

Water vapor permeability of edible starch based films

M.A. Bertuzzi ^{*}, E.F. Castro Vidaurre, M. Armada, J.C. Gottifredi

Instituto de Investigaciones para la Industria Química (CONICET), Facultad de Ingeniería, Universidad Nacional de Salta, Buenos Aires 177 (A4402 FDC) Salta, Argentina

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Abstract

Water transport in edible films of starch based products is a complex phenomenon due to the strong interaction of sorbed water molecules with polymeric structure of starch. Water sorption isotherms on high amylose starch based films are highly non linear in the range studied (5–45 °C). So permeability is usually affected by a number of parameters such as temperature, film thickness and plasticizer content. This knowledge is required to simulate and predict transport patterns. In the present contribution water vapor permeability (WVP) of high amylose corn starch (HACS) films, prepared in our laboratory, was determined following ASTM E-96 procedure. WVP increases as temperature increases between 5 and 40 °C and observed results can be correlated with an Arrhenius-type expression. Activation energy of WVP for the starch film investigated is 5.61 kJ/mol and values of WVP ranged between 2×10^{-10} and 1×10^{-9} g m⁻¹ s⁻¹ Pa⁻¹. It is also shown a direct relation between WVP with plasticizer content and film thickness. These observations could be explained in terms of variations in the number of potential intermolecular interactions in the film structure.

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1. Introduction

There has been a renewed interest in edible and biodegradable films. These films have the potential to replace conventional packaging in some applications. Polysaccharides, such as starches, cellulose derivatives and plant gums, have been reported as edible films and coatings in food packaging and preservation (Debeaufort, Quezada-Gallo, & Voilley, 1998; Donhowe & Fennema, 1994; Gilbert, 1986). They are known to be effective barrier to gas transport (O₂, CO₂), although they present high water vapor permeability (Donhowe & Fennema, 1994; Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; McHugh & Krochta, 1994). Generally the main functional properties of these hydrophilic materials strongly depend on their water content and therefore on the surrounding humidity (Chang, Cheah, & Seow, 2000; Wiles, Vergano, Barron, Bunn, & Testin, 2000). Particularly, the use of starch could

be an interesting solution since this polymer is abundant, cheap, biodegradable and edible. Several studies have been done to analyze starch based films properties (Arvanitoyannis & Biliaderis, 1998; Arvanitoyannis & Biliaderis, 1999; Mali, Grossmann, García, Martino, & Zaritzky, 2002; Rindlav-Westling, Standing, Hermansson, & Gatnholm, 1998; Ryu, Rhim, Roh, & Kim, 2002).

Water vapor permeability results can be useful to understand possible mass transfer mechanisms and solute and polymer interactions in edible films. According to the thermodynamic of irreversible process, water chemical potential difference is the driving force of the water transfer through a film. When the process occurs at constant temperature and pressure, the water chemical potential difference results proportional to water vapor concentration difference between the two faces (Morillon, Debeaufort, Blond, & Voilley, 2000).

Permeability can be defined as the product of diffusivity and solubility only when Fick and Henry laws fully apply. For most edible films the water vapor strongly interacts with polymer structure, which results in diffusion and solu-

^{*} Corresponding author. Tel./fax: +54 387 4251006.

E-mail address: bertuzzi@unsa.edu.ar (M.A. Bertuzzi).

bility coefficients dependent on driving force (Gennadios, Bradenburg, Park, Weller, & Testin, 1994a; Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002).

In the present study, starch based films, were prepared from high amylose corn starch using procedures deemed to be practical and economical at large scales. The films were targeted as packaging material for foods, which require controlled water vapor transport to extend the shelf life of products. The scope of this contribution is to investigate the effect of temperature, glycerol content and film thickness on water vapor permeability (sorption and diffusion phenomena) of high amylose corn starch based film.

2. Material and methods

2.1. Film preparation and casting

High amylose corn starch (Sigma Chemical Co., St. Louis, MO., USA) with an amylose content of about 70% and native lipid content of 1.2%, was used. Film-forming dispersion consisted of 1 g of starch, 10 mL 0.25 N sodium hydroxide and 10 mL distilled water. Film-forming dispersion was maintained 60 min under magnetic stirring. After that, the dispersion was gelatinized in a shaker water bath at 78–80 °C during 10 min. This procedure ensures the disintegration of starch granules to form a homogeneous dispersion. Glycerol (Merck, Whitehouse Station, NJ, USA.) was added as plasticizer. When starch solution temperature was around 50 °C, solution was poured on plastic Petri dishes. Dishes were placed in an air-circulating oven at 35 °C and 50% of RH until films were dry. After 15 h, the dishes were removed from the oven and the films were peeled off. Films present excellent transparency. Films of various thicknesses were prepared by pouring different amounts of starch solution onto the dishes.

2.2. Film thickness measurement

The thickness of film was measured with an electronic micrometer (0.001 mm accuracy, Fowler, Cole-Parmer Instruments Co.). Reported thickness was the mean value of five measurements and it was used as the specimen thickness for water vapor permeability calculations.

2.3. Determination of moisture sorption

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 COST-90 project (Argaiz & López-Malo, 1994), to cover a water activity range from 0.10 to 0.90. Table 1 shows water activity for all saturated salt solutions at different temperatures. All salts used were analytical grade. Film samples were cut into pieces approximately 2 cm². Samples were weighed and placed on a stainless steel lattice by holding it on a tripod inside the sorbostats that

Table 1
Water activity values of saturated salt solutions at different temperatures

Salt	a_w (5 °C)	a_w (25 °C)	a_w (35 °C)	a_w (45 °C)
LiCl	0.129	0.114	0.108	0.103
CH ₃ COOK	0.292	0.237	0.216	0.198
MgCl ₂	0.354	0.329	0.318	0.308
K ₂ CO ₃	0.459	0.443	0.436	0.430
Mg(NO ₃) ₂	0.584	0.536	0.516	0.497
NaBr	0.682	0.653	0.638	0.624
NaCl	0.805	0.762	0.743	0.726
KCl	0.934	0.855	0.821	0.791

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 days more. Equilibrium was judged to have been attained when the difference between two consecutive sample weightings was less than 1 mg/g dry solid. Results at equilibrium were reported for each relative humidity as gram water sorbed/100 g dry film. Absorption tests were done in triplicate at each a_w . The moisture sorption determination was done at 5, 25, 35 and 45 °C. Experimental sorption data were fitted using BET equation. The heat of sorption (ΔH_s) was deduced from the sorption isotherm data at a number of temperatures by applying Clausius–Clapeyron equation (Al-Muh-taseb, McMinn, & Magee, 2002; Mulet, García-Reverter, Sanjuán, & Bon, 1999; Viollaz & Rovedo, 1999).

2.4. Water vapor permeability (WVP) determination

The apparatus and methodology described in the ASTM E96 (ASTM, 1995) were used to measure the WVP of the film. Film specimens were conditioned for 48 h in a chamber at 25 °C and 52% relative humidity (Mg(NO₃)₂ saturated solution) before being analyzed. Films were sealed on cups containing distilled water. Test cups were placed in a desiccator cabinet maintained at temperature and relative humidity (LiCl saturated solution) controlled. To determine film thickness and plasticizer effect on WVP, tests were done at 30 °C. To study temperature influence on WVP, samples were analyzed in a temperatures range between 5 and 40 °C. A fan was used to maintain uniform conditions at all test locations over the specimen. Periodical weightings monitored the weight changes. Weight loss was plotted over time and when steady state (straight line) was reached 6 h more were registered. The WVP was calculated from the slope (G) of a linear regression of weight loss versus time.

$$WVP = \frac{G \cdot x}{A \cdot \Delta p} \quad (1)$$

where x is the film thickness; A is the area of exposed film and Δp is the differential water vapor partial pressure across the film. This method uses Fick's first law and Henry's law to calculate film WVP and assume that film

solubility and diffusivity are constant. WVP measured values were corrected for air gap distance between water level and the film position according to procedures outlined in Gennadios, Weller, and Gooding (1994b).

3. Results and discussion

3.1. Factors affecting permeability

3.1.1. Effect of temperature

The diffusion and solubility coefficients of permeants are affected by temperature. The temperature dependence on solubility obeys the Van't Hoff law, while diffusion obeys Arrhenius law. Usually, over small temperature ranges, the temperature dependence of permeability also can be represented by an Arrhenius type equation (Arvanitoyannis, Nakayama, & Aiba, 1998; Chinnan & Park, 1995; Donhowe & Fennema, 1994; McHugh & Krochta, 1994; Morillon et al., 2002, 2000).

$$S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \quad (2)$$

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (3)$$

$$\text{WVP} = \text{WVP}_0 \exp\left(\frac{-E_P}{RT}\right) \quad (4)$$

where E_D and E_P are the apparent activation energies for diffusion and permeation phenomena (kJ mol^{-1}), respectively, ΔH_s is the enthalpy change of sorption (kJ mol^{-1}), R is the gas constant ($8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K). From permeability definition, the relationship between energies is:

$$E_P = E_D + \Delta H_s \quad (5)$$

Usually, an increase in temperature causes a slight decrease in the solubility and an increase in the diffusion of water vapor through edible films. The increase in diffusivity with increasing temperature is due to the enhanced motion of polymer segments and to increased energy levels of the permeating molecules. As a result, permeability increases with increasing temperature.

Temperature and relative humidity effects on water vapor solubility in the polymer can be deduced from water sorption isotherm. On other hand, influence of temperature and water content on diffusivity is much more difficult to be established. Experimental data of moisture sorption at 25 and 45 °C for high amylose corn starch films as a function of water activity are shown in Fig. 1. Isotherms at 5 and 35 °C are not shown for sake of clarity. Sorption data at all temperature were adequately fitted by BET equation ($r^2 > 0.99$). Sorption curves are typical of water vapor sensitive polymers, and sorption levels are within the range reported for autoclaved high amylose corn starch (Bader & Göritz, 1994), cellulose films and protein based films (Chinnan & Park, 1995; Cuq, Gontard, Cuq, & Guilbert, 1997; Gennadios et al., 1994a; Velázquez, Torres, & Mar-

tín-Polo, 2001). Adsorption and mixing processes are exothermic since the moisture content decreases with increasing temperature at a given value of water activity. This behavior is usual for most dehydrated food materials, such as corn protein, starch and gelatin gels, fish muscle, meat products and also for gluten and myofibrillar protein based films (Al-Muhtaseb et al., 2002; Cuq et al., 1997; Gontard, Guilbert, & Cuq, 1993; Viollaz & Rovedo, 1999). The heat of sorption (ΔH_s) was obtained from sorption isotherms by applying Clausius–Clapeyron equation. Changes in enthalpy provide a measure of the energy changes occurring on the condensation and mixing of water molecules within the film during sorption process, wherefore is a function of water content. Enthalpy change of film sorption process as a function of water content is shown in Fig. 2. As water vapor is brought in contact with the film surface, where active sites of different energy are present, the most active sites are those first sorbed by water molecules followed by those less active until film saturation. So a decaying function of ΔH_s against moisture con-

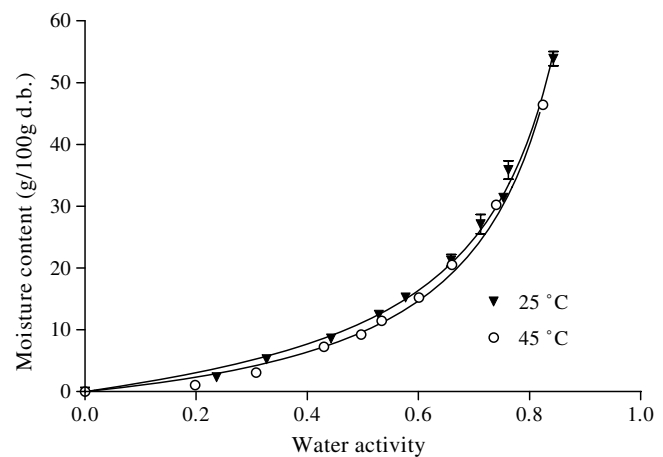


Fig. 1. Experimental data and isotherms curves predicted by BET equation for moisture sorption of high amylose corn starch based films.

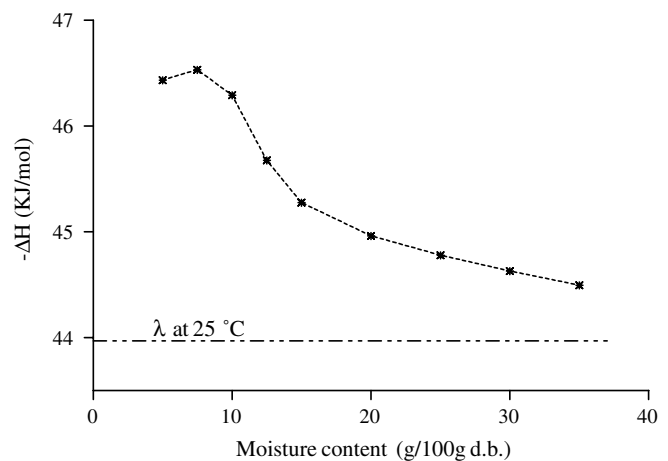


Fig. 2. Enthalpy change of water sorption for high amylose corn starch based films and latent heat of water condensation at 25 °C.

tent is observed. There is a continuous decrease of the affinity between film sorbed structure with water molecules as moisture content increase. Heat of sorption data obtained from Clausius–Clapeyron equation, have been reported in the literature for several foods and food components (Al-Muhtaseb et al., 2002; Mulet et al., 1999; Viollaz & Rovedo, 1999). However no data were reported for edible films.

In this work, film WVP were measured at different temperatures in a range of 5–40 °C. Temperature dependence of WVP of films is shown in Fig. 3. Results were fitted with an Arrhenius type expression (Eq. (4)). Activation energy for permeation process was determined from the slope of $\ln(\text{WVP})$ versus $1/T$ ($R^2 = 0.92$). The activation energy of high amylose starch films was 5.611 kJ/mol. Activation energy values of water vapor permeation in cellophane reported by Rogers, Fels, and Li (1982) was 1.67 kJ/mol. Chinnan and Park (1995) observed activation energies of hydroxypropyl cellulose and methyl cellulose were 14.56 and 16.43 kJ/mol, respectively. Due the hydrophilic nature of these materials, the energy barrier of water vapor permeation phenomenon is lower than energy barrier of hydrophobic films. Packaging synthetic films such as polyvinylidene chloride (61.9 kJ/mol), polypropylene (42.2–65.3 kJ/mol), polyethylene (33.4–61.7 kJ/mol) (Rogers et al., 1982) present higher activation energies. Kester and Fennema (1989) observed a rather large activation energy values (59.4 kJ/mol) for waxed laminated cellulose films. Gennadios, Weller, and Testin (1993) reported protein films activation energies ranging from 46 to 50 kJ/mol.

According to the obtained results, in the light of Eq. (5), diffusion is the preponderant mechanism of the moisture transfer. E_D and E_P are both positives, i.e., diffusion and permeation increase with increasing temperature.

3.2. Effect of thickness

In ideal polymeric structures gas and vapor permeabilities are independent of film thickness (Schwartzberg, 1986). However, there is experimental evidence (McHugh, Avena-

Bustillos, & Krochta, 1993; Park & Chinnan, 1995) of non ideal behavior. In this study it was observed that WVP of high amylose corn starch films increased linearly with film thickness over the range of thickness studied (Fig. 4). The linear fittings of the experimental values display a regression coefficient (R^2) of 0.98. This positive deviation from the ideal behavior indicates that starch films have an affinity for moisture that is not taken into account in Fick's and Henry's laws as can be seen in Fig. 1 (non linear isotherms). Previous studies have indicated similar relationships in hydrophilic film systems: amylose films (Rankin, Wolff, Davis, & Rist, 1958), cellulose derivatives films (Hagenmaier & Shaw, 1990); protein and other edible films (Gennadios et al., 1994a; Longares, Monahan, O'Sullivan, & O'Riordan, 2004; McHugh et al., 1993; Park & Chinnan, 1995; Park, Weller, Vergano, & Testin, 1993; Sobral, 2000). Several explanations for thickness effects on edible films have been reported. McHugh et al. (1993) observed that, as film thickness increased, the film provided an increased resistance to mass transfer across it; consequently, the equilibrium water vapor partial pressure at inner film surface increased. Other authors attributed thickness effect to film swelling as a result of attractive forces between polymer and water (Park et al., 1993). Film swelling could result in varying film structures.

From Eq. (1) and experimental data it becomes quite clear that water vapor flux through the film (G/A) ($\text{g s}^{-1} \text{m}^{-2}$) remains independent of film thickness, which would imply that flux in this type of edible films does not depend on x in the range of film thickness studied (40–150 μm). Due to the strong hygroscopic nature of starch films and the influence of glycerol it could be possible that during permeation process the film matrix, exposed to the high relative humidity side, sorbed enough water that desorption rate becomes independent of thickness resistance. As a whole the film behaves as only a thin portion of it, at the low relative humidity side, which is responsible of the mass transfer resistance. Under these conditions the

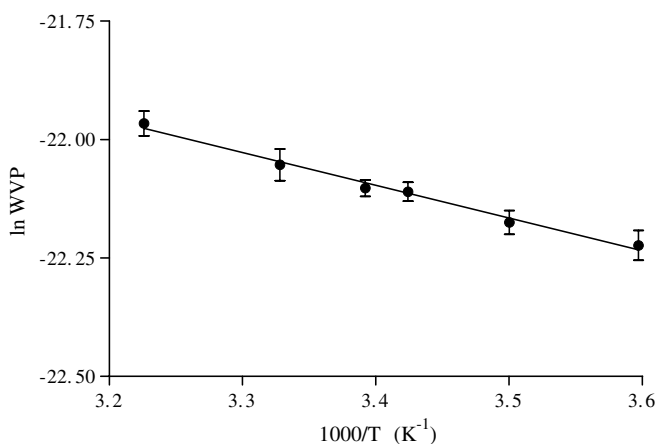


Fig. 3. Temperature dependence of water vapor permeability of high amylose starch film.

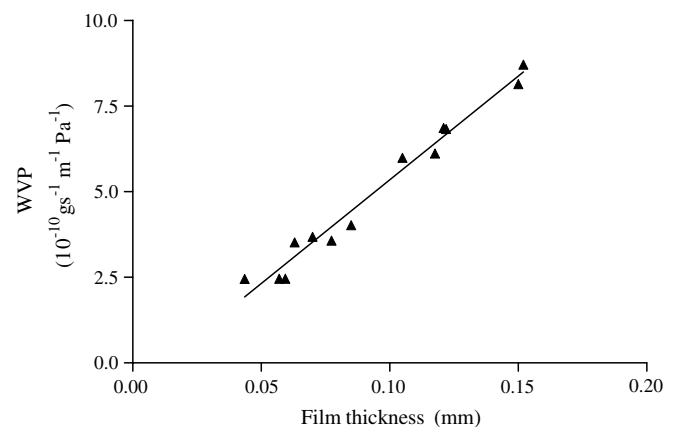


Fig. 4. Effect of film thickness on water vapor permeability for high amylose corn starch based films.

flux can become thickness independent and permeability will increase linearly with x .

Fig. 5 shows the thickness resulting values as function of film-forming gel amount poured in Petri dishes. Films were conditioned at different relative humidity (varying between 11% and 100%) during 72 h before measuring film thickness. It can be clearly seen that mean film thickness increases linearly with the amount of gel poured ($R^2 > 0.97$). This confirms that the retraction rate during drying is constant and homogeneous whatever the initial poured amount of film-forming gel.

However the observed variation of film thickness with relative humidity is congruent with sorption data shown in Fig. 1. Below 60% RH, thickness values are independent of relative humidity conditioning. A single line could approximate all experimental data. In Fig. 1 curves presented a relative slight slope at low values of a_w , but take an exponential course at high relative humidities (above 0.60). When $a_w > 0.60$ film thickness shows significant increase dependence with relative humidity and with the original film thickness. Thus under these conditions high amylose corn starch film, full of almost liquid water, offers a great water molecule mobility resulting in a dramatic increase in the rate of diffusion. Since ASTM E-96 method implies the presence of high relative humidity conditions in one side of the film, the observed behavior of Fig. 5 could explain the anomalous dependence of WVP with film thickness presented in Fig. 4.

3.3. Effect of plasticizer

Amylose is responsible for the film-forming capacity of starch based films. In the absence of plasticizers, films made from starch or amylose are brittle (Koskinen, Suortti,

Autio, Myllärinen, & Poutanen, 1996). The addition of a plasticizing agent to edible films is required to overcome film brittleness caused by extensive intermolecular forces. Plasticizers reduce these forces, thereby improving flexibility and extensibility of the films (Forssell et al., 2002; Gontard et al., 1993; Koskinen et al., 1996). Since plasticizers extend, dilute and soften the structure effectively, the chain mobility is increased and diffusion coefficients for gas or water markedly increase (Guilbert, 1986).

Jangchud and Chinnan (1999) found glycerol was the best plasticizer for water soluble polymers among several studied in their work. Based on this finding, glycerol was used as plasticant. The WVP of high amylose corn starch films as a function of glycerol content is presented in Fig. 6. As can be seen, WVP increased linearly as the concentration of glycerol increased in the range of glycerol content studied ($R^2 = 0.90$). These results could be related to structural modifications of the starch network produced by the plasticizer and to the hydrophilic character of glycerol, which favors the absorption and desorption of water molecules. Plasticizer causes a greater flexibility in polymeric structure, which increases water sorbed mobility within the structure. As a result WVP increases with plasticizer film content.

This behavior is common with hydrophilic edible films and was reported by several authors (Cuq et al., 1997; Genadios et al., 1994a; Nazan Turhan & Sahbaz, 2004; Sothornvit & Krochta, 2001). Park and Chinnan (1995) observed similar trends on cellulose films in the range of plasticizer composition used in our study. Ryu et al. (2002) reported high amylose corn starch films, without plasticizer, WVP as large as $117 \times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$, increasing up to $147 \times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ when glycerol concentration was increased to 100 g/100 g of starch. Their reported values are one order of magnitude larger than those observed in this contribution. Such deviation can only be explained by procedure differences on preparing films.

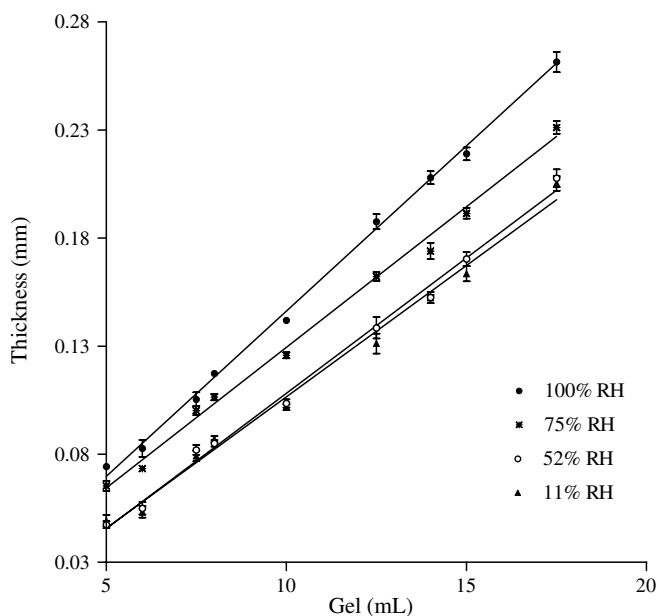


Fig. 5. Film thickness as a function of volume of gel poured onto Petri dishes conditioned at different relative humidity (RH).

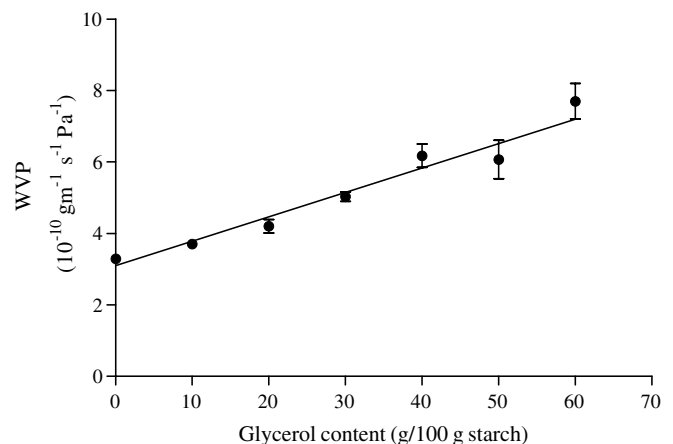


Fig. 6. Effect of glycerol content on water vapor permeability for high amylose corn starch based films.

4. Conclusions

HACS based film characterization requires the knowledge of barrier properties as well as their dependence with temperature, relative humidity gradients, film thickness and plasticizer content. In this work it is shown that temperature seriously affects both equilibrium (solubility) and kinetics (diffusion) phenomena through complex involved mechanisms.

Water vapor sorption experimental data shows an exothermic process. Sorption equilibrium can be well described with simple BET equation. Thus water solubility is expected to be a decreasing function of temperature. It should be noticed that, above $a_w = 0.6$, water content starts to increase in an exponential fashion producing film structural changes which allow a facilitated water transport phenomenon. ASTM E-96 method requires experiments in which one of the film surfaces is exposed to high relative humidity and the other to low relative humidity. Thus a sorbed water concentration gradient is built within the membrane along the diffusion reaction path. As clearly shown, when relative humidity is greater than 52% swelling is noticeable and the polymer matrix expand and water transport is facilitated. In the other region, near the surface subject to low relative humidity, the polymer matrix is much less influenced by water sorbed concentration. Then, it could be possible that water sorbed diffusion resistance is concentrated in a small region of low water content, so WVP becomes independent of film thickness.

It is also shown that plasticizer (glycerol) favors WVP due to its hydrophilic nature and also increases water diffusion rate within the film by allowing greater polymer chain mobility.

As general conclusion this work shows that permeability data on high amylose corn starch based films must be provided with other characteristic parameters such as plasticizer content, water activity gradient, film thickness and temperature to be comparable.

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