular to reduce drying of moist foods. The barrier properties to water vapour depends on both the molecular diffusion coefficient D_w and the solubility of water in the film S_w [17–20]. The kinetics of water sorption gives information about the mobility of the water in the film by determining the diffusion coefficient D_w . In addition, at equilibrium, kinetics experiments give values of solubility of water S_w . Therefore, it is particularly important to characterize the hydration of the film through kinetics of water uptake.

3.2.1. Effect of glycerol

Fig. 3 displays the plots representing the kinetics of water sorption at 90% r.h. of films with glycerol contents of 0, 10, 20, 30% w/w d.m. at the different thicknesses studied.

The curves connecting the experimental data in Fig. 3 were the best fittings using Eq. (2) (Crank model). Table 1 shows parameters obtained from fitting of experimental data. Kinetics data of Fig. 3 revealed that

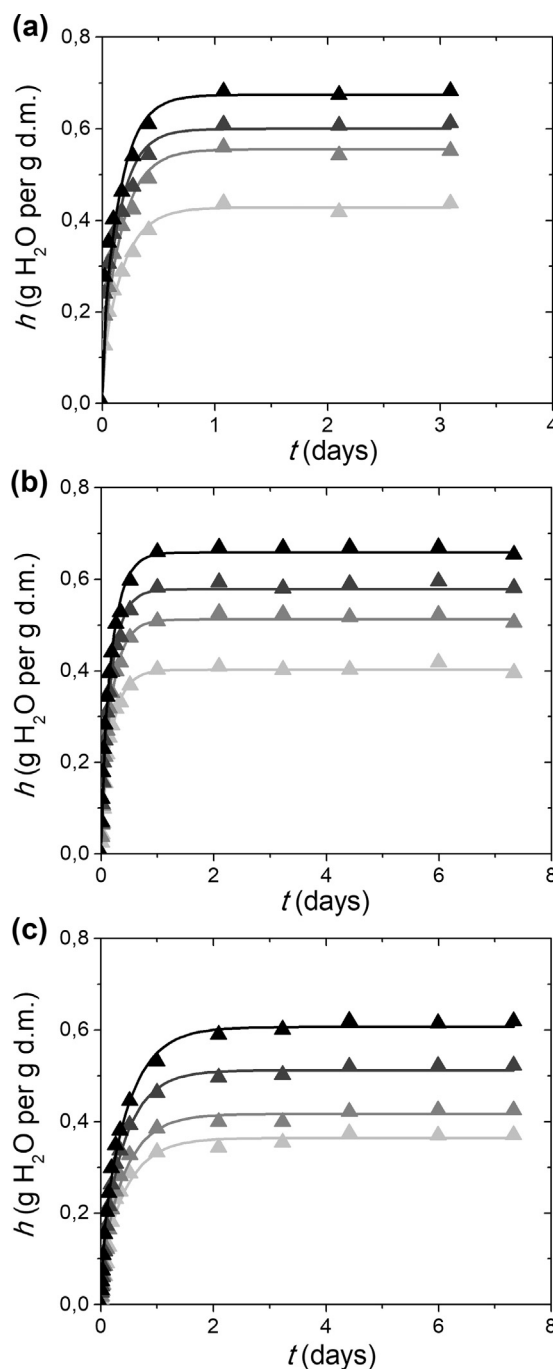


Fig. 3. Kinetics of water sorption at 90% r.h. of films with glycerol content of \blacktriangle , \blacktriangle , \blacktriangle , \blacktriangle 0, 10, 20, and 30% w/w d.m. (a) Films of $7 \pm 0.6 \times 10^{-5}$ m of thickness (b) Films $15 \pm 0.8 \times 10^{-5}$ m of thickness (c) Films of $30 \pm 1.3 \times 10^{-5}$ m of thickness. Experimental data were fitted with Eq. (2). Best fitting parameters are given in Table 1.

for all thicknesses studied, the hydration water h increased when glycerol content in films increased. As can be seen in Fig. 3 and Table 1, the addition of glycerol produced an increase in h_{∞} , the water content at equilibrium at 90% r.h. Glycerol reduces intermolecular forces between polymer chains, spacing them, and in this way, the plasticizer increases the amount of water molecules hydrating the film [39,40].

Table 1 displays values of the apparent diffusion coefficient D_w^{eff} obtained by Crank model (Eq. (2)). In fact, when a fully dehydrated film is exposed to a high relative humidity environment, the film undergoes to gradually transformations in the mobility of polymer chains (in some cases from glassy to rubber state at room temperature) due to the advance of the water front, therefore D_w^{eff} represents an average value

Table 1

Values of the parameters D_w^i ($10^{-13} \text{ m}^2 \text{ s}^{-1}$), D_w^{eff} ($10^{-13} \text{ m}^2 \text{ s}^{-1}$), h_∞ (g of H_2O per g d.m), k , and n , as determined by best fit analysis of water sorption kinetics experiments at 90% r.h. displayed in Fig. 2. Parameters were fitted using different models: Short Time Lapse (STL) (Eq. (4)), Crank (Eq. (2)), and Korsmeyer & Peppas (KP) (Eq. (5)). S_w ($\text{g m}^{-3} \text{ Pa}^{-1}$) was calculated from Eq. (3) using h_∞ obtained from Crank model.

Thickness L	% Glycerol content	STL model	Crank model				KP model		
		D_w^i	D_w^{eff}	h_∞	S_w	R^2	k	n	R^2
$7.0 \pm 0.6 (10^{-5} \text{ m})$	0	6.1 ± 0.9	1.2 ± 0.2	0.43 ± 0.02	182 ± 10	0.991	1.6 ± 0.1	0.42 ± 0.02	0.998
	10	6.2 ± 0.9	1.3 ± 0.2	0.56 ± 0.03	267 ± 11	0.991	1.3 ± 0.1	0.35 ± 0.03	0.998
	20	6.7 ± 0.9	1.5 ± 0.3	0.60 ± 0.03	306 ± 14	0.990	1.2 ± 0.1	0.28 ± 0.02	0.999
	30	6.6 ± 0.9	1.4 ± 0.3	0.68 ± 0.04	368 ± 19	0.990	1.0 ± 0.1	0.24 ± 0.01	0.999
$15.0 \pm 0.8 (10^{-5} \text{ m})$	0	21 ± 1	5.0 ± 0.4	0.40 ± 0.02	153 ± 11	0.992	4.3 ± 0.3	0.89 ± 0.03	0.998
	10	21 ± 2	5.1 ± 0.3	0.51 ± 0.02	216 ± 10	0.991	2.4 ± 0.2	0.67 ± 0.03	0.992
	20	22 ± 2	5.4 ± 0.2	0.58 ± 0.02	251 ± 11	0.995	1.8 ± 0.1	0.53 ± 0.02	0.997
	30	21 ± 2	5.1 ± 0.2	0.66 ± 0.02	310 ± 11	0.994	1.7 ± 0.1	0.52 ± 0.02	0.994
$30.0 \pm 1.3 (10^{-5} \text{ m})$	0	41 ± 1	9.3 ± 0.9	0.36 ± 0.01	132 ± 11	0.990	2.2 ± 0.1	0.93 ± 0.03	0.997
	10	42 ± 2	9.6 ± 0.9	0.42 ± 0.02	157 ± 11	0.991	1.7 ± 0.1	0.75 ± 0.03	0.995
	20	43 ± 2	9.9 ± 0.8	0.51 ± 0.02	209 ± 12	0.994	1.6 ± 0.1	0.70 ± 0.03	0.994
	30	42 ± 3	9.1 ± 0.8	0.61 ± 0.02	262 ± 13	0.991	1.4 ± 0.1	0.64 ± 0.02	0.995

throughout the process. Table 1 also shows values of the initial diffusion coefficient D_w^i obtained from STL model, fitting the initial period of sorption with Eq. (4). D_w^i takes into consideration the diffusion of water in the film during the initial twelve hours of sorption, and it can be considered constant during the hydration at this period of time [34], where the increment of volume is not remarkable. According to values displayed in Table 1, in all experimental conditions D_w^{eff} is lower than D_w^i , but both showed similar behaviour with the presence of plasticizer; this is, for a given thickness, the glycerol content did not cause any perceivable change considering experimental errors in those values. Similar results were reported for diffusion coefficients determinations in films obtained with cassava starch [41] and keratin [42]. In these works, the authors calculated diffusion coefficient indirectly through values measured of P_w^{exp} and S_w via $D_w = P_w^{\text{exp}}/S_w$, and observed that D_w was not altered by the incorporation of glycerol [41,42].

It is interesting to note that water and glycerol are plasticizers that produce changes in polymer mobility, but those changes were not produced in the same way. Other authors have observed the difference between water and glycerol through the study of fluorescein diffusion in iota-carrageenan films [43]. They observed that diffusion coefficient is more influenced by water than glycerol, in particular they detected that diffusion is independent of glycerol content below 31% w/w.

From values of h_∞ and Eq. (3), the solubility of water in the matrix at 90% r.h., S_w , was obtained. Fig. 4(a) and (b) show S_w and D_w^i respectively, both as function of glycerol content in films of different thickness.

The increase in the hydration at equilibrium h_∞ due to the glycerol content is manifested on the behaviour of S_w (Fig. 4(a)). The addition of glycerol increased the amount of hydration water of biopolymeric films, and consequently water solubility, as reported elsewhere [39,40,48]. However, those studies did not explore how the relationship between water solubility and glycerol was. The present study demonstrated that S_w increased linearly with the amount of glycerol, for each thickness studied. Moreover, as it can be observed in Fig. 4(b) glycerol content did not cause any perceivable change in D_w^i considering experimental errors.

3.2.2. Effect of thickness

The effect of thickness on the hydration properties of films was evident from the results showed in Fig. 4(a) and (b). To further characterize the effect of thickness, the data shown in Fig. 4(a) and (b) were replotted in Fig. 5(a) and (b) displaying S_w and D_w^i respectively, both as function of thickness, for films of glycerol content of 0, 10, 20, and 30% w/w d.m.

As displayed in Fig. 5(a) and (b), S_w and D_w^i were affected in a different way regarding the thickness of film. Fig. 5(a) shows that for all

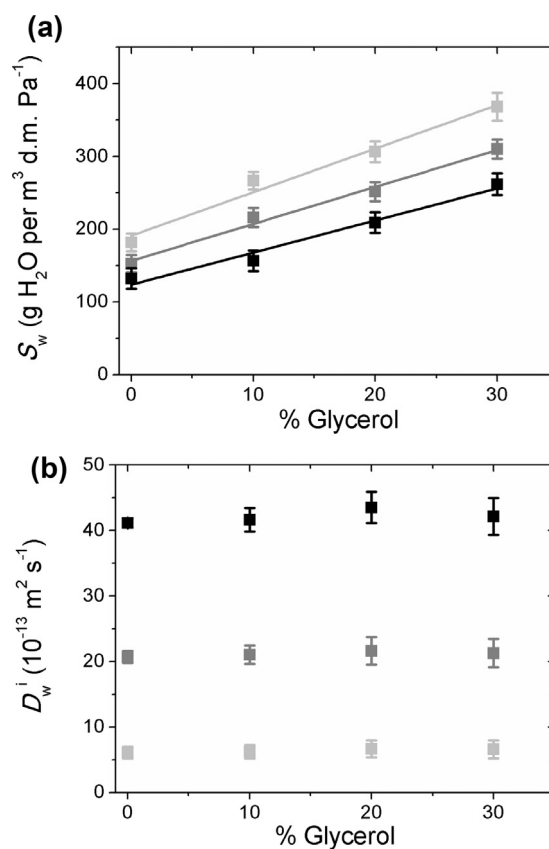


Fig. 4. Dependency of S_w and D_w^i with glycerol concentration of films of thickness ■ $7 \pm 0.6 \times 10^{-5} \text{ m}$, ■ $15 \pm 0.8 \times 10^{-5} \text{ m}$, and ■ $30 \pm 1.3 \times 10^{-5} \text{ m}$. (a) Plot of S_w as function of % of glycerol. (b) Plot of D_w^i as function of % of glycerol.

glycerol content, S_w decreased linearly when thickness increased. As shown in Table 1, the amount of water incorporated per gram of dry matter, h_∞ , decreased when thickness was increased. Although results were given per unit of gram of dry matter, considering the entire volume of film, in the lower thickness the gram included more superficial area than the same gram in higher thicknesses. This suggested an important role of surface adsorption effects in water uptake for these films.

Regarding water diffusion coefficient, Table 1 shows that both values, D_w^{eff} and D_w^i , increased with the increasing film thickness. Fig. 5(b) demonstrates that D_w^i increased linearly when thickness

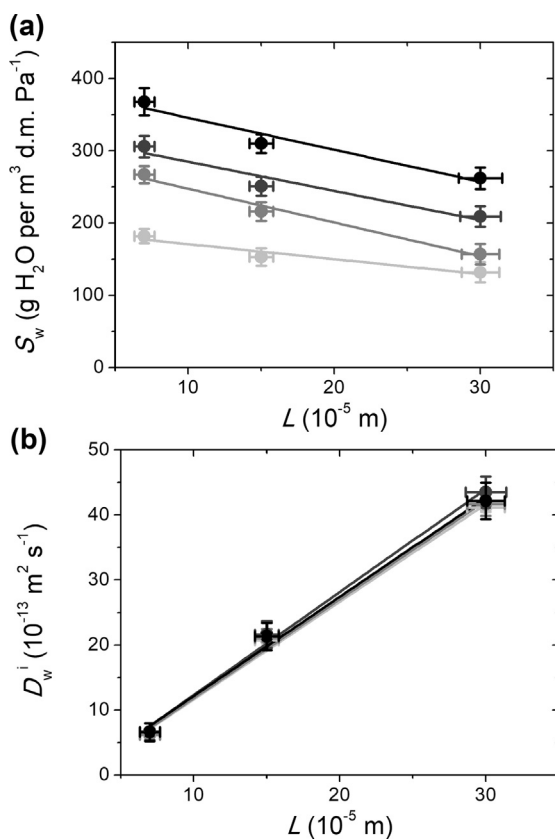


Fig. 5. Dependency of S_w and D_w^i with thickness L of films with glycerol content of ●0, ●10, ●20, and ●30% w/w d.m. (a) Plot of S_w as function of L . (b) Plot of D_w^i as function of L .

increased, straight lines for all glycerol contents studied were practically the same and confirm that the diffusion of water in the film was not altered by the presence of plasticizer.

It has been suggested that when thickness was reduced, the boundary layers increased their relevance in the overall resistance of water movement [44]. This performance might be reflected by the decreasing diffusion coefficient with the reduction of the thickness of film. On the other hand, solvent evaporation rate during film formation may be implicated in the final polymeric structure of the matrix [45]. Therefore, different structures may be formed in films of different thickness in casting method; because the constitution of the matrix occurs faster in thinner films due that there are less water to evaporate. This effect may alter the diffusion of water through the film.

Comparing the influence of thickness on S_w and D_w^i displayed in Fig. 5(a) and (b) respectively, it is possible to see that the total decrement of S_w throughout the range of thickness studied was 1.5 times, while the total increment of D_w^i was around 6.6 times. This demonstrates that the effect of thickness is more important on D_w^i than S_w .

3.2.3. Type of diffusion of water through the film

Table 1 shows values of the diffusional exponent n , characterizing the type of diffusion of water through the film. Values of n were obtained by fitting experimental kinetics data with Korsmeyer & Peppas (KP) model described previously (Eq. (5)). Results demonstrated that a quasi-fickian behaviour ($n < 0.5$) was observed for thinner films (7×10^{-5} m), turning to a non-fickian or anomalous behaviour ($0.5 < n < 1$) for those thicker samples (15×10^{-5} m and 30×10^{-5} m). At the same thickness value, n decreased with the incorporation of glycerol. Fickian transport of water molecules occurs in a situation that diffusion process is much slower than relaxation of the polymer, so diffusion becomes the bigger resistance. When diffusion process controls the global transfer, there is a concentration gradient of

water in the film because the relaxation process rate of the polymeric matrix is higher than the diffusion process, so the preponderant barrier to the transfer is imposed by the diffusion mechanism, in accordance to Fick's law [19,36,46]. On the other hand, the mobility of polymer chains is strongly affected by the presence of water and other plasticizers. When water transport occurs under a process controlled by polymer relaxation, the swollen front moves in a constant equilibrium concentration and a sharp cut off between zones with different T_g (generally glassy and rubbery zones) is established, producing a non fickian or anomalous diffusion [25]. As can be seen in Table 1, at a given thickness, the increase in plasticizer concentration turned the water transport into a fickian behaviour (n decreases) because plasticizer raises the velocity of relaxation due to the increased mobility of the polymer chains. Plasticizers decrease the T_g value because they reduce the cohesive forces between polymer chains and increase the freedom of movement [28,47]. When glycerol was incorporated, the transfer became gradually fickian and this is clearly shown in Table 1, following the value of n from films with 15×10^{-5} m and 30×10^{-5} m of thickness. Films with 7×10^{-5} m of thickness demonstrated quasi-fickian behaviour that was accentuated when glycerol content was increased. Table 1 also shows that at a given glycerol content the index n increased with the increment of thickness separating from the fickian behaviour. This may be due to structural differences in the polymeric matrix of films with different thickness produced during film formation by casting.

3.3. Water vapour permeability

Water vapour permeability is a measure of how easily a film could be penetrated by water vapour [20]. Experimental water vapour permeability P_w^{exp} was obtained through Eq. (8), which was derived from a combination of Fick's and Henry's laws [13,19,38]. Permeability should not be confused with transport through pores. Permeability consist of a process of sorption, diffusion, and desorption, where water vapour dissolves on one side of the film, then diffuses through to the other side, and finally emerges to the atmosphere. Therefore, water vapour permeability P_w is defined by Eq. (6) [18,19,24]. In permeability experiments, sorption occurs on the side of the film exposed at 90% r.h. and desorption on the other side exposed at 10% r.h. In order to compare the experimental value P_w^{exp} with the theoretical one, $P_w = S_w D_w$, S_w and D_w^i values obtained from kinetics of hydration experiments performed at 90% r.h. were used. D_w^i was determined taking into account the diffusion of water in the film during the initial period of sorption (first twelve hours in the present study), where the increment of volume due to hydration is not significant. The reason of the use of D_w^i is because represent the diffusion process that occurs at steady state, during the experimental permeability test performed.

3.3.1. Effect of glycerol

Fig. 6(a) displays the water flux J_w through the film and Fig. 6(b) the experimental permeability P_w^{exp} , as function of glycerol content, for films of thickness of 7×10^{-5} m, 15×10^{-5} m, and 30×10^{-5} m.

Both J_w and P_w^{exp} increased linearly with the glycerol content in the film. A linear relation between permeability and glycerol content was also observed in high amylose corn starch based films [48]. The fact that glycerol increased water vapour permeability is commonly observed in protein based films, such as myofibrillar and β -lactoglobulin films [27,28], and in polysaccharides films as cellulose [49].

Fig. 6(c) shows the values of $P_w = S_w D_w^i$ as function of glycerol content. As it can be seen in Table 2, and comparing Fig. 6(b) and Fig. 6(c), both permeabilities P_w^{exp} and P_w were in good agreement considering experimental errors. This agreement allowed studying the effect of the glycerol on the permeability in a more comprehensive way seeing as the plasticizer affects to S_w and D_w^i .

Observing Fig. 4(a) it can be seen that for a given thickness, S_w increased linearly with the amount of glycerol, while, as shown in

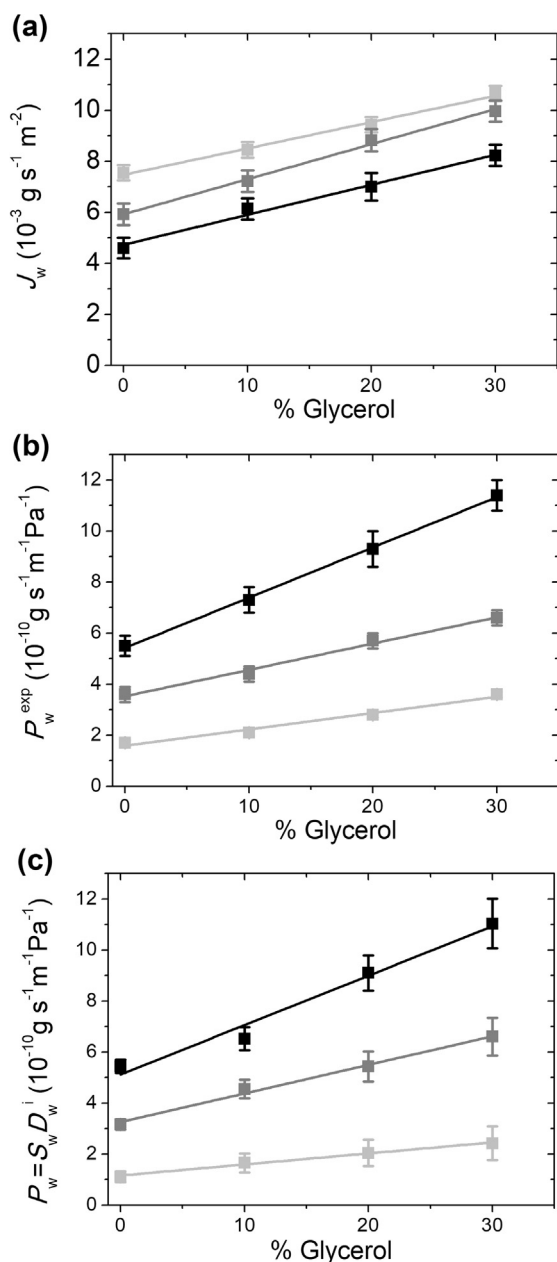


Fig. 6. Dependency of J_w , P_w^{exp} , and $P_w = S_w \cdot D_w^i$ with glycerol concentration of films of thickness $\blacksquare 7 \pm 0.6 \times 10^{-5}$ m, $\blacksquare 15 \pm 0.8 \times 10^{-5}$ m, and $\blacksquare 30 \pm 1.3 \times 10^{-5}$ m. (a) Plot of J_w as function of % of glycerol (b) Plot of P_w^{exp} as function of % of glycerol (c) Plot of $P_w = S_w \cdot D_w^i$ as function of % of glycerol.

Fig. 4(b), D_w^i was not affected by the content of plasticizer added. This suggested that the linear growth of water vapour permeability due to the addition of glycerol was given only by the linear increase in water solubility.

3.3.2. Effect of thickness

An effect of thickness on the water flux J_w through the film, and on the experimental permeability P_w^{exp} , was evident from results showed in Fig. 6(a) and (b) respectively. To further characterize the effect of thickness these data were replotted and displayed J_w and P_w^{exp} both as a function of thickness in Fig. 7(a) and (b) respectively, for films of 0, 10, 20, and 30% w/w d.m. of glycerol content. Therefore, Fig. 7(a) and (b) show for a given glycerol content how J_w and P_w^{exp} were affected by the thickness of film in a different manner.

Fig. 7(a) shows that J_w decreased linearly when thickness increased.

Table 2

Experimental values of water vapour flux J_w ($10^{-3} \text{gs}^{-1} \text{m}^{-2}$), and comparison of the experimental water vapour permeability P_w^{exp} ($10^{-10} \text{gs}^{-1} \text{m}^{-1} \text{Pa}^{-1}$) and the water vapour permeability obtained from water sorption kinetics experiments $P_w = S_w \cdot D_w^i$ ($10^{-10} \text{gs}^{-1} \text{m}^{-1} \text{Pa}^{-1}$).

Thickness L	% Glycerol content	Water sorption kinetics $P_w = S_w \cdot D_w^i$	Experimental permeability	
			J_w	P_w^{exp}
$7.0 \pm 0.6 (10^{-5} \text{ m})$	0	1.1 ± 0.2	6.8 ± 0.3	1.7 ± 0.1
	10	1.7 ± 0.4	8.4 ± 0.3	2.1 ± 0.1
	20	2.0 ± 0.5	9.4 ± 0.3	2.8 ± 0.1
	30	2.4 ± 0.7	10.7 ± 0.3	3.6 ± 0.1
$15.0 \pm 0.8 (10^{-5} \text{ m})$	0	3.2 ± 0.2	5.7 ± 0.4	3.6 ± 0.3
	10	4.6 ± 0.4	7.2 ± 0.4	4.4 ± 0.3
	20	5.4 ± 0.6	8.9 ± 0.4	5.7 ± 0.3
	30	6.6 ± 0.7	10.0 ± 0.4	6.6 ± 0.3
$30.0 \pm 1.3 (10^{-5} \text{ m})$	0	5.4 ± 0.3	4.6 ± 0.4	5.5 ± 0.4
	10	6.5 ± 4.5	6.1 ± 0.4	7.3 ± 0.5
	20	9.1 ± 0.7	7.0 ± 0.5	9.3 ± 0.6
	30	11.0 ± 0.9	8.2 ± 0.4	11.4 ± 0.5

Comparable linear behaviour of water flux with thickness was observed for myofibrillar protein-based film [24]. On the other hand, Fig. 7(b) shows that, for a given glycerol content, P_w^{exp} increased linearly with the increment of thickness. Similar linear performance of P_w^{exp} with thickness was observed for myofibrillar protein-based film [24] and high amylose corn starch based films [48].

In an ideal polymeric film, water vapour permeability is independent of film thickness [50]. For homogeneous ideal polymers, Fick's law requires that water vapour flux, under a given water vapour pressure gradient, should vary inversely with film thickness [51]. Thus, when calculating the permeability through Eq. (8), it becomes independent of thickness L . However, it has been shown that for hydrophilic polymeric films, water vapour permeability raised when the film thickness was increased [22,23,52]. Many authors have reported this anomalous behaviour and asserted that this effect is present in thin membranes of thicknesses lower than 6×10^{-5} m [14], however several works in the literature informed this behaviour above this level of thickness [48,53]. The reason of this deviation is clearly related to the hydrophilic nature of the polymeric matrix, but there is not a complete answer that explains the phenomenon at a microscopical level.

Some explanations have been reported to clarify the thickness effect on water vapour permeability. Hwang & Kammermeyer (1974) proposed two reasons to understand this dependence [44]. Firstly, when thickness is reduced, the boundary layers increase their relevance in the overall resistance. The other reason is due to the variation of the permeability coefficient along the membrane, because in hydrophilic films, the water content gradient intensifies the differences in mobility of polymer chains and in water solubility alongside the film. These reasons were manifested in the differences in diffusion coefficient described in Section 3.2.2. Meanwhile, Hauser and McLaren (1948) attributed the thickness effect on water vapour permeability in cellulose films to different structures formed at different thicknesses [51]. McHugh, Avenabustillos & Krochta (1993) [22] and Gennadios, Weller & Gooding (1994) [23] proposed some corrections in cup method (ASTM-E96) to measure permeability in high hydrophilic materials. They observed that, as film thickness increased, the resistance to mass transfer across the films also increased; consequently, the equilibrium water vapour partial pressure at the underside of the film increased, resulting in higher values of permeability [22]. Another explanation of the thickness effect is due to the swelling of the macromolecular matrix that may occur because of the water sorption during water transfer [54]. Such swelling occurs on the film side in contact with the highest humidity atmosphere and affects only a thin part of the film. The proportion of such swelling could thus be lower as the film becomes thicker.

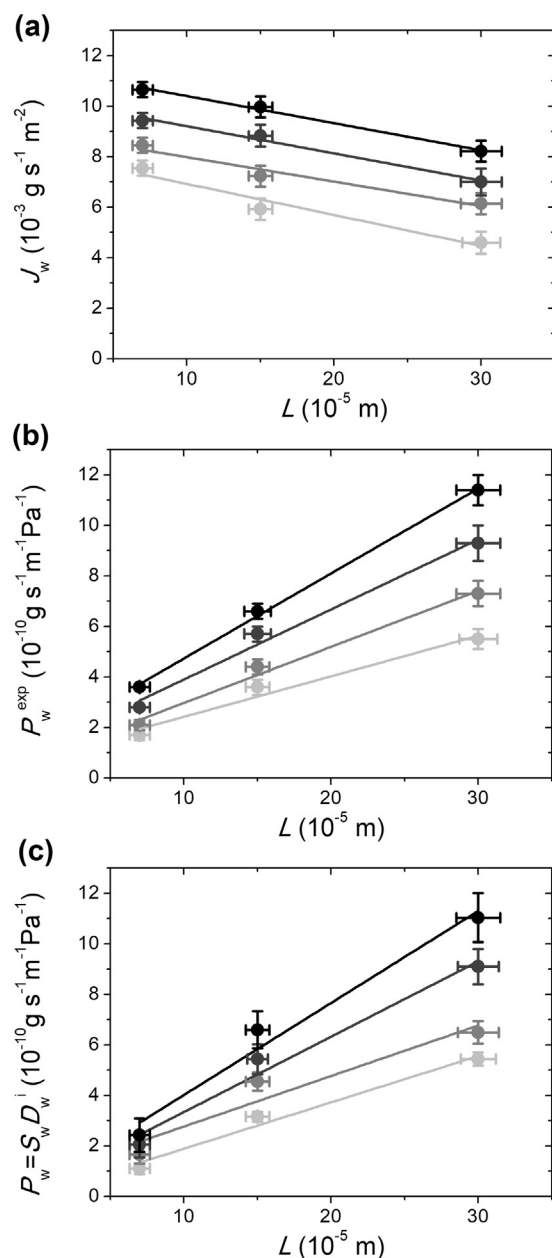


Fig. 7. Dependency of J_w , P_w^{exp} , and $P_w = S_w D_w^i$ with thickness L of films with glycerol content of \bullet 0, \bullet 10, \bullet 20, and \bullet 30% w/w d.m. (a) Plot of J_w as function of L . (b) Plot of P_w^{exp} as function of L . (c) Plot of $P_w = S_w D_w^i$ as function of L .

Therefore in thinner films where the proportion of swelling becomes remarkable, the movement of water could be retarded decreasing diffusion and permeability. The basis of this behaviour is the strong interaction between permeant and matrix film.

Similar behaviour with thickness was observed on the permeability of gases in hydrophobic materials [55]. A strong dependence of the permeability of CO_2 and He with respect to thickness was reported in polydimethylsiloxane membranes [55]. Researchers concluded that the effect of thickness on CO_2 and He permeability was important in the range of 2×10^{-7} m to 5×10^{-5} m, but above 5×10^{-5} m permeability did not depend on film thickness as proposed by Fick.

Modelling water transport through hydrophilic films is extremely complex due to nonlinear water sorption isotherms and water content dependency of diffusion [22]. To better understand the effect of thickness on the water vapour permeability, Fig. 7(c) shows the values of $P_w = S_w D_w^i$ as a function of thickness for films with glycerol at 0, 10,

20, and 30% w/w d.m. From Table 2 and comparing Fig. 7(b) and Fig. 7(c), it was possible to observe that both permeabilities: $P_w = S_w D_w^i$ and P_w^{exp} , are again similar considering experimental errors. This fact allowed studying the effect of thickness on the permeability coefficient observing separately the effect on S_w and D_w^i . As shown in Fig. 5(a) and (b), S_w and D_w^i display opposite behaviour but the increment of D_w^i is greater than the decrease of S_w with thickness. Therefore the increase in the permeability with thickness is governed by the increase in D_w^i with thickness.

Table 2 shows the great correspondence between experimental permeability P_w^{exp} measured by cup method and the permeability P_w calculated from the initial diffusion coefficient D_w^i and solubility S_w . Therefore is remarkable to note that the effect of glycerol content and thickness in water vapour permeability of films was also encountered in an indirect determination, different that the cup method. This suggests that these behaviours were not due to an error in the cup method to be corrected as suggested, but to a proper behaviour of the matrix film and its interaction with water and glycerol.

4. Conclusions

In this work the effect of film thickness and the addition of plasticizer on the hydration, water diffusion, and water vapour permeability were studied in biodegradable films based on yeast biomass.

The effect of thickness on the permeation process was remarkable, as demonstrated with two different experiments: the classical experimental cup method and an indirect kinetics method. Both methods gave the same permeability coefficient values considering experimental errors. To arrive to this agreement in the calculation of water vapour permeability, the initial diffusion coefficient D_w^i must be considered, since it is related to the conditions done in permeability experiments.

The glycerol added as plasticizer increased water vapour permeability because it affected the solubility of water in the matrix, but it did not modify diffusion coefficient. Instead, the change in thickness affected both diffusion and solubility in a different way, and the present work shows that the main cause of the decrease in permeability when thickness is decreased is due to a remarkable decrease of diffusion coefficient.

A practical conclusion in the application of hydrophilic membranes and the effect of film thickness can be reached from the results exposed in this work, where the phrase “less is more” could be applied, since in certain thickness range, a narrower membrane presents lower permeability coefficient than a thicker one, giving a better barrier effect against water vapour.

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