Water Vapor Absorption and Permeability of Films Based on Chitosan and Sodium Caseinate

Mariana Pereda, Mirta I. Aranguren, Norma E. Marcovich

Institute of Research in Materials Science and Technology, Department of Chemical Engineering,
AQ1 *Universidad Nacional de Mar del Plata, Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina*

ABSTRACT: The objective of this work was to characterize the moisture sorption and water vapor permeation behavior of edible films made from sodium caseinate and chitosan for future applications as protective layers on foods. Glycerol was used as a plasticizer, and the films were obtained by a casting/solvent-evaporation method. The moisture sorption kinetics and water vapor permeability (WVP) were investigated. The effect of the addition of glycerol on the WVP characteristics of the films was determined at 25°C with a relative humidity (RH) gradient of 0–64.5% (internal to external). Experimental data were fitted with an exponential function with two fitting parameters. WVP increased with increasing glycerol content in both films, chitosan samples being much more permeable than caseinate ones at any glycerol content. WVPs of sodium caseinate, chitosan, and chitosan/caseinate films with 28 wt % glycerol were also determined for two RH gradients, 0 to 64.5% and 100 to 64.5%, higher WVPs being measured at higher RHs. The moisture sorption kinetics of caseinate films prepared with various glycerol contents were determined by the placement of the films in environments conditioned at 20°C and 75% RH. Peleg's equation and Fick's second law were used to predict the moisture sorption behavior over the entire time period. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2008

Key words: biodegradable; proteins; renewable resources; thin films

INTRODUCTION

Edible films from renewable natural products not only are degraded readily after their disposal but also can extend the food shelf life, thus improving the quality of food. Caseinate-derived edible film wraps may be able to partially replace some conventional synthetic packaging materials used to preserve and protect foods because of their renewable and biodegradable nature.[1,2] Caseinates, obtained by acid precipitation of casein, easily form aqueous solutions because of their random-coil nature and ability to form extensive intermolecular hydrogen bonds.[3]

Chitosan is available from waste products of the shellfish industry.[4] Its importance resides in its antimicrobial properties in conjunction with its cationicity and film-forming properties.[5] Chitosan, bearing positively charged groups, can interact and form three-dimensional networks with molecules containing opposite charges, such as caseinate. Chitosan is known to be biodegradable, nontoxic, biocompatible, and bioadhesive.[6]

Moisture transfer is often the most important factor leading to changes in food quality during distribution and storage. Critical levels of water activity of food products must be maintained for optimal quality and acceptable safety.[7] Moisture transfer in finished products can seriously affect food quality, stability, and safety during storage and distribution. Edible films contribute to food preservation by controlling the mass-transfer phenomena. In fact, films controlling the rate at which small-molecular-mass compounds permeate inside or outside the package can slow down the detrimental phenomena responsible for the unacceptability of the packed foodstuff. Therefore, the effectiveness of edible coatings is generally related to their mass-transport properties.[8] Thus, to use the films as food packaging, it is necessary to understand their permeability characteristics and moisture sorption behavior. In accordance with the previous statements, the objective of this work was to characterize the moisture sorption and water vapor permeation behavior of edible films made from sodium caseinate and chitosan for future applications as protective layers on foods.

EXPERIMENTAL

Materials

AQ5 Sodium caseinate powder, containing 88.9 wt % protein (the rest being lactose, lipids, attached moisture, and ashes), was obtained from Lactoprot Deutschland GmbH (Germany). Chitosan (deacetylation degree = 90%) was supplied by Acofar (Mar del Plata, Argentina). Glycerol was purchased from DEM Chemicals (Mar del Plata, Argentina).

Methods and techniques

Film preparation

Sodium caseinate solutions with protein concentrations of 2.5% (w/v) were prepared by the dispersion of the sodium caseinate powder in distilled water and continuous stirring for 3 h at room temperature. Appropriate amounts of glycerol were added to achieve glycerol/protein weight ratios of 0.15, 0.28, 0.37, 0.43, and 0.5.

Chitosan solutions (2% w/v) were prepared by the dispersion of chitosan powder in an acetic acid solution (1 vol %). Different glycerol contents were added to achieve glycerol/chitosan weight ratios of 0.15, 0.28, 0.37, and 0.5.

Chitosan/sodium caseinate films were prepared through the mixing of 100 mL of the 2% (w/v) chitosan solution with 100 mL of 2.5% (w/v) sodium caseinate. Glycerol was added to achieve a glycerol/(protein + chitosan) weight ratio of 0.28, which represents 22% of the total solid weight.

Films were prepared according to the usual procedure,[9–14] and aliquots of each solution were then poured into Teflon Petri dishes (diameter = 14 cm) and dried at a constant temperature for approximately 10 h in a convection oven. The obtained films were peeled off from the plates after the excess water was evaporated and kept in a closed reservoir at 64.5% relative humidity (RH) and 23 ± 2°C for 3 days. The films were further characterized and tested.

The nomenclature used for the prepared edible films in the figures was as follows: SC for sodium caseinate films, CH for chitosan films, and CH/SC for hybrid films.

Thickness measurements

The thickness of the films was determined with a 0–25-mm manual micrometer with an accuracy of 0.01 mm. The reported values are the average of four readings taken randomly on each film sample. The measured thickness was used in the calculation of the film water vapor permeability (WVP).

Moisture sorption

The films were dried at 40°C for 3 days in a vacuum oven to ensure that they reached a constant weight. After that, they were placed into an environmental chamber maintained at 75% RH and a fixed temperature (23 ± 2°C) to obtain water sorption isotherms. Samples were taken out of the chamber at regular time intervals and weighed with a precision of ±0.0001 g. This experiment was performed on four specimens of each sample to ensure the reproducibility of the results.

The moisture content of the films as a function of time was obtained from the total mass balance over the sample as follows:

$$M_t = \frac{(W_t - W_0)}{W_0} \times 100 \qquad (1)$$

where M_t is the moisture content of the sample at a fixed time expressed on a dry basis (%), W_t is the weight of the sample at a fixed time (g), and W_0 is the initial dry weight of the sample (g).

Theoretical considerations

When studying the sorption of small molecules by a matrix, we must consider the assumptions underlying the applied theoretical models. In particular, the absence of a reaction between the solute and the matrix is assumed.[15] Generally, in solid systems such as food products or polymers, mass-transfer processes include not only Brownian diffusion but also other phenomena such as convection, capillary forces, chemical reactions, or transport resistance.[16] Diffusivity is highly dependent on the molecular properties and reactivity of the diffusing substance with the medium. Physicochemical interactions between a macromolecular system and a small diffusing molecule affect its diffusion, as has been observed in the case of aroma compounds in polymers.[17] Finally, water diffusion into hydrophilic polymers results in polymer chain relaxation with volume expansion. Thus, a simple analysis of the experimental data can lead only to an apparent diffusion coefficient.

A number of authors have proposed models for the absorption of water in hydrophilic films. These can be divided into two broad categories: empirical and fundamental.

Empirical models, which do not account for the fundamental physical processes occurring during water absorption, are often preferred to fundamental ones because of their easy computation. In this category, the Peleg equation is particularly popular for the empirical description of the sorption process for many food systems such as milk powders, rice and sago starches,[18] and edible polymeric films.[19] This

FILMS BASED ON CHITOSAN AND SODIUM CASEINATE 3

expression relates the instantaneous moisture content (M_t) to the initial moisture content (M_0):

$$M_t = M_0 + \frac{t}{K_1 + K_2 \cdot t} \qquad (2)$$

AQ3 where K_1 and K_2 are fitting parameters. K_1 is Peleg's rate factor [h/(g of water/g solid)] and is associated with the initial absorption rate; the higher K_1 is, the lower the initial absorption velocity is. K_2 is Peleg's capacity parameter (g of solid/g of water) and is related to the final absorption capacity. K_2 decreases as the absorption capacity increases.

Fundamental models describing water absorption in films are usually based on Fick's second law of diffusion, which, in the specific case of mass transport through a plane sheet with constant boundary conditions, reduces to the following expression:[20]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-D\frac{(2n+1)^2\pi^2 t}{l^2}\right] \qquad (3)$$

AQ2 where M_∞ is the amount of water absorbed at equilibrium, D is the effective diffusion coefficient, and l is the average thickness of the film. Edge effects being neglected, the early stages of diffusion-controlled uptake can be predicted in a simplified way as follows:[21]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2} \qquad (4)$$

WVP

The water vapor transfer rate (g/s m^2) through films was determined gravimetrically with ASTM Method E96-95.[22] The films were placed in a chamber maintained at room temperature and 64.5% RH for at least 2 days before each test. A fan located inside the chamber was used to move the internal air, ensuring uniform conditions at all test locations. During this period, the samples reached equilibrium conditions. After that, film specimens were mounted on acrylic cups containing dehydrated Cl_2Ca or distilled water. The corresponding RHs were 0% for the desiccant and 100% for the water. The weights of the assembled cups were recorded every hour for 6 h. Linear regression was used to fit the data (weight versus time) and to calculate the slope of the resulting straight line (g/s).

Six specimens were tested for each film type. Permeability values are reported as WVP (g m/Pa s m^2) as follows:

$$WVP = \Delta W y [A \Delta t (p_2 - p_1)]^{-1} \qquad (5)$$

where ΔW is the weight of water absorbed in the cup (g); Δt is the time for weight change (thus $\Delta W/\Delta t$ is the calculated slope); A is the area of the exposed film (m^2); y is the film thickness (m); and $p_2 - p_1$ is the vapor pressure difference across the film (Pa), which was calculated on the basis of the RH and temperature inside and outside the cup.

A two-parameter exponential equation was used to fit the experimental data:[23]

$$WVP = WVP_0 \exp(kx) \qquad (6)$$

where x is the glycerol concentration [g $(100 \text{ g})^{-1}$], k is a parameter related to the efficiency of glycerol to plasticize the film, and WVP_0 corresponds to the WVP of the films without glycerol.

RESULTS AND DISCUSSION

WVP

The WVP values measured at $23 \pm 2^\circ$C for caseinate and chitosan films at an RH gradient of 0–64.5% are shown in Figure 1. The reported values are of the same magnitude as data available in the literature for similar materials, that is, 2.6×10^{-10} to 4×10^{-10} g m/Pa s m^2 for chitosan films modified with garlic oil,[24] 8.3×10^{-10} g m/Pa s m^2 for glycerol-plasticized sodium caseinate films,[2] 3.6×10^{-12} to 5.2×10^{-11} g m/Pa s m^2 for cellophane films,[25] and 0.07×10^{-11} to 5×10^{-11} g m/Pa s m^2 for chitosan/gelatin films plasticized with water and glycerol,[5] all tested under similar temperature and RH gradient conditions.

As a rule, the incorporation of hydrophilic plasticizers into protein and polysaccharide films increases the WVP.[26] The inclusion of glycerol molecules in the polymer network increases the interchain spacing by reducing intermolecular interactions. The added plasticizer disrupts hydrogen bonding between the polymer chains, reducing the
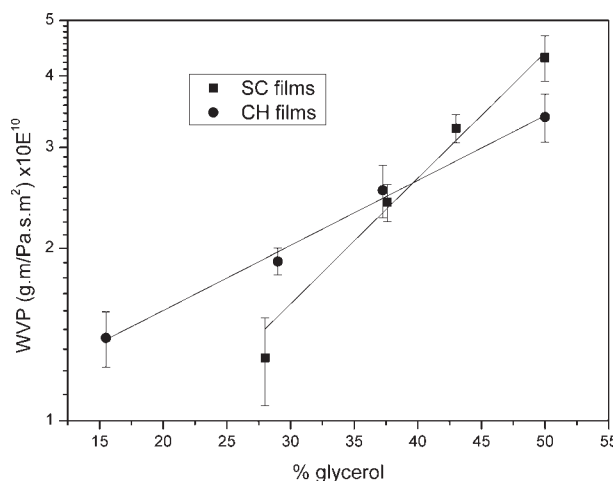
Figure 1 WVP as a function of the glycerol content for chitosan (CH) and sodium caseinate (SC) films: (■) experimental values and (—) modeled curves.

TABLE I
Fitting Parameters for Curves of WVP Versus the Glycerol Content for Caseinate and Chitosan Films

Film	$WVP_0 \times 10^{10}$	$k \times 10^2$	R^2
Chitosan	0.924	2.61	0.994
Sodium caseinate	0.35138	5.052	0.9878

TABLE II
WVP for Chitosan Films (Initial Thickness = 0.085 mm) Plasticized with 15% Glycerol at Three Different RH Gradients

Test condition (% RH)	$WVP \times 10^{10}$ (g m/Pa s m^2)
0/78	2.022 ± 0.11
0/71	1.55 ± 0.13
0/64.5	1.394 ± 0.153

interchain bonds and thus facilitating the diffusion of water molecules through the film.[27] In addition, because of the hydrophilic nature of glycerol, this compound acts as a humectant, enhancing the water-holding capacity of the polymer matrix and also contributing to higher WVP values of the films. At low glycerol contents, chitosan films show higher WVP values than sodium caseinate ones. However, the opposite behavior has been observed in samples prepared with more than 40 wt % glycerol. A higher sensitivity of the protein matrix to changes in the plasticizer concentration has also been noted.

Figure 1 also shows that WVP values present an exponential functionality with the glycerol content. This behavior has also been observed for the WVPs of several protein and polysaccharide films plasticized with water or glycerol.[28–31]

Equation (6) was used to model the experimental results. The corresponding WVP_0 value was not measured but was kept as a fitting parameter instead because of the difficulty of measuring WVP on nonplasticized films (brittle materials that break easily and cannot be manipulated without cracking).[32] WVP_0, k, and the regression coefficients for caseinate and chitosan films are given in Table I. The calculated k values are well in the range of those reported in the literature; a k value of 0.042 has been reported for gliadin films equilibrated at 75% RH.[23] As shown by the regression coefficients, eq. (6) provides a good fitting of the experimental values. Moreover, the larger k value calculated for the caseinate samples indicates that glycerol is more efficient in plasticizing protein films than chitosan ones.

The effect of the RH gradients on the WVP of chitosan films prepared with a constant glycerol content (15%) was also investigated, as shown in Table II.

As anticipated, testing conditions have a strong effect on the measured WVP. An increase in the RH gradient (by increasing the chamber humidity in this case) has a substantial impact on this property. WVP values increase as the humidity gradient increases because of the higher diffusivity caused by moisture plasticization and, consequently, the increased solubility.[33]

The mechanism involved in water transport through hydrophilic films such as chitosan ones is very complex. This complexity leads to nonlinear water sorption isotherms; therefore, the water vapor transport varies nonlinearly with the water vapor pressure, and water-content-dependent diffusivities are the result.[10]

To analyze the effect of the humidity level on the WVPs of caseinate, chitosan, and chitosan/sodium caseinate films prepared with 28 wt % glycerol, WVP measurements were performed at two RH gradients: 0/64.5 and 100/64.5 (Table III).

In this case, the WVP of films increased with increasing internal humidity (actually, with the overall average humidity). Again, it should be associated with the larger effect of plasticization resulting from increasing average humidity, independently of the gradient. Under high-humidity conditions, water, acting as a plasticizer, favors polymeric chain relaxation, allowing an increase in the penetrant flow, which leads to an increase in WVP.

Both chitosan and caseinate films showed a similar increase in WVP with respect to those obtained at 0/64.5. However, the WVP of the hybrid film chitosan/sodium caseinate is an intermediate value between the WVPs of pure chitosan and sodium caseinate films at the 0/64.5 gradient, although it is the maximum value at 100/64.5.

TABLE III
WVP for Sodium Caseinate, Chitosan, and Chitosan/Sodium Caseinate Films at Different RH Gradients

Film	Temperature (°C)	Initial thickness (mm)	$WVP \times 10^{10}$ (g m/Pa s m^2) 0/64.5[a]	100/64.5[a]
Chitosan	25	0.0861	1.898 ± 0.102	9.630 ± 1.783
Sodium caseinate	23	0.088	1.288 ± 0.226	7.075 ± 1.186
Chitosan/sodium caseinate = 0.8	24	0.092	1.655 ± 0.075	10.133 ± 1.1083

All samples contained 28% glycerol.
[a] RH values (%) inside and outside the test cup.

This behavior is still under study, but it may be related to the effect of the high-humidity conditions on the interactions that develop between the cationic polymer (chitosan) and the sodium caseinate carboxyl groups, which should lead to polyelectrolyte complexation in forming the hybrid film.[32] Another explanation that could be reasonable is that under high-humidity conditions, film swelling could take place, facilitating polymer chain relaxations. Thus, swelling would cause a conformational change in the microstructure of the complex film and open up the polymer structure, allowing an increase in the flux of the penetrant, which would lead to a higher than expected WVP. Changes in the polymer structure that occur in response to stresses generated within the film during sorption are a result of swelling.[34] These hypotheses are also supported by observations made by other authors. Arvanitoyannis et al.[5] indicated that the cohesion of chitosan/gelatin blends increases in the presence of several self-associated molecules, such as water and polyols, provided that they do not exceed 20%. In this case, there was a relatively high concentration of glycerol in the complex film (22 wt % with respect to the total mass), which, added to the moisture adsorbed from the high-RH environment, may exceed the percentage for self-associated molecules that ensure cohesion in the film.
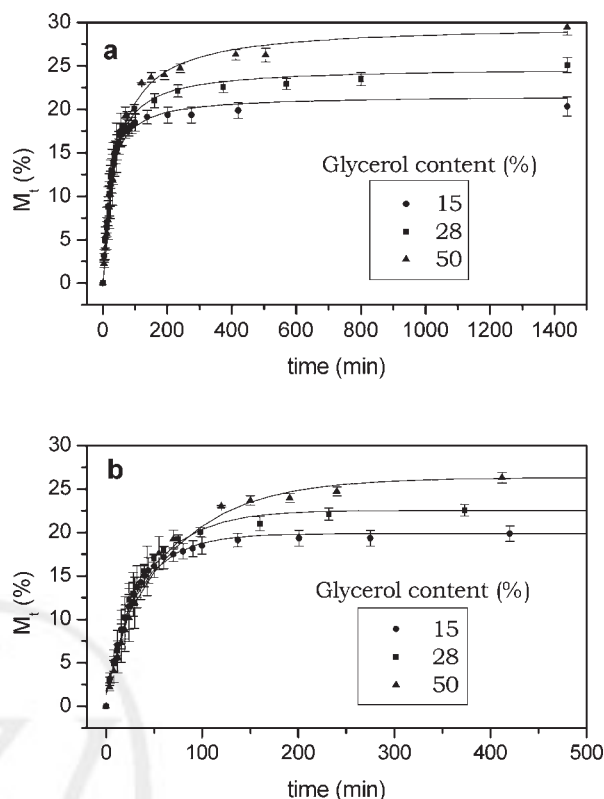

Figure 2 Moisture sorption of sodium caseinate films at 23°C and 75% RH as a function of time: (a) solid lines represent the fitting from the Peleg equation and (b) solid lines represent the Fickian model [eq. (3)].

Moisture absorption kinetics

To investigate the plasticizing effect of glycerol, a water sorption study for caseinate films was conducted at 23°C. The rate of moisture absorption is comparable but the equilibrium moisture content is higher with increasing concentrations of glycerol because of the hydrophilic nature of glycerol, as shown in Figure 2. The increasing moisture affinity of the films with increasing plasticizer concentrations is consistent with the findings for sorbitol- and/or glycerol-plasticized soy protein films,[35] for

glycerol-plasticized whey protein films,[19] for glycerol-plasticized gelatin films,[36] and for glycerol-plasticized whey protein films.[37]

Experimental moisture sorption data were fitted with the Peleg empirical equation [eq. (2)] over the entire time period, and the fitting parameters are reported in Table IV. The solid curves in Figure 2(a) are the results of the fitting process and show good agreement with the experimental data, as can be noticed from the R^2 parameters (Table IV).

TABLE IV
Fitting Parameters of the Peleg Equation and Effective Diffusion Coefficients for Sodium Caseinate (Different Glycerol Contents), Chitosan, and Chitosan/Sodium Caseinate Films

Film	Glycerol content (%)	Peleg equation [Eq. (2)]			Fickian model	
		Fitting parameters			Effective diffusion coefficient $\times 10^{13}$ (m^2/s)	
		K_1 (min/% weight)	K_2 (%$^{-1}$)	R^2	Eq. (4)	Eq. (3)
Sodium caseinate	15	0.915	0.0463	0.987	5.943	5.284
	28	1.060	0.0403	0.992	2.792	2.831
	50	1.452	0.0336	0.994	3.687	3.409
Chitosan	28	1.189	0.0161	0.997	1.512	1.144
Chitosan/sodium caseinate	28	0.743	0.0445	0.988	6.232	3.641

Experimental moisture sorption data were also fitted to eqs. (3) and (4), which correspond to the Fickian model, to calculate the effective diffusion coefficient (with the effective diffusion coefficient considered the fitting parameter).

Figure 2(b) shows the fitting curves corresponding to eq. (3) with the glycerol content as a parameter. The agreement between the theoretical curves and the experimental points is good in the early stages of sorption, but the model prediction slightly deviates at longer times (not shown in the figure). Moreover, the deviation increases as the glycerol content increases. The last data of the absorption test show non-Fickian behavior [the last experimental points can be observed in Fig. 2(a)] because after a period of time in which the samples appeared to reach the equilibrium (from ∼ 300 to 500 min), they started to absorb water again, although at a very slow rate. For that reason, the ultimate value of water absorption used in the fitting process with eqs. (3) and (4) was taken at 400 min. The effective diffusivities obtained are also reported in Table IV.

The values of the diffusion coefficients obtained with eq. (4) (short times) are also in good agreement with those obtained with eq. (3). This is understandable because the largest non-Fickian effects appear at long times.

As previously pointed out, Fick's model describes mass transport related to Brownian motions in which the penetrant flow is exclusively driven by a concentration gradient. However, the diffusion of low-molecular-weight compounds in polymers is generally governed by two simultaneously occurring phenomena, Fickian mass transport and a relaxation phenomenon driven by the distance from the local segmental position to that of the equilibrium.[38] The last limiting behavior is encountered when a very thin slab of the polymer is put in contact with a swelling penetrant. In this case, the characteristic diffusion time is much lower than the polymer relaxation time; hence, polymer relaxation becomes the limiting phenomenon controlling the solvent uptake kinetics.[38] Moreover, water sorption in moderately hydrophilic polymers is a rather complex phenomenon because of the presence of specific interactions between water molecules and the hydrophilic sites on the polymer backbone. In fact, the adsorbed molecules are in part randomly dispersed into the polymer matrix (sorbed water) and in part physically bonded to the hydrophilic sites (adsorbed water).[39] In this work, it is assumed that the diffusion coefficient depends only on the temperature (ideal Fickian diffusion); however, in this case, this assumption may not be strictly fulfilled because of the specific interactions between the polymer and the water molecules. Besides, as water penetrates the hydrophilic polymer, it induces its plasticization. This effect is
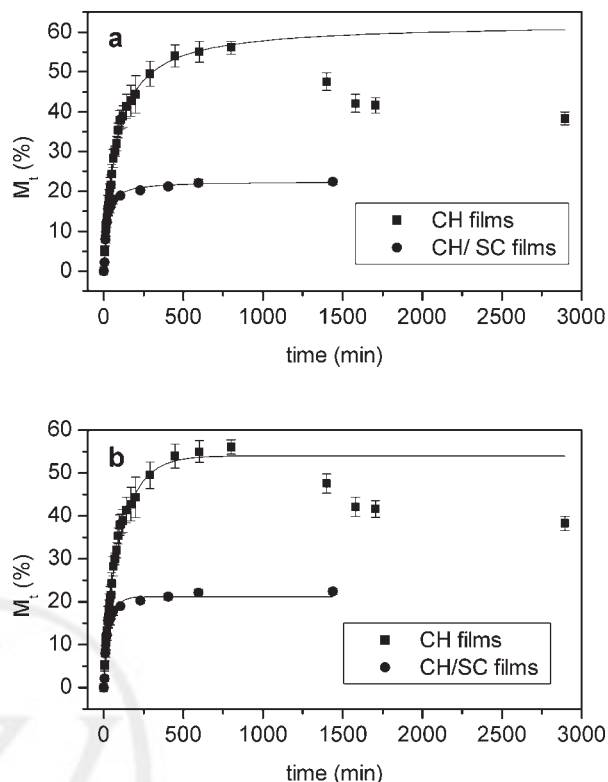

Figure 3 Moisture sorption of chitosan (CH) and chitosan/sodium caseinate (CH/SC) films at 23°C and 75% RH: (a) solid lines represent the fitting from the Peleg equation and (b) solid lines represent the Fickian model.

more critical as the glycerol content increases. In this sense, Karbowiak et al.,[15] who investigated the diffusion of a reference molecule (fluorescein) introduced into a biopolymer film of i-carrageenan, revealed the underlying mechanism of diffusion with the existence of a population of molecules that are retained in the mesh of the film as the water concentration remains below a critical level but that acquire complete mobility when the water concentration surpasses that critical level. In this case, as glycerol (the plasticizer) surpasses 28 wt %, the molecular structure becomes open and flexible enough to allow the passage of the water molecules.

The water sorption behavior of chitosan/caseinate and chitosan films prepared with 28 wt % glycerol was also evaluated, and the resulting Peleg parameters and effective diffusion coefficients are also included in Table IV.

Figure 3(a,b) shows the fitting curves corresponding to the Peleg equation and the Fickian model, respectively. As before, the equilibrium moisture content used in the fitting process with eqs. (3) and (4) was measured at about 400 min; such values were approximately 20% for chitosan/caseinate and 55% for chitosan films, the latter being comparable to literature data.[40] The K_1 parameter is lower for the chitosan/caseinate complex film and higher for

the neat chitosan film in comparison with the corresponding value for a caseinate (28 wt % glycerol) sample, and this indicates that the initial absorption rate is higher for the complex film and lower for the chitosan one. The same conclusion is obtained from the analysis of the effective diffusivity values. Moreover, the low K_2 value of the chitosan sample clearly indicates that this sample had a higher final absorption capacity; thus, it was the most hydrophilic film, as previously deduced from the permeability tests. From Figure 3(b), it is clear that both the chitosan and chitosan/caseinate films also deviated from Fickian behavior at times longer than 600 min. In fact, after that time, the weight of the chitosan films decreased instead of increasing or remaining constant, and this indicated that a competition between degradation and water absorption processes took place.

The strong interactions between caseinate and chitosan in forming polyelectrolyte complex films lead to fewer sites in the polymer matrix at which water can be held, and they are responsible for the reduced final water content (in comparison with chitosan). For the same reason (reduced interactions with the penetrant water), the rate of water diffusivity is higher than in the chitosan case because the small molecules are not retained by the polymer.

Similar conclusions can be extracted from the analysis of the Peleg fitting or the Fickian model, although in the latter case, the extent of non-Fickian effects introduces uncertainties into the values of the fitted diffusivities.

CONCLUSIONS

Sodium caseinate, chitosan, and chitosan/sodium caseinate films plasticized with glycerol were successfully prepared. WVP values showed an exponential growth relationship with the glycerol content. A two-parameter exponential growth equation was used to fit the experimental data. Although chitosan samples seemed to be much more permeable than caseinate ones at any glycerol content, glycerol was more efficient in plasticizing the caseinate films than the chitosan ones. Analyzing the permeability obtained at two different RH gradients, we found that the WVP of the films increased with increasing humidity and that the increment of WVP at 100 : 64.5 (with respect to those obtained at 0 : 64.5) was similar for the chitosan and caseinate pure films, but it was highest for the chitosan/sodium caseinate hybrid sample.

With respect to the water uptake measurements, the rates of moisture sorption for the caseinate films were similar but the equilibrium moisture contents were higher with increasing glycerol concentrations because of the hydrophilic nature of glycerol. Chito-

san films prepared with 28 wt % glycerol showed the lowest rate of moisture sorption but reached a higher equilibrium moisture content, whereas the chitosan/caseinate ones exhibited the opposite behavior. This last feature is related to the strong interactions that developed in the polyelectrolyte complex.

Experimental moisture sorption data were well fitted with Peleg's empirical equation over the entire time period with very good agreement. Additionally, the Fickian model for a one-dimensional sheet was used to estimate an effective diffusion coefficient. In this case, the agreement between the theoretical solid curves and the experimental points was good in the early stages of sorption but deviated slightly at longer times, and this was attributed to the changes in the matrix structure induced by plasticization. These non-Fickian effects were more noticeable for chitosan samples.

References

1. Audic, J.; Chaufer, B. Eur Polym J 2005, 41, 1934.
2. Schou, M.; Longares, A.; Montesinos-Herrero, C.; Monahan, F. J.; O'Riordan, D.; O'Sullivan, M. Food Sci Technol 2005, 38, 605.
3. McHugh, T. H.; Krochta, J. M. Food Technol 1994, 48, 97.
4. Wong, D. W. S.; Gastineau, F. A.; Gregorski, K. S.; Tillin, S. J.; Pavlath, A. E. J Agric Food Chem 1992, 40, 540.
5. Arvanitoyannis, S.; Nakayama, A.; Aiba, S. Carbohydr Polym 1998, 37, 371.
6. Remuñán-López, C.; Bodmeier, R. J Controlled Release 1997, 44, 215.
7. Baker, L. D.; Ferguson, J. D.; Chalupa, W. J Dairy Sci 1995, 78, 2424.
8. Buonocore, G. G.; Del Nobile, M. A.; Di Martino, C.; Gambacorta, G.; La Notte, E.; Nicolais, L. J Food Eng 2003, 60, 99.
9. Lazaridou, A.; Biliaderis, C. G. Carbohydr Polym 2002, 48, 179.
10. Fernández Cervera, M.; Karjalainen, M.; Airaksinen, S.; Rantanen, J.; Krogars, K.; Heinämäki, J.; Colarte, A. I.; Yliruusi, J. Eur J Pharm Biopharm 2004, 58, 69.
11. Zhai, M.; Zhao, L.; Kume, T. Carbohydr Polym 2004, 57, 83.
12. Xu, Y. X.; Kim, K. M.; Hanna, M. A.; Nag, D. Ind Crops Prod 2005, 21, 185.
13. Bourtoom, T.; Chinnan, M. S. Food Sci Technol, to appear.   AQ4
14. Ziani, K.; Oses, J.; Coma, V.; Maté, J. I. Food Sci Technol, to appear.   AQ4
15. Karbowiak, T.; Gougeon, R. D.; Rigole, S. Food Chem 2008, 106, 1340.
16. Masaro, L.; Zhu, X. X. Prog Polym Sci 1999, 24, 731.
17. Debeaufort, F.; Voilley, A.; Meares, P. J Membr Sci 1994, 91, 125.
18. Nashed, G.; Rutgers, R. P. G.; Sopade, P. A. Starch 2003, 55, 131.
19. Coupland, J. N.; Shaw, N. B.; Monahan, F. J.; O'Riordan, E. D.; O'Sullivan, M. J Food Eng 2000, 43, 25.
20. Crank, J. The Mathematics of Diffusion, 1st ed.; Clarendon: Oxford, 1956.
21. Deb, S.; Braden, M.; Bonfield, W. Biomaterials 1995, 16, 1095.
22. Annual Book of Standards; American Society for Testing and Materials: Philadelphia, 1993; E96-95, p 697.
23. Hernández-Muñoz, P.; López-Rubio, A.; Lagarón, J. M.; Gavara, R. Biomacromolecules 2004, 5, 415.

24. Pranoto, Y.; Rakshit, S. K.; Salokhe, V. M. Food Sci Technol 2005, 38, 859.
25. Del Nobile, M. A.; Fava, P.; Piergiovanni, L. J Food Eng 2002, 53, 295.
26. Kolodziejska, I.; Piotrowska, B. Food Chem 2007, 103, 295.
27. Chen, H. J Dairy Sci 1995, 78, 2563.
28. McHugh, T. H.; Aujard, J. F.; Krochta, J. M. J Food Sci 1994, 59, 416.
29. Mate, J. I.; Krochta, J. M. J Agric Food Chem 1996, 44, 3001.
30. Gontard, N.; Guilbert, S.; Cuq, J. L. J Food Sci 1993, 58, 206.
31. Gounga, M. E.; Xu, S.; Wang, Z. J Food Eng 2007, 83, 521.
32. Pereda, M.; Aranguren, M. I.; Marcovich, N. J Appl Polym Sci 2008, 107, 1080.

33. Coma, V.; Sebti, I.; Pardon, P.; Pichavant, F. H.; Deschamps, A. Carbohydr Polym 2003, 51, 265.
34. Rogers, C. E. In Polymer Permeability; Comyn, J., Ed.; Elsevier: New York, 1985; p 11.
35. Cho, S. Y.; Rhee, C. Food Sci Technol 2002, 35, 151.
36. Lim, L. T.; Mine, Y.; Tung, M. A. J Food Sci 1999, 64, 616.
37. Mahmoud, R.; Savello, P. A. J Dairy Sci 1992, 75, 942.
38. Del Nobile, M. A.; Mensitieri, G.; Netti, P. A.; Nicolais, L. Chem Eng 1994, 49, 633.
39. Netti, P. A.; Del Nobile, M. A.; Mensitieri, G.; Ambrosio, L.; Nicolais, L. Bioact Compat Polym 1996, 11, 312.
40. Vargas, M.; Albors, A.; Chiralt; A.; González-Martínez, C. Food Hydrocolloids, to appear.   AQ4