

# Barrier Properties of Paper–Chitosan and Paper–Chitosan–Carnauba Wax Films

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**ABSTRACT:** A gas barrier and biodegradable multilayer material was processed with a paper substrate, chitosan, and carnauba wax. The first step consisted of the study of the chitosan coating to obtain a dense polymer layer at the paper surface. The influence of the molecular weight and the concentration of the chitosan solution were studied, and a chitosan coating of 7 g/m<sup>2</sup> was achieved, which led to interesting gas barrier properties in the anhydrous state. Nevertheless, the hydrophilic character of both cellulose and chitosan did not allow us to preserve these properties in the

hydrated state. A layer of carnauba wax was then deposited on the chitosan face of the bilayer. Because of the hydrophobic character of this external layer, the water sorption in the multilayer decreased greatly, and CO<sub>2</sub> and O<sub>2</sub> permeability coefficients lower than 0.5 barrer were obtained in the hydrated state. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 704–710, 2005

**Key words:** barrier; chitosan; biodegradable; films

## INTRODUCTION

Paper is widely used in packaging applications, but its porous structure makes it highly permeable to gases. When gas barrier properties are requested, paper is often coated with ethyl vinyl alcohol (EVOH), a well-known material that is impermeable to gas.<sup>1,2</sup> This polymer fills the paper pores and forms a dense layer at the paper surface. Hydrogen bonds formed between the polar groups of EVOH mainly explain the high cohesive energy density of this film and its good gas barrier properties in the anhydrous state. However, these polar groups are also at the origin of the hydrophilic character of the polymer at high relative humidity<sup>1</sup> and, as a consequence, at the origin of the loss in this domain of the gas barrier properties.<sup>2</sup> An additional polymer layer is thus used to prevent water sorption, and polyolefins are generally chosen. Unfortunately, due to the addition of these two synthetic polymer layers, the multilayer material thus loses its natural and biodegradable properties as well as its recyclability.

The aim of this study was to process a biodegradable film from a porous substrate (paper) that would exhibit interesting gas barrier properties in a wide

range of relative humidities. The approach consisted of the elaboration of a multilayer material. Composite films based on natural polymers have already been proposed, especially for edible packaging.<sup>3–5</sup> These composites usually combine polysaccharides or proteins that present good mechanical and barrier properties, respectively, to lipids. Some studies have focused on methylcellulose and candelilla wax systems.<sup>3</sup> Methylcellulose brings interesting gas barrier properties to the composite but is often used with a plasticizer to obtain the appropriate mechanical properties.<sup>6–8</sup> Compared to methylcellulose, chitosan is a natural polysaccharide with good mechanical properties that can be obtained without any additive. Its gas permeability has been studied for several years to evaluate its potency for packaging applications,<sup>9–11</sup> and very low gas fluxes were measured on films in the anhydrous state. Nevertheless, due to its hydrophilic character,<sup>12</sup> like methylcellulose and EVOH, chitosan loses its gas barrier properties in the hydrated state. Therefore, we decided to associate this polymer with a natural wax, carnauba wax, and we focused on the processing and properties of a multilayer material consisting of paper, chitosan, and carnauba wax.

## EXPERIMENTAL

### Materials

Two different polymers and a wax were used in this study, and their main characteristics are presented hereafter.

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### Cellulosic material

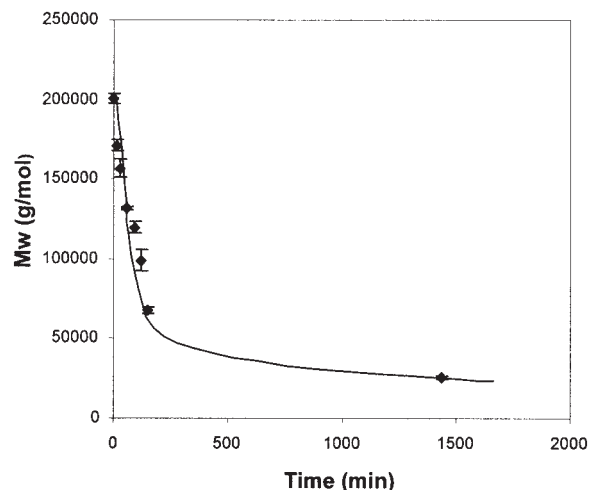
We used a 100% cellulose model paper composed of pure cellulose wood fibers without any additives included in the final fibrous dispersion. A blotting paper was first prepared; then, a parchment paper was processed by the immersion of the initial paper in concentrated sulfuric acid. During this treatment, cellulose fibers were partially dissolved, which formed a gel and thus allowed partial filling of the paper pores. The thickness of the paper sheet was  $40 \pm 5 \mu\text{m}$ . As the goal of this study was to obtain a barrier material, we chose to work on the parchment paper, which was assumed to be less porous than the blotting paper.

### Chitosan

Previous studies<sup>9–11</sup> have already shown the good gas barrier properties of chitosan in the anhydrous state. Detailed analysis of the transport properties of this material also underlined the dependence of the gas flux as a function of the relative humidity. Thus, the material was chosen to be used as an intermediate layer in the composite system. To optimize the deposit of this second layer, a chitosan provided by France Chitin (Marseille, France) with a weight-average molecular weight ( $M_w$ ) of 200,000 g/mol was taken as a reference, and chitosan polymers with lower average molecular weights were obtained by the hydrolysis of the reference material. Among the various possible hydrolysis methods,<sup>12–15</sup> we chose a chemical method based on the use of  $\text{NaNO}_2$ .<sup>16,17</sup> This quite simple and rapid method presented only the disadvantage of the formation of a 2,5-anhydro-D-mannose at one chain end that could impede the crystallization of the formed oligomers.<sup>18</sup> The experimental hydrolysis conditions used were as follows: a  $\text{NaNO}_2$  solution (10 g/L) was added to a chitosan solution (0.14%) in 0.2 M acetic acid/0.1 M sodium acetate. After different treatment times, chitosan was isolated from the solution by precipitation. Successive washings were applied to the precipitates to obtain neutral materials. The samples were then lyophilized, and their  $M_w$  values were characterized by size exclusion chromatography. The evolution of  $M_w$  as a function of the treatment time is presented in Figure 1. A previous study<sup>19</sup> showed that the gas barrier properties of the polymer remained in the whole range of molecular weights used.

### Carnauba wax

A pure natural carnauba wax was initially chosen for this study, but the optimization of the coating conditions required us to heat the paper substrate before immersion in the melt wax at  $65^\circ\text{C}$ . Because these conditions could not be easily transferred to the paper industry, a commercial emulsion of carnauba wax



**Figure 1** Evolution of  $M_w$  as a function of time during the hydrolysis of chitosan with a  $\text{NaNO}_2$  solution.

(Michem Lube 160PF. E from Michelman) was finally used.

### Coating method

Chitosans with different  $M_w$ 's were dissolved at various concentrations in an aqueous acetic acid solution. A hand coater (K. Control Coater) was used to deposit the chitosan solutions on the paper at a speed of 10 m/s. To determine the amount of chitosan deposited on the paper ( $M_{\text{chit}}$ ), half of a paper sheet was coated with the chitosan solution. The paper sheet was then dried at  $110^\circ\text{C}$ . A sample ( $10 \times 10 \text{ cm}$ ) was taken from the coated part, and another one was taken from the uncoated part. The amount of deposited chitosan corresponded to the weight difference between the two samples, and it was expressed in grams per meter squared.  $M_{\text{chit}}$  was defined as the mean value of three measurements, and the precision was better than 5%.

The same method was used for wax deposition, but in that case, the wax emulsion was deposited on paper sheets already coated with chitosan.

### Transport properties analysis

#### Water sorption analysis

Water sorption isotherms were determined at  $20^\circ\text{C}$  by a gravimetric method with a Setaram B92 microbalance (Lyon, France).<sup>19</sup> The sample was introduced in the microbalance, and a desorption *in vacuo* ( $2 \times 10^{-6}$  mbar) was performed to determine the weight of the anhydrous sample. The sample was then exposed to a given water activity, and its water uptake was followed as a function of time until the sorption equilibrium was achieved. Experiments performed at differ-

ent activities allowed us to determine the water sorption isotherm.

### Permeation measurements

For all experiments, the permeation cell consisted of two compartments (the upstream and downstream compartments) separated by the studied membrane. The coated face of the membrane was always placed in the upstream side. The cell was thermostated at  $20 \pm 1^\circ\text{C}$ . A desorption *in vacuo* ( $2 \times 10^{-6}$  mbar) was performed before each experiment.

**Gas permeation measurement**<sup>19</sup> For gas permeation in the anhydrous state, a  $3.0 \times 10^5$ -Pa gas pressure ( $P_1$ ) was introduced in the upstream compartment. The pressure in the downstream compartment ( $P_2$ ) was measured as a function of time with a Datametrics pressure sensor. A steady-state line was obtained after a transitory state. The permeability coefficient ( $P$ ) was calculated from the slope of the steady-state line according to the following equation:

$$P = \frac{eV_2}{76SP_1} \frac{dP_2}{dt} \quad (1)$$

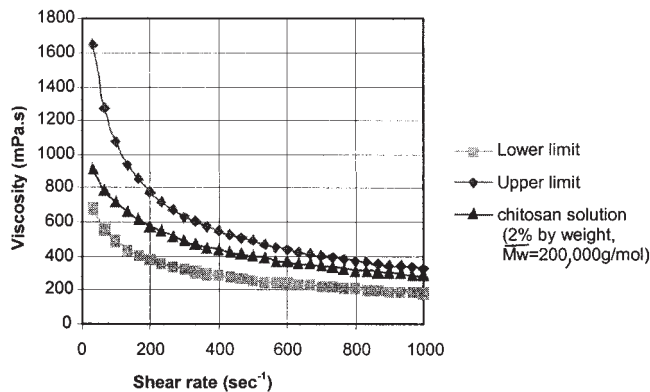
where  $e$  is the thickness of the membrane,  $S$  is the surface of the membrane, and  $V_2$  is the volume of the downstream compartment.

For gas permeation experiments on hydrated membranes, the upstream and downstream compartments were exposed to the same chosen relative humidity, which allowed the membrane placed between these two compartments to be equilibrated in these conditions. When the sorption equilibrium was reached, a  $3.0 \times 10^5$ -Pa gas pressure was introduced in the upstream compartment.  $P$  was calculated according to eq. (1) from the slope of the straight line representative of the evolution of  $P_2$  as a function of time.

**Water vapor permeation measurement** The upstream side of the membrane was exposed to a chosen activity, thus to a given water vapor pressure ( $P_1$ ). The variation of the pressure ( $P_2$ ) in a defined  $V_2$  allowed us to determine the amount of vapor diffusing through the membrane in the steady state and to calculate  $P$  according to the following equation:<sup>19</sup>

$$P = \frac{eV_2}{76S} \frac{d \left[ \ln \left( \frac{P_1}{P_1 - P_2} \right) \right]}{dt} \quad (2)$$

In all cases, the  $P$  values are given in barrers ( $1 \text{ barrer} = 10^{-10} \text{ cc}_{\text{STP}} \text{ cm}_{\text{film}} \text{ cm}_{\text{film}}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ ).



**Figure 2** Upper and lower limits of the solution viscosity that was used for coatings.

## RESULTS

### Properties of the chitosan–cellulose bilayers

**Influence of the processing conditions on the chitosan deposition**

The first goal of this study was to deposit on the porous cellulosic substrate a continuous layer of chitosan to improve the gas barrier properties in anhydrous conditions. A hand coater was used to process the bilayers, and the optimal range of the solution viscosity was determined first. Figure 2 represents the upper and lower limits of the viscosity for this process. Chitosan solutions were prepared in an aqueous acetic acid solution, and two parameters were optimized to adapt the viscosity of the chitosan solutions to the previously described conditions: the concentration (expressed in weight percentage) and the molecular weight of the polymer. For the reference chitosan ( $M_w = 200,000$  g/mol), the concentration of the solution could only be varied in the range 1–2% (Fig. 2). For the hydrolyzed chitosan with a  $M_w$  of 120,000 g/mol, the concentration could be increased up to 4%, and for hydrolyzed chitosan with a  $M_w$  of 60,000 g/mol, the maximum concentration was 8%.

$M_{\text{chit}}$  was determined for the different chitosan solutions (Table I). It increased as the polymer concentration increased in the chitosan solution.  $M_{\text{chit}}$  was thus strongly related to the chitosan molecular weight, allowing higher concentrations as it decreased. The value of  $M_{\text{chit}}$  obtained after two consecutive coatings with a solution containing 4 wt % chitosan ( $M_w = 120,000$  g/mol) did not increase in proportion to the number of coatings. Moreover, it remained below the value measured after a single coating with a solution containing 8 wt % chitosan ( $M_w = 60,000$  g/mol). All these results clearly show that the polymer concentration that was directly related to the chitosan molecular weight seemed to be the major parameter for the control of the chitosan coating.

To obtain additional information on the different coatings, we performed a morphological study. Figure

**TABLE I**  
**CO<sub>2</sub> and O<sub>2</sub> *P* Values Measured on Anhydrous Chitosan-Paper Bilayer Films as a Function of the Coating Parameters (Average Molecular Weight of Chitosan, Concentration of the Solution, and Number of Coatings)**

Chitosan <i>M<sub>w</sub></i> (g/mol)	Concentration of the coating solution (wt %)	Number of coatings	<i>M<sub>chit</sub></i> (g/m <sup>2</sup> )	<i>P<sub>CO<sub>2</sub></sub></i> (barrer)	<i>P<sub>O<sub>2</sub></sub></i> (barrer)
—	—	0	0	1635	685
200,000	1	1	0.9	820	588
200,000	2	1	1.5	594	231
120,000	4	1	3	75	36
120,000	4	2	4.5	3.1	3.3
60,000	8	1	7	0.28	0.12

3 presents scanning electron microscopy (SEM) photographs relative to the paper and the bilayer with  $M_{\text{chit}} = 4.5 \text{ g/m}^2$ . For this last sample, the cellulose fibers were fully coated with chitosan. IR spectra (Fig. 4) confirmed the presence of chitosan because the peak relative to the free amine function centered at  $1575 \text{ cm}^{-1}$  was observed as well as the amide I and II peaks based at  $1635$  and  $1540 \text{ cm}^{-1}$ , respectively. IR microscopy analysis was performed on paper coated with  $1.5$  and  $7 \text{ g/m}^2$  chitosan. In Figure 5, the blue areas correspond to cellulose fibers, and the green, yellow, and red areas correspond to chitosan. The chitosan deposit was heterogeneous in the case of paper coated with  $1.5 \text{ g/m}^2$  chitosan, whereas it became quite uniform and homogeneous for  $7 \text{ g/m}^2$ . The influence of these different coatings was studied on the gas transport properties.

Gas transport properties in the anhydrous state of the reference materials and the bilayers

In Table I, the CO<sub>2</sub> and O<sub>2</sub> transport properties of the anhydrous parchment paper and the anhydrous bilayers from the different chitosan solutions are listed. For comparison, all *P* values are given in barrers (1 barrer =  $10^{-10} \text{ cc}_{\text{STP}} \text{ cm}_{\text{film}} \text{ cm}_{\text{film}}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ ).

The high values of the gas permeability determined for the paper underlined its porous morphology. On the contrary, very low values of gas fluxes were measured for both the reference chitosan film ( $M_w = 200,000 \text{ g/mol}$ ) and the hydrolyzed chitosan film ( $M_w = 26,000 \text{ g/mol}$ ). The CO<sub>2</sub> and O<sub>2</sub> *P* values were 0.03 and 0.025 barrer, respectively, for both films. These results confirm the high gas barrier character of chitosan and the low dependence of the transport properties as a function of the mean-average molecular weight in the range we studied.

The gas permeability of the bilayers decreased as  $M_{\text{chit}}$  increased. Nevertheless, for the paper coated with  $4.5 \text{ g/m}^2$  chitosan, the *P* values were still higher

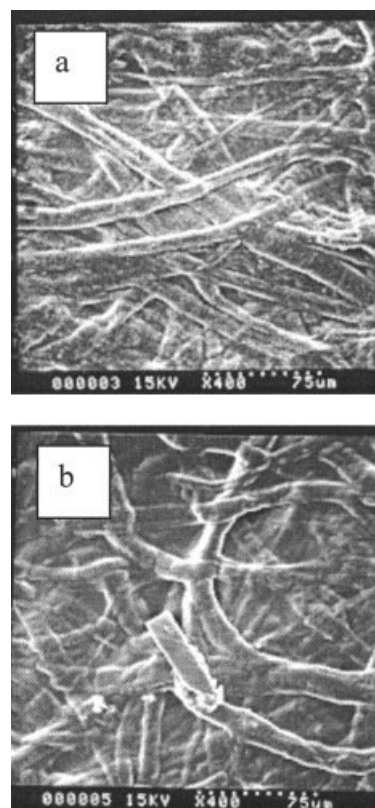
than 1 barrer. Thus, even if the fibers were fully coated with chitosan, the amount of deposited polymer did not seem to be sufficient to form a continuous chitosan layer. On the other hand, good gas barrier properties were obtained when  $M_{\text{chit}}$  was  $7 \text{ g/m}^2$  (Table I). *P* was indeed equal to 0.28 barrer for CO<sub>2</sub> and 0.12 barrer for O<sub>2</sub>. As the morphological analysis showed that, in this case a homogeneous coating was obtained, we used the permeability law developed for the multilayer systems to determine the thickness of the chitosan layer:

$$\frac{e}{P} = \frac{e_{\text{paper}}}{P_{\text{paper}}} + \frac{e_{\text{chit}}}{P_{\text{chit}}}$$

$$e = e_{\text{paper}} + e_{\text{chit}}$$

where *e* is the thickness; *P* is the permeability coefficient of the multilayer;  $e_{\text{paper}}$  and  $e_{\text{chit}}$  are the thicknesses of the paper and chitosan layers, respectively; and  $P_{\text{paper}}$  and  $P_{\text{chit}}$  are the permeabilities of the paper and chitosan layers, respectively. When *P*,  $P_{\text{paper}}$ ,  $e_{\text{paper}}$ , and  $P_{\text{chit}}$  were determined, we could deduce  $e_{\text{chit}}$ . A thickness of about  $5 \mu\text{m}$  was determined with CO<sub>2</sub> data.

A fully biodegradable bilayer material with a thin chitosan layer presenting good gas barrier properties in anhydrous conditions was thus optimized.



**Figure 3** SEM photographs of (a) paper and (b) paper coated with chitosan ( $M_{\text{chit}} = 4.5 \text{ g/m}^2$ ).



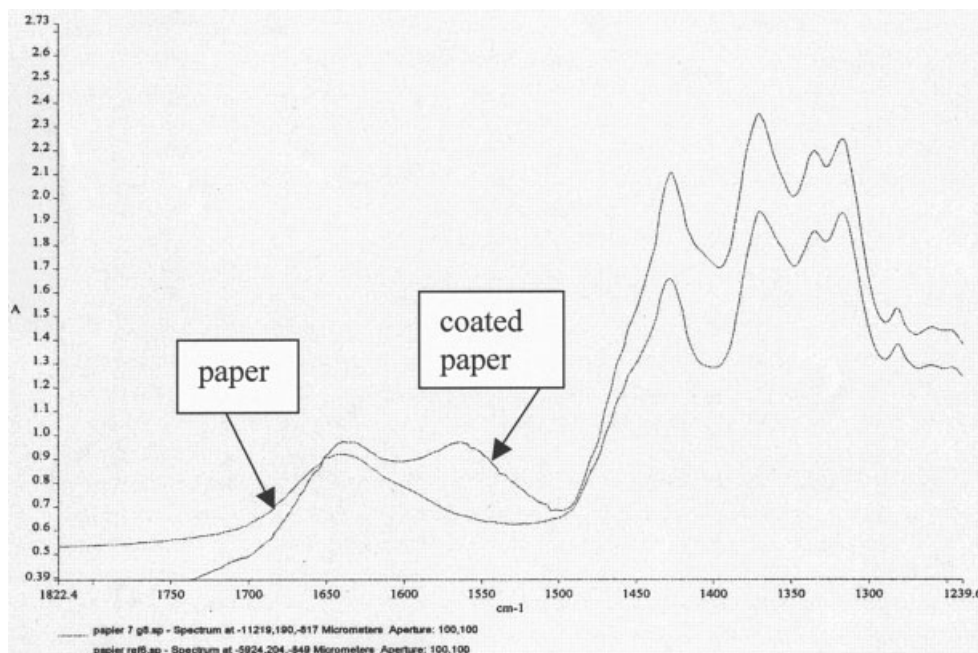


Figure 4 IR spectra relative to paper and paper coated with chitosan ( $M_{\text{chit}} = 7 \text{ g/m}^2$ ).

Water and gas transport properties under various hydration conditions for the paper coated with  $7 \text{ g/m}^2$  chitosan

The second step of the work was to determine, for the bilayer material containing  $7 \text{ g/m}^2$  chitosan, the water and gas transport properties under various hydration conditions. Indeed, chitosan and cellulose are well known as hydrophilic materials, and in a previous study,<sup>9</sup> we showed that chitosan became a poor water and gas barrier material at a high relative humidity.

The water sorption isotherms relative to paper, chitosan, and the bilayer material are presented in Figure 6. In all cases, these isotherms were of Brunauer, Emmett,

and Teller type II. Chitosan was more hydrophilic than paper, and this tendency was particularly observed at high activity ( $a > 0.9$ ). Indeed, in this range, the deviation from linearity of the water uptake as a function of the activity was much more pronounced for chitosan than for paper. The water contents sorbed by the bilayer resulted exactly from the contribution of each layer as underlined by the good agreement observed between the experimental results and the theoretical values calculated with an additivity law (Fig. 6). For this bilayer, the chitosan weight deposition on the paper was low (16%) and could thus explain why the isotherm relative to the bilayer was close to the isotherm relative to the paper.

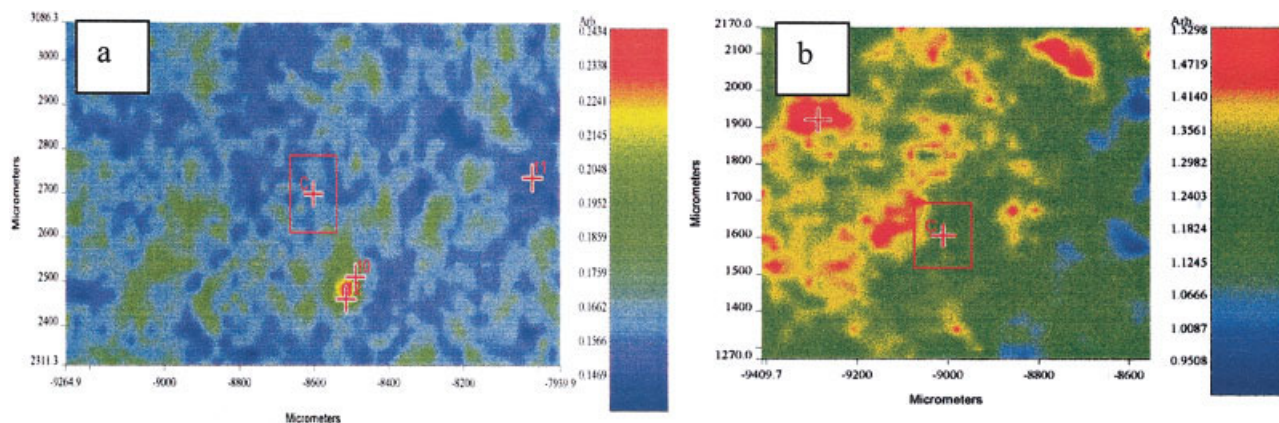
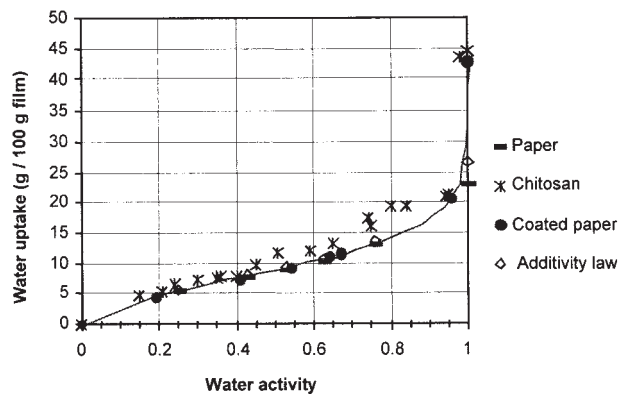


Figure 5 IR microscopy analysis of paper coated with chitosan:  $M_{\text{chit}} =$  (a)  $1.5$  and (b)  $7 \text{ g/m}^2$ . The blue areas correspond to cellulose fibers, and the green, yellow, and red areas correspond to chitosan. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



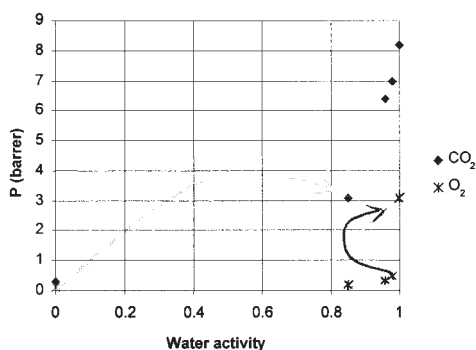
**Figure 6** Water sorption isotherms of (—) paper, (\*) chitosan, and (●) paper coated with chitosan ( $M_{\text{chit}} = 7 \text{ g/m}^2$ ). The additivity law is represented with a full line.

The effects of relative humidity were studied on the gas permeability. The membranes were equilibrated at the desired activity before the gas experiments were performed. As shown on Figure 7, a loss of gas barrier properties was observed at high relative humidities. As for chitosan,<sup>9</sup> the increase of gas flux was more important for  $\text{CO}_2$  than for  $\text{O}_2$ .

In conclusion, a good gas barrier material was optimized under the form of a chitosan–paper bilayer material, but its application was limited to a low relative humidity. To broaden the water activity range in which the material could be used, an additional layer was deposited on the material. The nature of this layer was chosen with a marked hydrophobic character.

#### Properties of the multilayer material as a function of the processing

A three-layer material, carnauba wax–chitosan–paper, was processed for permeation measurements according to the method presented in the Experimental section. Thus, after the paper was coated with a chitosan solution (8% w/w), the bilayer was dried at  $110^\circ\text{C}$ , and  $M_{\text{chit}}$  was



**Figure 7** Evolution of the (◆)  $\text{CO}_2$  and (\*)  $\text{O}_2$   $P$  values as a function of the relative humidity for paper coated with chitosan ( $M_{\text{chit}} = 7 \text{ g/m}^2$ ).

**TABLE II**  
Water Vapor  $P$  Values of the Three-Layer Material (Carnauba Wax–Chitosan–Paper) and of the Chitosan Film at Different Water Activities

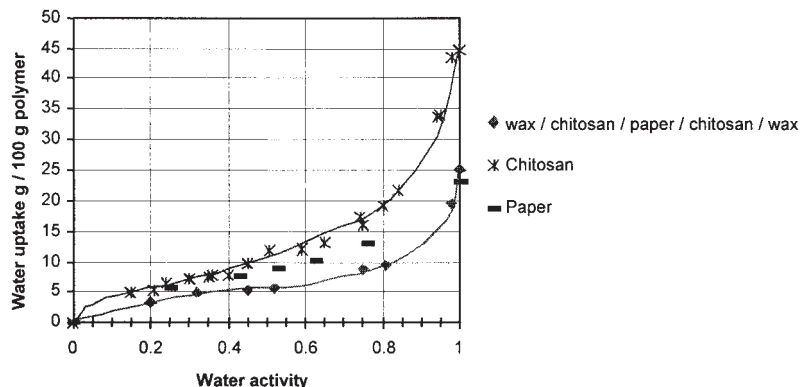
Water activity (a)	0.7	0.96	1
Water $P$ (barrer) of the three-layer material	55	423	7650
Water $P$ (barrer) of the chitosan film (thickness = $20 \mu\text{m}$ )	1,900	13,000	78,500

evaluated as  $7 \text{ g/m}^2$ . The carnauba wax solution was then deposited on the chitosan layer, and after it was dried at  $110^\circ\text{C}$ , the amount of wax present at the surface was measured by weight analysis as close to  $2 \text{ g/m}^2$ . The wax layer was placed in the upstream side of the permeation cell for gas permeability measurements in the anhydrous state and water vapor permeability measurements. As the studied sample was surrounded by water molecules, for water vapor sorption and for gas permeation under various hydrations, a symmetrical multilayer material (carnauba wax–chitosan–paper–chitosan–carnauba wax) was processed according to the previously described steps.

The gas permeability values measured in the anhydrous state of the three-layer material were equal to 0.08 barrer for  $\text{CO}_2$  and 0.04 barrer for  $\text{O}_2$ . Good gas barrier properties were thus obtained for this material with interesting mechanical properties retained. Indeed, in the experiments, the films were at first desorbed in the permeation apparatus. A 3-bar pressure was then applied on one side of the sample. This generally leads to the formation of cracks for brittle materials. No cracks were evident after the measurements on the multilayer material, which showed that good mechanical properties were retained even with the wax coating.

The coefficients of water vapor permeability were determined in the activity range 0.7–1, where a loss of the water barrier character was observed for pure chitosan films.<sup>9</sup> The results reported in Table II showed that the water fluxes relative to the three-layer material were lower than those measured on the chitosan films. They remained in the range of few hundred barrers up to an activity equal to 0.96, showing a significant reduction in the hydrophilic character of the material.

Water sorption was also studied for the five-layer material, and the corresponding sorption isotherm is shown on Figure 8. The sorption isotherms relative to the chitosan film and to the paper were also reported in Figure 8. The water contents sorbed by the multilayer were much lower than those determined for the two reference materials based on chitosan and cellulose. The amount of water sorbed by the multilayer at an activity of 0.75 corresponded to the water sorbed by the chitosan film at an activity of 0.35. Thus, due to



**Figure 8** Water sorption isotherms of (—) paper, (\*) chitosan, and (◆) the carnauba wax–chitosan–paper–chitosan–carnauba wax multilayer material.

its hydrophobic character, the wax layer decreased the amount of water molecules diffusing through the material. This new behavior had important consequences on the evolution of the gas permeability as a function of hydration. Indeed, the  $\text{CO}_2$   $P$  measured for the multilayer (carnauba wax–chitosan–paper–chitosan–carnauba wax) was equal to 0.24 barrer for a relative humidity equal to 0.91, whereas it achieved 6 barrer in the same conditions for the chitosan–paper bilayer. Moreover, the  $\text{O}_2$   $P$  remained below 0.1 in the whole range of relative humidities.

## CONCLUSIONS

A natural multilayer material based on a porous substrate (parchment paper), a hydrophilic polymer (chitosan), and a hydrophobic material (carnauba wax) was processed for food-packaging applications. A step-by-step study of the multilayer formation and multilayer properties allowed us to show the parameters that played a major role in the achievement of good gas barriers. The first deposited layer, the chitosan layer, determined the level of gas barrier properties in the anhydrous state. The quality of this first layer was shown to be strongly related to the concentration of the chitosan solution used in the coating process. A polymer concentration of 8 wt % in the solution, which implied the use of a low-molecular-weight chitosan ( $M_w = 60,000$  g/mol), was necessary to form a continuous layer of chitosan at the paper surface. A decrease in the  $\text{CO}_2$  permeability in the anhydrous state from 1635 barrer, the permeability of the parchmented paper, to 0.08 barrer for the chitosan–paper bilayer was thus obtained. The hydrophilic character of chitosan did not allow us to preserve these gas barrier properties in the hydrated state. A layer of carnauba wax, a hydrophobic mate-

rial, was then coated on the chitosan side of the bilayer. For a coating of 2 g of wax per square meter, gas  $P$  values lower than 0.5 barrer were obtained in the hydrated state.

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