

# Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach

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## Abstract

The effects of glycerol and sorbitol on the water sorption isotherms and water vapor permeability ( $K^w$ ) of cassava starch films prepared by casting were investigated.  $K^w$  values were determined in three ranges of relative humidity, RH, (2–33%, 33–64% and 64–90%) and the GAB model was used to fit experimental water sorption isotherms. These data were used to determine the relative influence of the diffusion coefficient of water ( $D^w$ ) and the average solubility coefficient ( $\bar{\beta}$ ) of water in the films on the  $K^w$  value. In all cases, an increase in  $K^w$  values were observed with increasing plasticizer concentration and RH. The  $D^w$ ,  $\bar{\beta}$  and  $K^w$  values of films prepared with glycerol were greater than those of films prepared with sorbitol. For high RH, the  $\bar{\beta}$  values increased 6-fold for films with glycerol and 7-fold for films with sorbitol, while  $D^w$  values did not change significantly. These results indicate that  $K^w$  values are dependent on the solubility coefficient ( $\bar{\beta}$ ) of water in the film, which is not consistent with the proposal that an opening of polymer chains promoted by plasticizers leads to an increase in  $D^w$  and  $K^w$ .

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## 1. Introduction

The increase in non-biodegradable waste material and the difficulty in recycling most of the available synthetic packaging have been pushing researches toward the development of new biodegradable materials, which are suitable for packaging. In this regard, the production of edible films may play an important role in food preservation (Krochta & Miller, 1997; Lu, Weng, & Cao, 2006; Monterrey & Sobral, 1999; Myllärinen, Partenen, Seppälä, & Forssell, 2002).

The obtainment of films based on biological materials involves the use of at least a film-forming agent (macromolecules like starch or proteins), a solvent and a plasticizer

(e.g., glycerol and sorbitol) (Krochta, Baldwin, & Nispero-Carriedo, 1994). Several studies have been carried out on the use of starches from different sources to obtain films and coatings with different properties. The reported results indicate that these carbohydrates are promising materials in this regard (Garcia, Martinho, & Zaritzky, 2000; Defloor, Dehing, & Delcour, 1998; Souza & Andrade, 2002; Avérous, Fringant, & Moro, 2001; Mali, 2002; Nogueira, Mazoni, Mali, & Grossmann, 2003; Myllärinen et al., 2002; Larotonda, Matsui, Sobral, & Laurindo, 2005).

Film characteristics are dependent on the cohesion of the polymeric matrix, which in turn is dependent on the structure of the polymer chains, the film obtainment process and the presence of plasticizer agents. The most used plasticizers for starch-based films are sorbitol and glycerol (Gontard & Guilbert, 1996; McHugh & Krochta, 1994; Krochta & Miller, 1997; Lourdin, Coignard, Bizot, & Colonna, 1997).

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The incorporation of plasticizers is necessary to reduce polymer intermolecular forces, increasing the mobility of the polymeric chains, and improving the mechanical characteristics of the film, such as the film extensibility (Krochta & Sothornvit, 2001; Mali, 2002). Also, plasticizers affect the water barrier property of the films, since they have a great affinity for water.

Godbillot, Dole, Joly, Rogé, and Mathlouthi (2006) reported that water content and interactions in starch films are dependent not only on plasticizer concentration, but also on the relative humidity (RH) to which these materials are exposed. They reported that the interactions between the components of the system, formed by starch, plasticizer and water, vary according to the relative quantities of these components. It is possible that, under some conditions, phase separation occurs.

Reports found in the literature describe the behavior of water vapor permeability and the simultaneous behaviors of water diffusivity and solubility in a polymeric matrix (Krochta & Miller, 1997; Krochta & Sothornvit, 2001; Larotonda et al., 2005; Martelli, Moore, Paes, Gandolfo, & Laurindo, 2006a; Martelli, Moore & Laurindo, in press; Moore, Martelli, Gandolfo, Sobral, & Laurindo, 2006). However, no specific studies were found in the literature regarding the relative influences of these parameters on the water vapor permeability of starch films.

Larotonda et al. (2005), working with Kraft paper impregnated with starch acetate, investigated the influence of the impregnation on the values for the water vapor permeability ( $K^w$ ), water diffusion coefficient ( $D^w$ ) and the solubility coefficient of water in this material. Through the first derivative of the water sorption isotherm of Kraft paper (represented by the GAB model) in relation to the water activity ( $a_w$ ), divided by the water vapor pressure at the sorption isotherm temperature, the value of the solubility coefficient ( $\beta$ ) of water in the film was calculated and called film hydrophilicity by these authors. From the behavior of the average  $\beta$  value (averaged over a relative air humidity range and represented by  $\bar{\beta}$ ) in relation to the water activity of the films, the water diffusion coefficients ( $D^w$ ) were determined, since  $K^w$  is dependent on the product of these variables. This procedure is summarized by Eqs. (1)–(3)

$$K^w = \rho_s \cdot D^w \cdot \bar{\beta} \quad (1)$$

where the  $K^w$  unit is  $\text{g m/m}^2 \text{ h Pa}$ ,  $\rho_s$  is the film density ( $\text{g/m}^3$ ),  $D^w$  is given in  $\text{m}^2/\text{h}$  and  $\bar{\beta}$  is given in  $\text{g of water/g of dry solid} \times \text{Pa}$ .

$$X_w = \frac{C k m_o a_w}{[(1 - k a_w)(1 - k a_w + C k a_w)]} \quad (2)$$

$$\beta = \frac{C k m_o}{p_s} \left[ \frac{\frac{1}{(1 - k a_w)(1 - k a_w + C k a_w)} - \frac{a_w}{[(1 - k a_w)(1 - k a_w + C k a_w)]^2} [-k(1 - k a_w + C k a_w)]}{+(1 - k a_w)(-k + C k)} \right] \quad (3)$$

In Eqs. (2) and (3),  $a_w$  is the water activity (RH/100),  $X_w$  the equilibrium water content on a dry weight basis,  $m_o$  the water content on a dry weight basis related to the monomolecular water layer,  $C$  the Guggenheim constant relating to the monolayer heat sorption, and  $k$  the constant relating to the multilayer heat sorption. The saturation pressure of water, at the temperature at which the sorption curve was obtained, is represented by  $p_s$ .

Moore et al. (2006) reported data on the influence of  $\bar{\beta}$  and  $D^w$  on the water vapor permeability of keratin-based films plasticized with glycerol. These authors report that the value of  $K^w$  increased about 6-fold when 0.09 g glycerol/g of keratin was added to the film-forming solution. This large increase in  $K^w$  was explained by the increase in the solubility coefficient ( $\bar{\beta}$ ) of the water in the films. For relative air humidity (film water activity) values ranging from 0.62 to 0.96,  $\bar{\beta}$  varied from  $3.18 \times 10^{-6}$  to  $5.43 \times 10^{-5}$  g water/g dry mass Pa (17-fold increase), while the value of the diffusion coefficient  $D^w$  decreased from  $5.83 \times 10^{-6}$  to  $1.26 \times 10^{-6}$   $\text{m}^2/\text{s}$ . Small variations in the thickness and density of the films also influenced the  $K^w$  values of the films, but the overall results indicated that  $K^w$  values of keratin films are dependent on the  $\bar{\beta}$  values.

The objective of this study was to investigate the effects of glycerol and sorbitol concentrations and of the relative air humidity on the water vapor permeability, water diffusion coefficient and the solubility coefficient of water in cassava starch films.

## 2. Materials and methods

### 2.1. Film preparation and characterization

Starch films were prepared through the casting technique using a film-forming solution containing 3% of commercial cassava starch (Yoki, Brazil). Glycerol and sorbitol were used as plasticizers, at concentrations of 0.25, 0.30 and 0.35 g/g dry starch. The mixture was heated to 80 °C in a thermal bath under constant stirring, and poured homogeneously onto Plexiglas plates. The plates with the film forming solution were then dried in an oven with air circulation, at 40 °C, for 16 h. The dry films were removed from the plates and conditioned for 48 h in glass desiccators at a relative humidity of 58% (using a saturated solution of sodium bromide) and temperature of 25 °C.

### 2.2. Film thickness and density

The film thicknesses were determined using a digital micrometer (Mitutoyo Co., Japan) from the average of ten random measurements performed for each film. Square samples of the films (20 × 20 mm) were kept in desiccators with phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) for 20 days, at 25 °C, and then weighed. The thicknesses of these films were measured at five different points of each sample. The film den-

sity was determined directly from the film weight and dimensions (volume) and the values considered were the average of ten determinations.

### 2.3. Water sorption isotherms

The water adsorption isotherms of the films were determined through the static method, using saturated saline solutions to obtain different relative humidities (Labuza & Ball, 2000). Sorption isotherms were determined using film samples previously dehydrated in desiccators containing phosphorus pentoxide ( $P_2O_5$ ) for 15 days, at 25 °C. The GAB model (Eq. (2)) was used to represent the experimental equilibrium data.

### 2.4. Water vapor permeability ( $K^w$ ) of films

The water vapor permeabilities were determined in appropriate diffusion cells (Sarantópoulos et al., 2002), using three different ranges of relative humidity (2–33%, 33–64% and 64–90%). The films (0.005 m<sup>2</sup> disks) were fixed into the openings of cells containing a salt solution that provided the lower relative humidity (2%, 33% or 64%, depending on the case) and placed in a hermetic chamber containing a salt solution that provided the higher relative humidity (33%, 64% or 90%, depending on the case). The chamber with the diffusion cells was kept at 25 °C and the changes in mass over time of each cell were determined by weighing them on an analytical scale. The water vapor permeability was determined using Eq. (4).

$$K^w = \frac{W \delta}{S p_s (a_{w1} - a_{w2})} \quad (4)$$

where  $\delta$  is the average film thickness,  $S$  is the film permeation area (0.005 m<sup>2</sup>),  $a_{w1}$  (RH<sub>1</sub>/100) is the water activity in the chamber,  $a_{w2}$  (RH<sub>2</sub>/100) is the water activity inside the cell,  $p_s$  is the water vapor pressure at the experimental system temperature (25 °C) and  $W = G/t$  (g of water/hour) was calculated using the linear regression of the mass variation over time under a steady state permeation condition.

### 2.6. Solubility coefficient of water in the film ( $\beta$ and $\bar{\beta}$ )

The solubility coefficient of water in the films,  $\beta$  (g of water/g of dry mass × Pa), was determined according to Larotonda et al. (2005), based on the experimental water sorption isotherms, GAB model and Eq. (3). The coefficients of water diffusion through the films were determined from data on water vapor permeability, solubility coefficient of water in the film and film density (Eq. (1)). The  $\bar{\beta}$  value used to determine the diffusion coefficient, in each case, was the median of the RH range used for the permeability measurement.

## 3. Results and discussion

### 3.1. Thickness and density of the starch films

The thicknesses of films plasticized with glycerol ranged from  $89 \pm 16 \mu\text{m}$  (0.25 g glycerol/g starch) to  $91 \pm 13 \mu\text{m}$  (0.35 g glycerol/g starch), while the density of dry films varied from  $1.98 \pm 0.31 \text{ g/cm}^3$  (0.25 g glycerol/g starch) to  $2.46 \pm 0.14 \text{ g/cm}^3$  (0.35 g glycerol/g starch). On the other hand, the thicknesses of films plasticized with sorbitol ranged from  $88 \pm 12 \mu\text{m}$  (0.25 g glycerol/g starch) to  $94 \pm 10 \mu\text{m}$  (0.35 g glycerol/g starch), while the density of these films after drying varied from  $1.89 \pm 0.34 \text{ g/cm}^3$  (0.25 g glycerol/g starch) to  $2.23 \pm 0.12 \text{ g/cm}^3$  (0.35 g glycerol/g starch). The similar thickness values were the result of a strict control of the dry mass in the film forming solutions used in the casting procedure. Films with a higher concentration of plasticizer showed higher densities, but the type of plasticizers did not influence the film densities.

### 3.2. Water sorption isotherms

The water sorption isotherms of films prepared with different plasticizer concentrations are shown in Fig. 1, while the GAB parameters and correlation coefficients are given in Table 1. The GAB model represented well the experimental data, as previously reported by other authors (Godbillot et al., 2006; Mali, 2002; Mali, Sakanaka, Yamashita, & Grossmann, 2005). For all concentrations, the films prepared with glycerol were more hygroscopic than films prepared with sorbitol. Also, glycerol had an important positive effect on the equilibrium water content as its concentration increased, which was not the case for films prepared with sorbitol, in which the equilibrium water content was less influenced by plasticizer concentration, over the concentration range investigated (0.25–0.35 g sorbitol/g starch). Moreover, glycerol increased the value of the monolayer water content ( $m_0$ ), while this value was almost

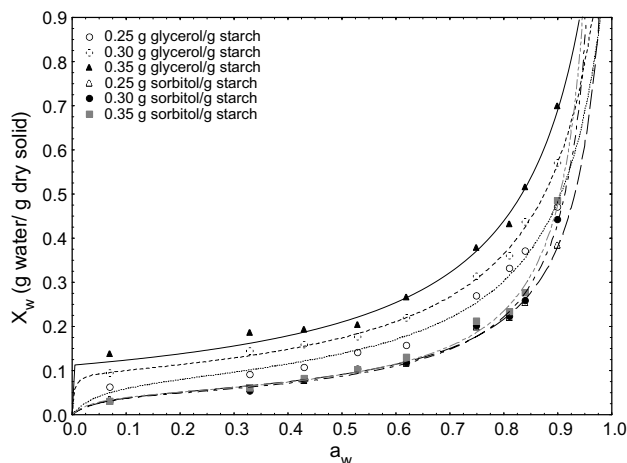


Fig. 1. Experimental data and GAB model adjustment of water sorption isotherms of starch films prepared with different plasticizer concentrations.

Table 1  
GAB model parameters of cassava starch films with different plasticizer concentrations

Sample	GAB parameters			$R^2$
	$m_o$	$K$	$C$	
0.25 g Glycerol/g starch	0.078	0.93	18	>0.99
0.30 g Glycerol/g starch	0.094	0.93	35	>0.99
0.35 g Glycerol/g starch	0.111	0.93	246	>0.99
0.25 g Sorbitol/g starch	0.046	0.97	22	>0.99
0.30 g Sorbitol/g starch	0.046	1.00	28	>0.99
0.35 g Sorbitol/g starch	0.047	1.00	30	>0.99

constant for the films prepared with sorbitol. These results may be related to the higher hygroscopicity of glycerol. Mali et al. (2005) reported data on starch films prepared with glycerol and sorbitol which are consistent with the results obtained in this study. The value for the parameter  $C$ , relating to the monolayer heat sorption, increased with the concentration of both plasticizers. On the other hand, the value for the parameter  $k$  does not appear to be affected by plasticizer concentration, as reported by Coupland, Shaw, Monahan, O'Riordan, and Sullivan (2000) and Mali et al. (2005). The values found in this study for the GAB constants are in agreement with the values reported in the literature (Bertan, 2003; Mali et al., 2005; Sakanaka, Müller, Grossmann, & Yamashita, 2004).

The behavior of the average solubility coefficient of water in the films ( $\bar{\beta}$ ), for different plasticizer concentrations, is shown in Fig. 2. The values of  $\bar{\beta}$  are high for low film water activity, mainly for films prepared with glycerol addition. This behavior may result from the strong activity of adsorption sites before the monolayer filling by water molecules. In the  $a_w$  range between 0.1 and 0.6,  $\bar{\beta}$  values showed low variation, but they increased from  $2.77 \times 10^{-6}$  to  $4.56 \times 10^{-5}$  g/g Pa for  $a_w$  values ranging from 0.6 to 0.9. Furthermore, for  $a_w < 0.75$ ,  $\bar{\beta}$  and  $\beta$  values for films prepared with glycerol addition were all higher

than those for films prepared with sorbitol. For  $a_w > 0.75$  some crossover of  $\beta$  curves was observed. This may be related to the poor performance of the GAB model at high water activity, although different behaviors of glycerol and sorbitol solutions, including possible phase separation, is also possible. Godbillot et al. (2006) reported results on the hygroscopicity of wheat starch films plasticized with different plasticizer concentrations and conditioned at different air RH values. They found that films with 20% of glycerol had a much higher water content when they were conditioned at air RH of 60% or higher. At RH lower than 60%, glycerol and water compete for amylose and amylopectin polar sites, while for higher relative humidities the increase in film hygroscopicity is due to the water absorption by glycerol. According to these authors, for a RH of 58%, in films with a glycerol concentration higher than 17%, phase separation occurs, resulting in the appearance of free glycerol.

### 3.5. Water vapor permeability, solubility coefficient and diffusion coefficient of water in the films

Table 2 shows data on the film water vapor permeabilities which represent the average values of three experiments. The  $K^w$  values varied between  $1.59 \times 10^{-07}$  and  $1.04 \times 10^{-06}$  g m/m<sup>2</sup> h Pa, when glycerol was used as the plasticizer and between  $4.89 \times 10^{-08}$  and  $9.71 \times 10^{-07}$  g m/m<sup>2</sup> h, when the films were prepared with sorbitol. For all investigated conditions,  $K^w$  values increased with plasticizer concentration, as expected and as previously reported in the literature. Table 2 shows also that the factor with the greatest influence on the  $K^w$  value increase was the large increase in the average solubility coefficient ( $\bar{\beta}$ ) of water in the film, because the coefficients for the water diffusion through the films were almost constant, in all cases. Glycerol and sorbitol hydroxyl groups made the films more hygroscopic, increasing the  $\bar{\beta}$  values. Moreover, for all film formulations, increasing the relative humidity resulted in higher  $K^w$  values. The  $K^w$  values of films prepared with 0.25 g glycerol/g starch increased by around 50% when the relative humidity difference used in the  $K^w$  experiments varied from 2–33% to 33–64% and by around a factor of 4 when the difference varied from 33–64% to 64–90%. For films prepared with sorbitol, a similar behavior was observed, but the increase in the permeability was smaller for the lower RH range. For films prepared with 0.25 g sorbitol/g starch, the  $K^w$  value did not vary when the air RH difference used in the experiments varied from 2–33% to 33–64%, but it increased by around 65% when the air RH difference varied from 33–64% to 64–90%. The effect of the relative humidity range on the water vapor permeability can be evaluated in two ranges. In the first range (2–33% to 33–64%) a small increase in  $K^w$  values was detected, while in the second range (33–64% to 64–90%) this property increased significantly. This may be explained by the positive effect of the air RH increases on the  $\bar{\beta}$  val-

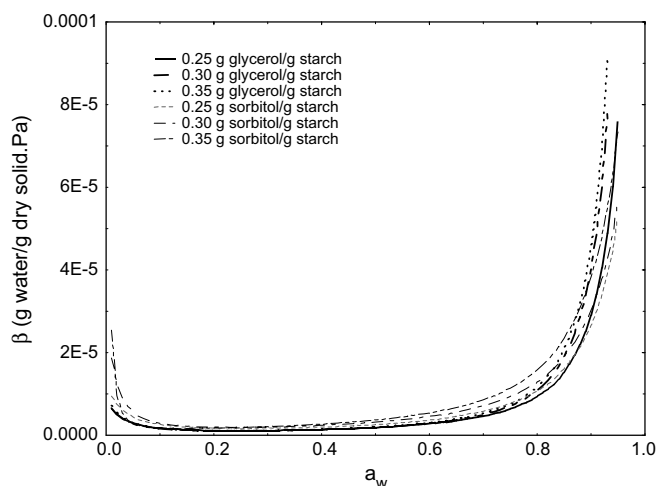


Fig. 2. Behavior of the solubility coefficient of water in the films with different plasticizer concentrations.



Table 2

Water vapor permeability ( $K^w$ ), median solubility coefficient of water in the film ( $\beta$ ) and coefficient of water diffusion through films prepared with different plasticizer concentrations

Plasticizer	RH gradients	$K^w$ (g/m <sup>2</sup> Pa h)	$\rho$ (g/m <sup>3</sup> )	$\bar{\beta}$ (g/g Pa)	$D^w$ (m <sup>2</sup> /h)
<i>0.25 g Plasticizer/g starch</i>					
Glycerol	2–33%	$1.59 \times 10^{-07}$	$1.98 \times 10^6$	$1.79 \times 10^{-06}$	$4.48 \times 10^{-08}$
	33–64%	$2.46 \times 10^{-07}$		$2.49 \times 10^{-06}$	$5.00 \times 10^{-08}$
	64–90%	$10.1 \times 10^{-07}$		$8.73 \times 10^{-06}$	$5.92 \times 10^{-08}$
Sorbitol	2–33%	$4.89 \times 10^{-08}$	$1.89 \times 10^6$	$1.21 \times 10^{-06}$	$2.14 \times 10^{-08}$
	33–64%	$5.08 \times 10^{-08}$		$1.81 \times 10^{-06}$	$1.49 \times 10^{-08}$
	64–90%	$8.39 \times 10^{-08}$		$7.40 \times 10^{-06}$	$6.00 \times 10^{-09}$
<i>0.30 g Plasticizer/g starch</i>					
Glycerol	2–33%	$2.33 \times 10^{-07}$	$2.46 \times 10^6$	$1.99 \times 10^{-06}$	$4.76 \times 10^{-08}$
	33–64%	$3.43 \times 10^{-07}$		$3.09 \times 10^{-06}$	$4.51 \times 10^{-08}$
	64–90%	$10.3 \times 10^{-07}$		$1.05 \times 10^{-05}$	$3.96 \times 10^{-08}$
Sorbitol	2–33%	$5.88 \times 10^{-08}$	$2.20 \times 10^6$	$1.13 \times 10^{-06}$	$2.37 \times 10^{-08}$
	33–64%	$5.88 \times 10^{-08}$		$1.82 \times 10^{-06}$	$1.47 \times 10^{-08}$
	64–90%	$8.81 \times 10^{-07}$		$8.29 \times 10^{-06}$	$4.83 \times 10^{-08}$
<i>0.35 g Plasticizer/g starch</i>					
Glycerol	2–33%	$2.42 \times 10^{-07}$	$2.19 \times 10^6$	$1.68 \times 10^{-06}$	$6.56 \times 10^{-08}$
	33–64%	$4.42 \times 10^{-07}$		$3.59 \times 10^{-06}$	$5.62 \times 10^{-08}$
	64–90%	$10.4 \times 10^{-07}$		$1.29 \times 10^{-05}$	$3.68 \times 10^{-08}$
Sorbitol	2–33%	$7.56 \times 10^{-08}$	$2.23 \times 10^6$	$1.17 \times 10^{-06}$	$2.90 \times 10^{-08}$
	33–64%	$8.15 \times 10^{-08}$		$1.92 \times 10^{-06}$	$1.90 \times 10^{-08}$
	64–90%	$9.71 \times 10^{-07}$		$8.94 \times 10^{-06}$	$4.87 \times 10^{-08}$

ues, while the  $D^w$  values did not vary considerably, in all cases.

The permeability of films prepared with 0.30 g glycerol/g starch was 4.4 times greater when the RH gradient changed from 2–33% to 64–90%. This  $K^w$  behavior is associated with the  $\beta$  increase since this parameter increased 5.3-fold for the same RH range, while  $D^w$  showed a relatively small variation.

Mali (2002) reported results for the water vapor permeabilities of yam starch films prepared with lower plasticizer concentrations and using a relative humidity difference of 2–75%. The  $K^w$  values were close to  $10^{-7}$  g m/m<sup>2</sup> h Pa, which is similar to the  $K^w$  values for the cassava starch films reported by Sakanaka et al. (2004). The results found in this study showed that water vapor permeability is greatly dependent on relative air humidity, since this variable has a great influence on the  $\beta$  values.

#### 4. Conclusions

The relative air humidity and the plasticizer type and concentration affect the solubility coefficient ( $\bar{\beta}$ ) of water in the films and, consequently, the film water vapor permeability. Water vapor permeability ( $K^w$ ) increases with plasticizer concentration and with air relative humidity. Therefore, the determination of water vapor permeabilities of hygroscopic films using the procedures developed to handle synthetic films may not to be satisfactory. The solubility coefficient of water in most synthetic films is independent on air RH. As  $K^w$  is dependent on the air

RH for hygroscopic films, it must be determined for the specific RH range conditions under which the films will be used.

The procedure used in this study is useful to understand how RH and plasticizer concentration affect the water diffusion coefficient ( $D^w$ ) of the films. It is surprising to find that  $D^w$  does not vary significantly with RH and plasticizer concentration, which is not consistent with the proposal that an opening of the polymer chains results in an increase in  $D^w$ . The hydrophilic groups of plasticizers could even reduce water molecule mobility and as a result reduce  $D^w$ . Thus, it is possible to conclude that water vapor permeability is controlled by the solubility coefficient ( $\bar{\beta}$ ) of water in the film.

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