Influence of the Physical State of Water on the Barrier Properties of Hydrophilic and Hydrophobic Films

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Water transfer through different films, as a function of the physical state of water in contact with the film, the relative humidity difference, and the water vapor pressure difference, was investigated. The films were two synthetic packagings (hydrophobic polyethylene and hydrophilic cellophane) and an edible film. The physical state of water affects water sensitive films, such as cellophane, inducing a higher liquid water transfer due to interactions with the polymer. For hydrophobic polymers, such as polyethylene, neither the physical state of water nor the relative humidity has an influence on the water permeability. In complex system, such as an edible film composed of hydrophilic particles dispersed in a lipid phase, barrier efficiency is influenced by the continuous hydrophobic phase but could also be affected by the physical state of water due to the presence of hydrophilic compounds.

Keywords: *Water transfer; permeability; physical state; edible films; packaging materials*

INTRODUCTION

The properties of edible films have been reviewed by Kester and Fennema (1986), Guilbert et al. (1995), Krochta (1997), and Debeaufort et al. (1998). Lipids are the most efficient as moisture barrier due to their hydrophobic character (Callegarin et al., 1997). Some studies have shown that barrier efficiency is mainly due to lipid phase, but it could be affected by the other compounds (Landmann et al., 1960; Biquet and Labuza, 1988). The composite film used in this study consists of hydrophilic particles (i.e., sugar, cocoa powder) dispersed in a hydrophobic continuous phase (lipid). One of the most used types of lipid film is chocolate. Permeabilities quantified the film efficiency to reduce mass transfers between food and its surrounding medium. Water transport through such films is complex, due to the sigmoidal shape of the water sorption isotherm. Water flux varies nonlinearly with water vapor pressure difference, and permeability is not an inherent property of hydrophilic films (Crank, 1975; McHugh et al., 1993). Most of the papers dealing with moisture transfer through edible or plastic films concern water vapor transfers. Little explanation has been offered for the influence of the physical state of water in contact with the film on its transfer through an edible packaging. Nevertheless, some studies take into account the direct contact of the moist product with the barrier (Kamper and Fennema, 1985; Rico-Peña and Torres, 1990) or water-filled packages as described by Labuza and Contreras-Medellin (1981), but they were not compared to water vapor transfer. Water transfer is due to the chemical potential difference between the two food compartments, but water molecules affect film properties such as plasticization, swelling, and solubilization, which could modify the barrier efficiency. Moreover, because the physical state of water could influence these phenomena, it should be interesting to study and compare liquid and vapor transfers of water.

To better understand the effects of the state of water on the edible film, two packagings were studied under the same conditions: cellophane, which is a hydrophilic cellulose membrane, and amorphous polyethylene (hydrophobic). The aims of this study are first to understand the influence of the physical state of water on its transfer through three types of films (cellophane, polyethylene, and an edible film) and second to explain the contribution of the different ingredients of the edible film compared with the model films.

EXPERIMENTAL PROCEDURES

Materials. The lipid-based, edible film was composed of hydrogenated vegetable fat, crystalline sucrose, cocoa powder, and lecithin. The commercial cellophane film (300P) was obtained from Courthauld's films (U.K.), and the ultralow-density polyethylene film (ULDPE) was from Enichem Polymeres France S.A. Their densities were, respectively, 1200 and 900 g L^{-1} at 25 °C.

Edible Film Preparation. Material was melted at 70 °C during 10 min, laminated on a plate at room temperature, and solidified at 5 °C. Disks of a defined thickness (650 ± 50 μm) were obtained and stored for 24 h over silica gel at 25 or 5 °C before permeation measurements, respectively, at 25 °C or at lower temperatures. The temperature profile of samples was the same in each preparation to induce the same fat crystallization. The disk thickness was controlled during the lamination step and accurately measured at room temperature (22 ± 2 °C), after cooling, with an electronic micrometer (Sodexim S.A., France). The cellophane films displayed a thickness of 20 μm and for polyethylene, 30 μm.

Water Transfer Rate (WTR) Determination. The WTR was determined gravimetrically using a derived AFNOR (NF

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Table 1. Water Activity of the Sucrose Solutions from the Larsen−UNIQUAC Model and at Their Experimental Temperature

exptl temp (°C)	concn (%, w/w)	a_w from Larsen−UNIQUAC model	a_w at exptl temp
40	71.0	0.818	0.840
25	68.5	0.840	0.852
25	50.0	0.934	0.939
15	68.5	0.840	0.848
5	68.5	0.840	0.843
−10	66.0	0.858	0.854

H00-030, 1974) procedure adapted by Debeaufort et al. (1993). The film was placed in a glass cell containing pure water or a sucrose solution (Prolabo, purity of 99.8%). The permeation cells were placed, for positive temperatures, in a commercial climate-controlled room from WTB binder (Tuttlingen, Germany) maintained at a relative humidity (RH) of 22%; and, for negative temperatures, in another climatic room maintained at 17% RH. All systems were ventilated and regulated in temperature at ±1 °C for positive temperatures and at ±0.5 °C for negative ones. Permeation cells were stood up with an air layer between the solution and the film to determine the water vapor transfer rate, or turned, inducing a direct contact between the solution and the film barrier to measure the liquid water transfer rate. In direct contact, a small quantity of solution was used (∼5 mL) to ensure that the pressure, due to the gravity, would not affect the water transfer. From preliminary studies, the use of saturated salt solutions to control the high RH in direct contact with the film induced an ingress of salt solution in the film, and as water evaporated on the other film face, the salt crystallized inside the barrier film, denaturing the structure. Sucrose solutions were used to control the RH because the edible film contained crystalline sucrose, avoiding migration of this molecule from the solution inside the film.

The sucrose solutions were prepared at concentrations slightly higher than the saturation for each temperature to obtain a saturated solution. The concentration were 71, 68.5, 68.5, 68.5, and 66% (w/w) for measurements at 40, 25, 15, 5, and −10 °C, respectively; a nonsaturated sucrose solution (50%) was prepared to study the effect of higher water activity difference at 25 °C. The water activity of these solutions was determined by a Larsen modified UNIQUAC model (Catté et al., 1994). As the sucrose−water binary mixtures were nonideal, their water activities changed with temperature (van der Berg and Bruin, 1981). Equation 1, given by Morin (1983),

$$a_{w2} = (a_{w1})^{T_1/T_2} \tag{1}$$

allowed the calculation of the water activity (a_w) of a solution at any temperatures. In eq 1, a_{wi} is the water activity at the temperature T_i (K).

The a_w values of the sucrose solutions used in this study were calculated with the Morin equation at their use temperature, considering that the water activity determined by the Larsen−UNIQUAC model corresponds to the absolute temperature (273.15 K), and they are given in the Table 1.

Water Permeability Calculation. Cells were accurately weighted at least two times by days at 5 and 25 °C and every 10 min at −10 °C (in a continuous system) with a precision of 0.1 mg. From the slope of the plotted curve of the cell weight versus time, for fixed operating conditions, water vapor transfer rate (WVTR) and water liquid transfer rate (WLTR) were determined at steady state. The water vapor or liquid permeability (WVP or WLP), denoted WP for the water permeability without consideration of the physical state of water, often called the permeability coefficient, was calculated from the WTR as follows:

$$WTR = \Delta w/\Delta t \times A \tag{2}$$

$$WP = (WTR \times e)/\Delta p \tag{3}$$

where $\Delta w/\Delta t$ is the transfer rate, that is, the amount of

Table 2. Water Permeability of the Three Films Determined at 25 °C (ΔRH = 22−85%)[a]

	water permeability (10^{-12} g m^{-1} s^{-1} Pa^{-1})		
	polyethylene	cellophane	lipid-based film
vapor water	1.4[d]	62.6[b]	31.6[c]
liquid water	1.5[d]	99.0[a]	28.6[c]

[a] Values having the same letter are not significantly different at a level of $p < 0.05$.

moisture loss per unit of time (g s^{-1}); A is the film area exposed to moisture transfer (8×10^{-4} m^2); e is the film thickness (m); and Δp is the water vapor pressure difference between the two sides of the film (Pa).

For each measurement, at least three repetitions were made. Differences among data means were tested for statistical significance at the $p < 0.05$ level by the Student−Newmans−Keuls test.

Determination of Water Vapor Sorption Isotherms. Sorption isotherms were determined according to the Cost 90 procedure adapted to our experiments and samples (Wolf et al., 1985). Samples were dried over P_2O_5 during at least 3 weeks. One gram of each product was weighed into vials and placed in seven boxes containing saturated salt solutions to maintain the relative humidities of 11.0, 33.0, 42.8, 57.7, 75.3, 84.3, and 90.2% at a temperature of 25 ± 1 °C. Respectively, the solutions of LiCl, MgCl$_2$, K$_2$CO$_3$, NaBr, NaCl, KCl, and BaCl$_2$ were prepared according to the procedure described by Multon (1984), and water activity was taken from the literature (Multon, 1991) and measured in the laboratory with Decagon (Tripette & Renault, France). The atmosphere in sorption chambers was stirred by small fans (∼5 s every 5 min). Measurements of water uptake by samples were done by weighing samples until equilibrium. For each measurement, at least four repetitions were made.

RESULTS AND DISCUSSION

Liquid and Vapor Water Permeabilities of the Films at 25 °C. The moisture permeabilities of the three films, polyethylene, cellophane, and lipid-based film, determined at 25 °C for an RH difference (ΔRH) of 22−85% with a direct contact with the solution (liquid water contact) or not (vapor water contact) are given in Table 2.

The hydrophobic film (polyethylene) displays low water permeabilities, which are indicative of a good barrier efficiency. The water vapor value is slightly higher than those found by other authors (Park et al., 1993; Krochta, 1997), probably due to the film's amorphous structure (crystallinity < 0.5%; Debeaufort, 1994) versus that of polyethylene generally studied as packaging, which contains at least 30−35% crystallinity. The physical state of water does not affect its transfer, which depends only on the water activity difference on both sides of the film. This result follows the general tendency explained by Lebovits (1966), who states that the physical state of the permeant molecule (e.g., water) has no influence on its transfer through a polymeric material (e.g., polyethylene) in which it has no interaction.

The hydrophilic film (cellophane) has poor water barrier properties, and thus its permeability is higher when compared to that of polyethylene. The water vapor permeability is in the same order as values obtained by Martin-Polo et al. (1992) or by Debeaufort (1994), higher than those found by McHugh et al. (1993), and lower than the value reported by Krochta (1997). These differences would be due to the different natures of the cellophanes and measurement conditions; the value reported by Krochta (1997) was determined at 38 °C with a relative humidity difference (ΔRH) of 0−90%.

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Our results indicate that the physical state of water in contact with the film affects significantly the barrier efficiency of the cellophane, because for a given ΔRH, the liquid permeability is significantly higher than the WVP. These results could be related to the hydrophilic nature of the film. The presence of similar functional groups in the polymeric film and the penetrant induces an important affinity between them as shown by water vapor sorption measurements of cellophane (Weisser and Liebenspacher, 1989; Debeaufort, 1994). In a recent study concerning pure water sorption of cellulose membranes in both liquid and vapor phases, Grigoriew and Chmielewski (1997) explain that water acts on the cellulose in two ways. The liquid−cellulose contact induces water ingress in the cellulose and the formation of nanometric water inclusions, also called clusters. The saturation is obtained very rapidly, in a few seconds, for the liquid water, whereas it is achieved in ∼1 h for water vapor and causes weight increases by factor of 2 and 20% for liquid and vapor water, respectively. The organization of molecular chains of cellulose is decreased in both cases but more so with liquid than vapor water. These structure changes could explain the loss of cellophane barrier efficiency for liquid water.

Water permeability of the edible film is intermediate between those of the hydrophobic film (polyethylene) and the hydrophilic film (cellophane). It is composed of hydrophilic particles (sucrose and cocoa powder) dispersed in a hydrophobic phase (fat). WVP, 31×10^{-12} g m^{-1} s^{-1} Pa^{-1}, is slightly higher than the values obtained by Landmann et al. (1960) or by Biquet and Labuza (1988) for chocolate, which were between 10×10^{-12} and 26×10^{-12} g m^{-1} s^{-1} Pa^{-1}. There is no published value for liquid water permeability. In terms of the quantity of water that transfers through the edible film (9.5×10^{-5} and 8.6×10^{-5} g m^{-2} s^{-1} for, respectively, vapor and liquid transfer rate), it is comparable to that with the polyethylene film (9.0×10^{-5} and 9.8×10^{-5} g m^{-2} s^{-1}, respectively), so the barrier efficiency is mainly due to the lipid phase. The physical state of water does not affect the barrier efficiency of the edible film exposed to a ΔRH of 22−85%, whereas it contains hydrophilic components.
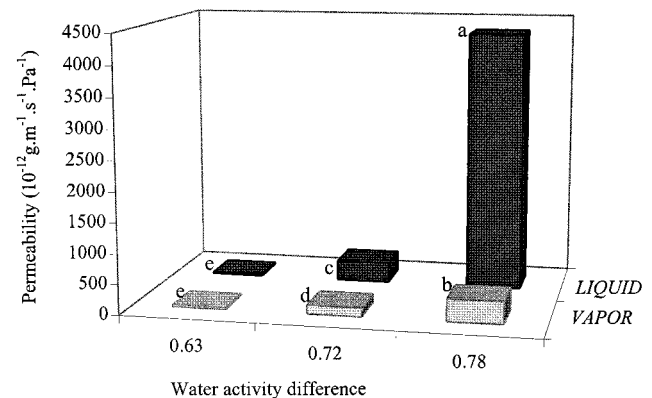
Influence of the Water Activity Difference on the Moisture Permeability at 25 °C. The state of water, for the same water activity, could affect its transfer through films interacting with the penetrant. To focus on these type of interactions, permeabilities were determined at 25 °C, for three ΔRH values varying at the highest RH value: 22−85, 22−94, and 22−100% (Figures 1 and 2).

According to our measurement conditions and method sensitivity, we observe that the water permeability of the polyethylene is not significantly affected either by the water activity difference, as shown by Myers et al. (1961) and McHugh et al. (1993), or by the physical state of water (Figure 1). The rate at which water (WTR) transfers through the film is directly proportional to the water vapor pressure difference (Δp), independent of the physical state of water in contact with the film. In others words, Henry's and Fick's laws can be applied; there is no strong interaction between polymer and water.

WP of cellophane increases with the water activity difference (Figure 1), as observed by Karel et al. (1959) for WVP. This non-Fickian behavior reveals the presence of interactions between water and film and/or film structure changes. The liquid state of water always
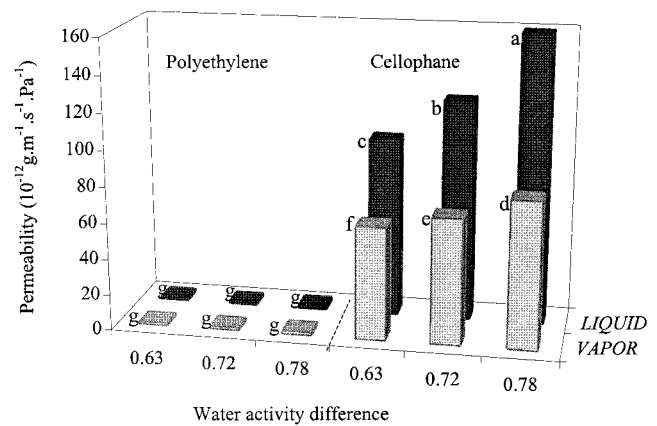
Figure 1. Water permeability of cellophane and polyethylene as a function of the water activity difference at 25 °C.
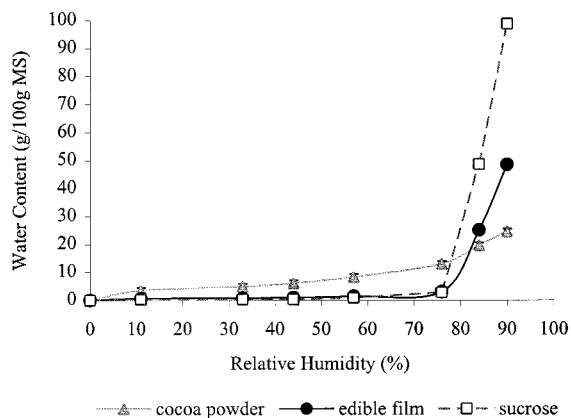

Figure 2. Water permeability of edible film as a function of the water activity difference at 25 °C.

induces higher permeability of cellophane than the vapor state. As explained previously, the liquid water interacts strongly with the hydrophilic polymer.

The edible film displays the same behavior as the hydrophilic film: the permeability increases with the water activity difference, especially for liquid water (Figure 2). Moreover, the liquid permeability is significantly higher than the vapor one, for each of the two highest water activity differences. The loss of barrier efficiency can be devoted to hydrophilic compounds, as observed by Landmann et al. (1960) and by Biquet and Labuza (1988) for water vapor transfers through dark chocolate. Hydrophilic particles are responsible of the edible film water affinity, as observed on their water vapor sorption isotherms (Figure 3). The shape of the water sorption isotherm of the edible film is mainly due to sucrose, with a slight influence of cocoa powder. This water affinity is particularly important in the case of liquid water, which could lead to a solubilization of edible film at high water activities. There is no difference between vapor and liquid water permeabilities for the lowest water activity difference (Figure 2), because the sucrose solution is a saturated one and cannot dissolve more sucrose crystals from the edible film. In this case, there is no influence of the physical state of water. These modifications of composition and structure affect strongly the barrier efficiency, and the barrier properties decrease by a magnitude of 100 when water activity differences vary from 0.22−0.85 to 0.22−1. The barrier efficiency provided by the fat phase is mainly affected by the water affinity of the dispersed phase.

WP as a Function of Water Vapor Pressure Differences and Temperature. The ΔRH affects the

Figure 3. Water vapor sorption isotherms of the edible film and the hydrophilic components at 25 °C (variability is included in the symbol size).

Table 3. Water Vapor Pressure Differences (ΔP) Used for the Permeability Measurements

(A) As a Function of the Temperature

	Δp: water vapor pressure difference (Pa)		
	at 25 °C	at 5 °C	at −10 °C
ΔRH = 22−85%	2001	543	183

(B) As a Function of the Relative Humidity Difference (ΔRH)

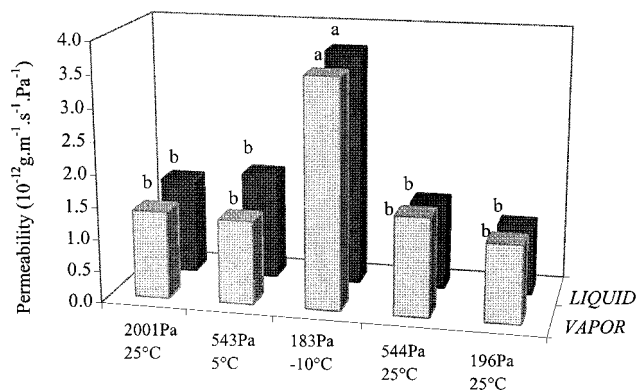|	Δp: water vapor pressure difference (Pa)		
	ΔRH = 22−85%	ΔRH = 68−85%	ΔRH = 78−85%
at 25 °C	2001	544	196
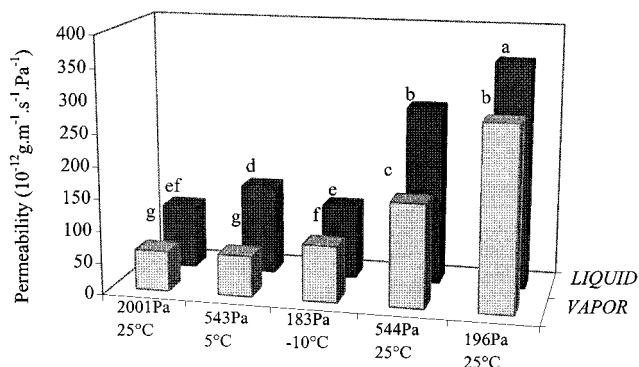
Figure 4. Water permeability of cellophane as a function of water vapor pressure difference (Pa) and temperature (°C).

barrier efficiency of films at 25 °C. The same ΔRH is maintained at several temperatures to analyze the influence of temperature on permeability.

For the same RH, the water vapor pressure varies with temperature. The 22−85% ΔRH at 25, 5, and −10 °C corresponds, respectively, to 2001, 543, and 183 Pa (Table 3A). These last vapor pressure differences could also be obtained at 25 °C for 68−85 and 79−85% ΔRH (Table 3B). These ΔRH values are studied in high relative humidities to focus on the influence of possible interactions between penetrant and film.

Permeabilities of water through cellophane measured for the same ΔRH (22−85%) at different temperatures are in the same range (bars 1, 2, and 3 in Figure 4). Measured at 25 °C for these vapor pressure difference (bars 4 and 5 in Figure 4), the permeabilities of water through cellophane for the same water vapor pressure differences (Δp) are always higher at 25 °C than at 5 and −10 °C (Figure 4). Liquid permeabilities are always significantly higher than vapor ones, whatever the


Figure 5. Water permeability of polyethylene as a function of water vapor pressure difference (Pa) and temperature (°C).

temperature or the ΔRH. The affinity of cellophane for water is responsible for the differences observed, because the high relative humidities used at 25 °C induce a great moisture sorption, whereas the water vapor pressure difference is the same. McHugh et al. (1993) have also observed that the highest RH gives the highest permeability of water sensitive film, due to plasticization of the film. At different temperatures, film barrier efficiency is more affected by ΔRH than by Δp.

The same measurements were made for the hydrophobic polyethylene film and are given in Figure 5. For this film, the moisture sorption is much lower (McCall et al., 1984; Gerlowski, 1990) and permeabilities measured for a Δp of 543 Pa (at 25 and 5 °C), are comparable (Figure 5). Moreover, there is no difference between the vapor and the liquid water permeabilities. This means that water diffusion in the film does not decrease significantly with temperature to lower the water transfer. The WVP and WLP measured at 25 °C for a pressure difference of 196 Pa are not significantly different from those obtained previously for a Δp of 543 Pa, as measured for a Δp of 2001 Pa (at 25 °C). These results confirm that when the film has no affinity for water, the influence of sorption is negligible and the transfer depends only on the Δp, whatever the physical state of water. Nevertheless, WP measured at −10 °C for a pressure difference of 183 Pa is 3 times higher than obtained at 25 °C for a similar Δp. This is probably due to a structure change of the film because its barrier efficiency is affected independently by the liquid or vapor state of water. This could not be attributed to the water sorption, because in that case we would expect that cellophane would exhibit the same behavior.

To determine the influence of the Δp, permeabilities were determined at two additional temperatures (40 and 15 °C) with constant ΔRH (22−85 or 22−100%). The curves as a function of the Δp obtained at these different temperatures (40, 25, 15, 5, and −10 °C) were analyzed in Figures 6 and 7. The WTR of polyethylene varies linearly with Δp at values >2000 Pa, that is, independently from the ΔRH, the temperature, or the physical state of water (Figure 6). This change at 2000 Pa could be due to water sorption of polyethylene as observed by Karel (1959), which plasticizes the polymer (Johansson and Leuven, 1994).

The WVTR through cellophane shows an evolution similar to that observed for polyethylene with a slope change at 5000 Pa (Figure 7). Nevertheless, WLTR displays a more complex evolution: it increases with Δp with a strong increase above 1000 Pa, and it is progressively reduced for Δp > 2000 Pa. The strong change at

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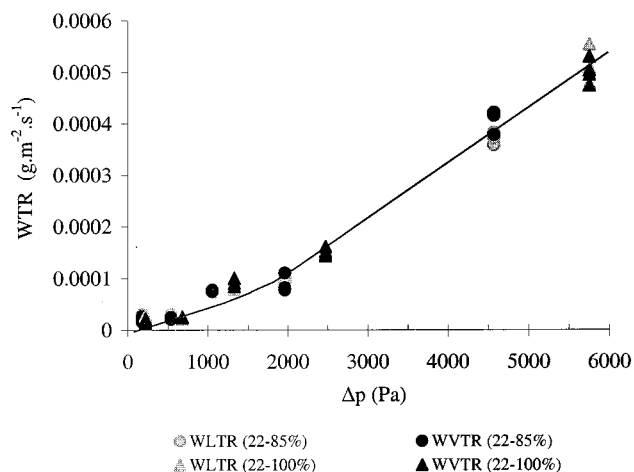
Figure 6. WTR through polyethylene as a function of the water vapor pressure difference (Pa) and the physical state of water.
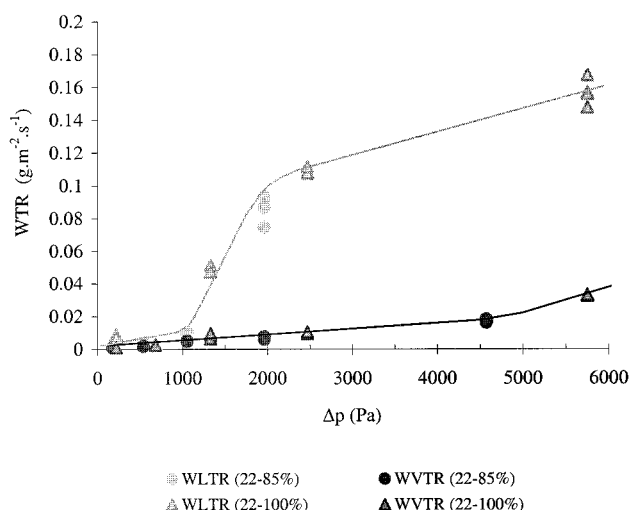
Figure 7. WTR through cellophane as a function of the water vapor pressure difference (Pa) and the physical state of water.

1000 Pa is probably due to plasticization of the film structure by the water, as observed previously. The WTR slowing at 2000 Pa could be due to the formation of clusters inside the cellophane film, which decrease the water diffusion and the WTR as observed by Debeaufort et al. (1994) for methylcellulose films. This hypothesis agrees with the results of Grigoriew and Chmielewski (1997), who showed that liquid water induces nanometric inclusions with an average size of 8 nm. Meares (1977) explains also that when hydrophilic polymers are saturated by contact with liquid water, this molecule is extensively clustered and located preferentially in the regions of the hydrated polar groups. It could be supposed that the WVTR through this film would exhibit the same behavior but at higher Δp due to the lower sorption from water vapor than liquid water (Grigoriew and Chmielewski, 1997). The influence of the ΔRH seems mainly due to the Δp value. Moreover, these results demonstrate that for films such as cellophane, the two factors of permeation (the sorption and the diffusion) could be strongly affected by the liquid state of water.

Conclusion. The physical state of water affects only water sensitive films, such as cellophane, inducing a higher liquid water transfer due to interactions with the polymer: higher water sorption, swelling, and changes in composition or in structure, which all decrease the barrier efficiency. In this case, the increase of the water activity difference has a tremendous effect, increasing the detrimental action of the liquid water during its transfer. For hydrophobic polymers, such as polyethylene, the water transfer depends only on the water vapor pressure difference on both sides of the film. Neither the physical state of water nor the relative humidity has an influence on the water permeability.

The edible film presents different aspects due to its composition: hydrophilic particles dispersed in a hydrophobic matrix. Its barrier efficiency is similar to those of polyethylene, due to the lipid phase. Nevertheless, the physical state of water affects this property due to the presence of hydrophilic compounds. In such complex systems, all of the components act and must be taken into account to predict the barrier efficiency.

ABBREVIATIONS USED

A = surface area (m²)
a_w = water activity
e = thickness (m)
T = temperature (K)
t = time (s)
ULDPE = ultralow-density polyethylene
WP = water permeability (g m^{-1} s^{-1} Pa^{-1})
WLP = water liquid permeability (g m^{-1} s^{-1} Pa^{-1})
WVP = water vapor permeability (g m^{-1} s^{-1} Pa^{-1})
WTR = water transfer rate (g s^{-1})
WLTR = water liquid transfer rate (g m^{-2} s^{-1})
WVTR = water vapor transfer rate (g m^{-2} s^{-1})

Greek Symbols

ΔRH = relative humidity difference (%)
Δp = water vapor pressure difference (Pa)
Δw = amount of transferred water (g)

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