JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Improvement of Water Barrier Property of Paperboard by Coating Application with Biodegradable Polymers

Jaejoon Han,[†] Stéphane Salmieri,[‡] Canh Le Tien,[‡] and Monique Lacroix*,[‡]

[†]Department of Food Science and Biotechnology, Sungkyunkwan University, Suwon, Gyeonggi-do, 440-746, Republic of Korea, and [‡]Research Laboratories in Sciences Applied to Food, Canadian Irradiation Centre, Institut National de la Recherche Scientifique−Institut Armand-Frappier, 531, Boulevard des Prairies, Laval, Québec, H7V 1B7, Canada

Biopolymeric coatings were prepared and applied onto paperboard to improve its water barrier property. To prepare whey protein isolate (WPI)/cellulose-based films, WPI and glycerol were dissolved in water with glutaraldehyde (cross-linking agent) and cellulose xanthate. The solution was cast, dried, and insolubilized by entrapment of WPI in regenerated cellulose. Films were combined with beeswax (BW) into a bilayer coating system and then applied onto paperboard by heating compression. Another coating solution consisting of poly(vinyl butyral) (PVB)/zein was prepared by dissolving poly(vinyl alcohol) (PVA) and zein in 70% ethanol with glutaraldehyde and butyraldehyde (functionalization agent). The PVB/zein solution was applied onto paperboard after BW was sprayed. The structure of the PVB/zein-based coatings was analyzed by Fourier transform infrared spectroscopy (FTIR). The water vapor barrier property of coated paperboards was evaluated by water vapor transmission rate (WVTR) measurements. From the FTIR spectra, PVA functionalization after cross-linking and efficient acetalization into PVB were confirmed. WPI/cellulose and PVB/zein coating treatments improved the water barrier properties of paperboard by decreasing the WVTR by 77−78%. Although the BW coating was more efficient (decrease of WVTR by 89%), bilayer coatings composed of BW and polymer coatings had a stronger barrier effect with a decrease of WVTR to 92−95%, hence approaching commercial attributes required to ensure water vapor barrier in paperboard-based food containers (10 g/m^2·day). These results suggest that surface coating by biodegradable polymers may be utilized for the manufacture of paperboard containers in industrial applications.

INTRODUCTION

Paperboard is known as the most widely used packaging material for industrial applications (*1*). Although highly recyclable and environmentally friendly, paperboard contains cellulose, whose hydrophilic nature causes poor water resistance (*2*). Paperboard offers mechanical strength and flexibility for package production, but its main composition and raw material, pulp, is highly water-soluble and has hygroscopic properties. Its lack of barrier properties requires treatment to improve the surface functionality (*3*). Paperboard may lose physical and mechanical strength by absorbing water during distribution and storage. To prevent or minimize the loss of physical strength and to improve the water barrier property, the surface of paperboard can be coated (*2*). A water barrier is formed on the paper surface by changing the wettability with sizing agents or by coating with hydrophobic materials. For example, paraffin wax emulsions and polyurethane- or styrene-based copolymers are typical hydrophobic sizing agents that are applied in molten form to the surface

of paper or paperboard and for improvement of the water vapor barrier property (*4*). The primary purpose of the wax is to provide a moisture barrier and a heat sealable laminant. However, paraffin wax has relatively poor durability and flexibility as a surface-coating material. Other synthetic polymers and modifiers, such as cellulose derivatives, rubber derivatives, vinyl copolymers, polyamides, polyesters, and butadiene−styrene copolymers, are compatible with wax to overcome its defects (*2*). Often, special resins or plastic polymers are added to the wax to improve adhesion and low-temperature performance and to prevent cracking as a result of folding and bending of the paper. These coating treatments endow the surface of the paperboard with a hydrophobic nature and thus prevent wetting of the paperboard. However, these synthetic polymer materials and modifiers are limited in the extent that they can be separated, recycled, or composted after use (*5*). In an effort to produce more environmentally friendly and renewable materials, biodegradable polymers have been investigated as surface-coating materials on paper or paperboard (*6−10*). Good coating materials generally have hydrophobic and film-forming characteristics that improve the water barrier property of paperboard when applied to the surface.

*To whom correspondence should be addressed. Tel: 450-687-5010 ext. 4489. Fax: 450-686-5501. E-mail: monique.lacroix@iaf.inrs.ca.

3126 *J. Agric. Food Chem.,* Vol. 58, No. 5, 2010

Han et al.

The purpose of this study was to develop a new bilayer coating method for the surface treatment of paperboard. A coating matrix based on (i) whey protein isolate (WPI) and cellulose xanthate or (ii) poly(vinyl butyral) (PVB) and zein, in combination with beeswax (BW), was formulated. WPI ($\approx$90% protein) is the low-cost byproduct of cheese manufacturing, commonly used for its nutritional value and ability to form gels and emulsions (*11*). WPI has a good film-forming property but a high water vapor transmission rate (WVTR) in the presence of plasticizers (*12*). Plasticizers increase the flexibility of protein films. They work as spacers between polymer chains, resulting in a less dense structure where the chain ends become more mobile and increase the water vapor permeability (*13*). By incorporating a lipid component, such as waxes or fatty acids, into protein hydrocolloid films, the water barrier property can be improved. Waxes and fatty acids would be effective barriers to water vapor transfer, but they are insufficient to form self-supporting films (*11*). They are also less durable to high temperatures and unstable to contact with lipophilic materials. Bilayer films consisting of protein and lipid components would possess an efficient water barrier property with structural strength and stability (*14*). White BW was selected for the first layer of a bilayer system on paperboard in this study. Cellulose xanthate is derived from water-insoluble cellulose by a chemical reaction. The synthesis of stable derivatives of cellulose xanthate is carried out by the action of methylxanthoacetic acid and the phenyl ester of methylxanthoacetic acid on cellulose (*15*). Cellulose xanthate is compatible with other polymers by dissolving it in a sodium hydroxide solution.

Another bilayer coating system was developed using PVB and zein in combination with BW. PVB was derived from poly(vinyl alcohol) (PVA), which is known as a biodegradable synthetic and excellent water-soluble polymer (*16*). PVB is prepared by reacting PVA with butyraldehyde in the presence of an acid catalyst. The hydroxyl groups of PVA react with butyraldehyde to form 1,3-dioxane rings (acetal rings) and partial or even almost complete exchange of the original functional group for a new copolymer, PVB (*17*). PVB is water-insoluble and compatible with other polymers, contributing to excellent commercial applications (*18*). Zein is a major protein in corn endosperm. The hydrophobic nature of zein is related to its high content of nonpolar amino acids (*19*). Zein has excellent film-forming properties with strong and elastic films. The zein film is formed through the development of hydrophobic, hydrogen, and limited disulfide bonds between zein chains (*20, 21*). Like other protein-based films, zein film is a poor moisture barrier due to the hydrophilic nature of proteins, but it has good barrier properties to gases such as oxygen and carbon dioxide (*21, 22*).

The objective of this study was to evaluate the capacity of biopolymer-based coatings to decrease the WVTR of paperboards used in the packaging of commercial cereal boxes. Our results argue for the replacement of nonbiodegradable petrochemical plastic packaging with biopolymer-coated paperboard.

MATERIALS AND METHODS

Preparation of Biodegradable Polymer Coatings. *Selection of Paperboard Substrate.* Paperboard was selected from a commercial breakfast cereal container (thickness, 441.0 ± 0.7 μm) manufactured by Cascades Inc. (Kingsey Falls, QC, Canada). Containers were printed on the external side, and the coating had to be applied on the raw internal side. Similar commercial containers were chosen to approach the food market and to obtain a repeatable thickness and WVTR of uncoated paperboard.

Formation of Preliminary Basic Coatings. This preliminary step was designed to compare different biodegradable polymers related to their capacity to offer a water vapor barrier as coatings on paperboard. In this

Scheme 1. Process Chart for the Preparation of WPI/Cellulose Films and Their Application onto Paperboard as a Part of a Bilayer System
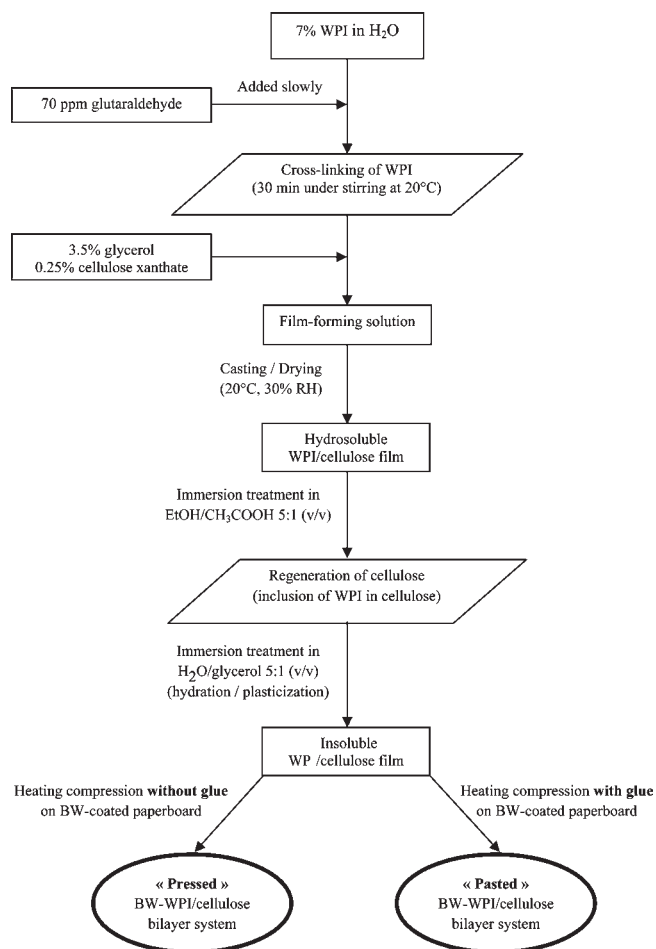
preliminary study, the barrier properties of chitosan (Chi; Kitomer, low M_w, 70% deacetylated, 100−500 cP; Marinard Biotech, Rivière-au-Renard, QC, Canada), polycaprolactone diol (PCL; average M_n 1250; Sigma-Aldrich Canada Ltd., Oakville, ON, Canada), WPI (BiPro, 97.8% total protein weight; Davisco Foods International Inc., Le Sueur, MN), and zein (Sigma-Aldrich Canada Ltd.) were independently tested in the presence of glycerol (Gly; Laboratoire Mat, Beauport, QC, Canada) as a plasticizer. Coating solutions were composed of (i) 2% Chi (w/v) and 0.5% Gly (dissolved in a 0.1 M acetic acid solution); (ii) 2% PCL and 0.5% Gly (dissolved in benzene); (iii) 10% WPI and 2.5% Gly (dissolved in deionized water); and (iv) 10% zein and 2.5% Gly [dissolved an ethanol−water mixture 70:30 (v/v)]. These coating formulations were prepared to obtain analogous viscosities (data not shown) and to prevent stretching of the paperboard due to water absorption. A 10% (w/v) concentration of WPI or zein was required to attain viscosity, spreadability, and wettability values comparable to those of 2% (w/v) Chi or PCL. All polymer solutions were prepared at room temperature, under magnetic stirring. For each coating, Gly was added after total solubilization of the polymer. Each coating solution was then spread onto the internal side of the paperboard (300 mg per cm^2) using a brush. Brushing allowed ensurance of a homogeneous thickness of the coating since the polymer was applied under liquid state-inducing gelation. Samples were then dried overnight at room temperature and 35% relative humidity (RH) (the coating surface was smooth after drying).

Formation of WPI/Cellulose-Based Film. WPI/cellulose-based films were prepared following a procedure developed by Le Tien et al. (*23*). The process chart for the preparation of WPI/cellulose films is presented in **Scheme 1**. A cellulose xanthate stock solution was prepared according to the Viscose process. Briefly, a solution consisting of 4% α-cellulose dissolved in 18% aqueous NaOH at 20 °C (alkali cellulose) was converted into cellulose xanthate by the addition of carbon disulfide (CS$_2$) up to

Scheme 2. Process Chart for the Preparation of PVB/Zein Coatings and Their Application onto Paperboard as a Part of a Bilayer System
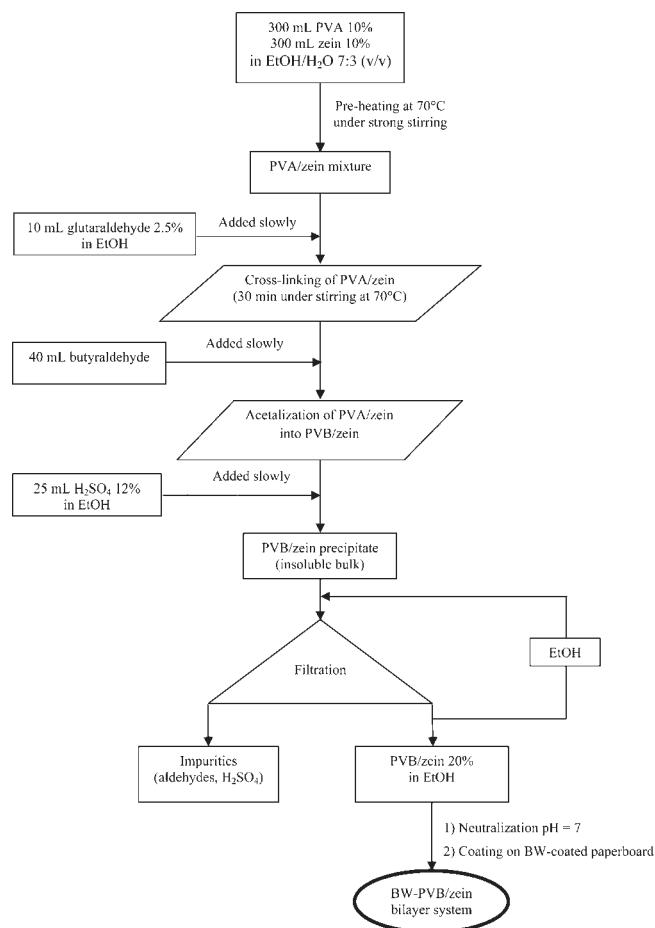
1.3−1.6%. After the solution was stirred for 2 h, excess CS_2 was removed from the solution by vacuum, followed by mild stirring for 24 h at room temperature. A solution containing 7% WPI and 3.5% Gly was prepared at room temperature, to which a 2.5% glutaraldehyde solution (Sigma-Aldrich Canada Ltd.) was added under stirring, at a concentration of 40 μL/g protein. At this step, a cross-linking reaction was performed for 30 min to promote intermolecular imine links between proteins and glutaraldehyde, as described by Kawahara et al. (*24*) and Han et al. (*25*). Cellulose xanthate (0.25%) was then added to the protein solution to induce protein inclusion into the cellulose matrix. Films were then cast by applying 5 mL of film-forming solution evenly onto Petri dishes (8.5 cm diameter; VWR Int., Ville Mont-Royal, QC, Canada), which were allowed to dry overnight at room temperature and 35% RH. The entrapment process (insolubilization of films) was performed as follows: Dried films were peeled and treated in baths containing ethanol/acetic acid 5:1 (v/v) solution for 15 min. This insolubilization step regenerated films by allowing protein fixation with ethanol and coagulation of soluble cellulose xanthate into insoluble cellulose with acetic acid. To remove excess acid, films were repeatedly washed in water baths and in Gly/water 1:5 (v/v), using Gly as a stabilizing agent. Films were then equilibrated for at least 48 h in desiccators containing a saturated NaBr solution to ensure a 59.1% RH at 20 °C. These films, with their interesting mechanical and barrier properties, very low solubility, and long-term biodegradability, were then combined with BW to form a bilayer coating system on the paperboard. The structural and functional properties of these films were characterized in our previous results (*23*), but films were not evaluated in any application until the present study. Hence, this formulation was compared to a PVB/zein formulation for their water vapor barrier properties.

Formation of PVB/Zein-Based Coating Solution. The process chart for the preparation of the PVB/zein coating is presented in **Scheme 2**. A PVB suspension was prepared using PVA (87−89% hydrolyzed, M_w 85000−146000; Sigma-Aldrich Canada Ltd.) and zein (Sigma-Aldrich Canada

Ltd.) as the major components. Glutaraldehyde and butyraldehyde (Laboratoire Mat), as the cross-linking agent and functionalization agent, respectively, promote acetalization of PVA to cross-linked PVB, which is insoluble and compatible with zein in alcoholic solution. A 300 mL volume of 10% (w/v) PVA solution was prepared in ethanol/water 7:3 (v/v) and preheated at 70 °C. An identical volume of 10% zein was added to the PVA solution, under stirring at 70 °C for 5 min. A 10 mL volume of 2.5% (v/v) glutaraldehyde was slowly added to the PVA/zein mixture, and the cross-linking reaction was maintained at 70 °C for 30 min under stirring. After reaction, a 25 mL volume of sulfuric acid (dissolved in ethanol) was added followed by 40 mL of butyraldehyde. The solution was stirred vigorously for 1 h at 70 °C to promote acetalization of PVA. The resulting precipitate (obtained from cross-linking/acetalization of PVA and zein inclusion) was successively filtered and washed twice with ethanol. The final resinlike precipitate was dissolved into ethanol for 2 h at 40 °C under vigorous stirring to obtain a final solution of 20% (w/v) PVB/zein-based resin. The suspension was neutralized to pH 7 before utilization. The structural properties of this formulation were characterized by FTIR analysis, and its water vapor barrier property was compared to the WPI/cellulose-based film formulation.

Preparation of BW-Polymer-Based Bilayer Coating Systems. BW (white BW; Laboratoire Mat) was used as the first layer in the testing of bilayer systems on paperboard. A comparison was made between the processing of a free-standing film (WPI/cellulose) versus a film-forming suspension (PVB/zein) applied to a BW layer on the WVTR of coated paperboards. The first bilayer system was characterized by a solid, insoluble, free-standing WPI/cellulose-based film applied onto a BW first layer (BW-WPI/cellulose film bilayer system; **Scheme 1**). The second bilayer system was characterized by an insoluble, spreadable PVB/zein coating solution applied on a BW first layer (BW-PVB/zein coating bilayer system; **Scheme 2**). Moreover, it is interesting to note that (i) the WPI/cellulose film formulation promoted the insolubilization of hydrosoluble polymers after the coagulation process of cellulose xanthate in acidic/alcoholic conditions, as described in **Scheme 1**, and (ii) the PVB/zein coating formulation helped to provide a readily insoluble polymer blend after acetalization of PVA, as described in **Scheme 2**.

Preparation of BW-WPI/Cellulose-Based Film Bilayer System. BW was preheated at 60 °C and spread using a brush onto the internal side of the paperboard (300 mg per cm^2). The coating layer was allowed to cool for 10 min at room temperature. After the layer cooled, the WPI/cellulose-based film (thickness in the range of 50−60 μm) was applied onto the paperboard by heating compression at 0.5 t/cm^2 for 30 s using a hydraulic Carver press (Carver Inc., Wabash, IN) with (i.e., pasted films) or without (i.e., pressed films) biodegradable starch-based glue paste (Pritt stick; Henkel Canada Corp., Mississauga, ON, Canada) as an interfacial sticking agent between layers. The samples were then equilibrated before WVTR measurements for at least 24 h in desiccators containing saturated NaBr solution to ensure 59.1% RH at 20 °C.

Preparation of BW-PVB/Zein-Based Coating Bilayer System. BW was preheated and spread onto paperboard as described above. The coating layer was allowed to cool for 10 min at room temperature. After it was cooled, 300 mg of PVB/zein suspension per cm^2 of paperboard was applied to the BW layer using a brush. The coated samples were then allowed to dry overnight at room temperature. After they were dried, samples were equilibrated before WVTR measurements for at least 24 h in desiccators containing saturated NaBr solution to ensure 59.1% RH at 20 °C.

Structural Analysis by FTIR Spectroscopy. FTIR spectra of PVA and PVB films were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high linearity lithium tantalate (HLLT) detector. Spectra were analyzed using the Spectrum software (version 3.02.1). Films were stored at room temperature for 72 h in a desiccator containing saturated NaBr solution to ensure a stabilized atmosphere of 59.1% RH at 20 °C. Films were then analyzed in a transmission chamber, and analysis was performed within the spectral region of 650−4000 cm^{-1} with 64 scans recorded at a resolution of 4 cm^{-1}. After baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units. The resulting spectra for the cross-linking reaction with glutaraldehyde and the functionalization of PVA by butyraldehyde were compared in relation with the intensity of IR vibrational bands.
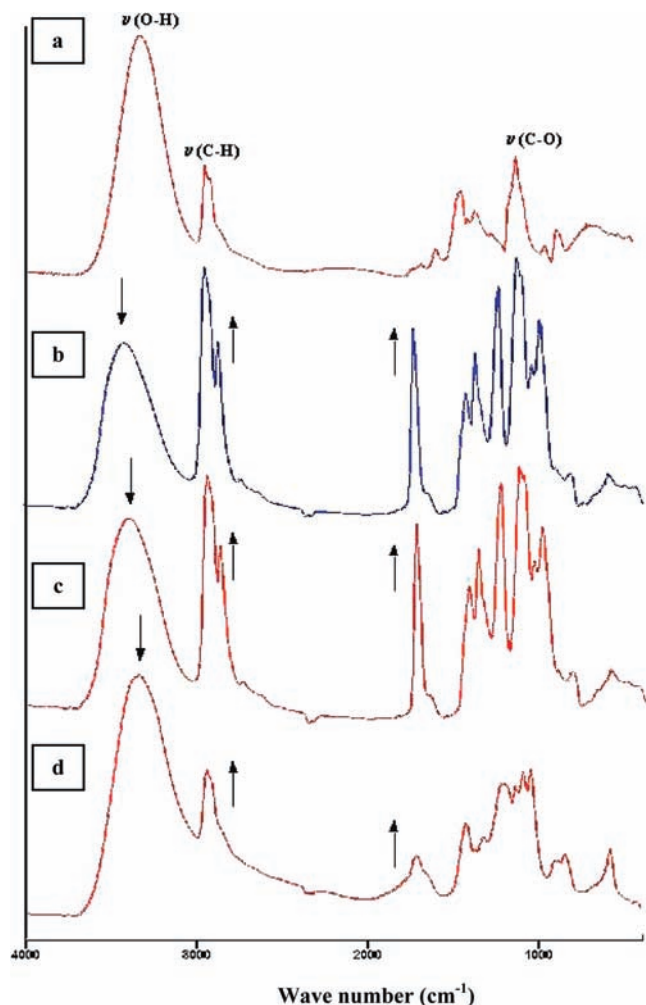
3128 *J. Agric. Food Chem.,* Vol. 58, No. 5, 2010

Han et al.

Figure 1. FTIR spectra of (**a**) PVA, (**b**) PVB, (**c**) PVA modified with butyraldehyde only, and (**d**) PVA modified with glutaraldehyde only.

WVTR. To compare WPI/cellulose film and PVB/zein coating formulations as efficient water vapor barriers on paperboard, their WVTRs were determined gravimetrically at 20 °C using the TAPPI method T 464 om-95 (*26*). Coated paperboards were mechanically sealed onto Vapometer cells (no. 68-1; Thwing-Albert Instrument Co., West Berlin, NJ) containing 30 g of anhydrous calcium chloride (0% RH). The cells were initially weighed and placed in a Shellab 9010 L controlled humidity chamber (Sheldon Manufacturing Inc., Cornelius, OR) maintained at 30 °C and 90% RH for 24 h. The amount of water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the cell. The assemblies were weighed initially and after 24 h for all samples and up to a maximum of 10% gain. Changes in weight of the cell were recorded to the nearest 10^{-4} g. The WVTR was calculated according to the combined laws of Fick and Henry for gas diffusion through coatings and films, represented in the following formula (*27*):

$$\text{WVTR } (\text{g/m}^2 \cdot 24 \text{ h}) = w/A$$

where w is the weight gain of the cell (g) after 24 h and A is the area of exposed film ($31.67 \times 10^{-4} \text{ m}^2$).

Statistical Analysis. For each measurement, three samples in each replicate were tested. Analysis of variance and Duncan's multiple-range tests were used to perform statistical analysis on all results, using SPSS Base 10.0 software (Stat-Packets Statistical analysis Software, SPSS Inc., Chicago, IL). Differences between means were considered to be significant when $p \leq 0.05$.

RESULTS AND DISCUSSION

FTIR Analysis. Figure 1 shows the FTIR spectra of (**a**) PVA, (**b**) PVB (cross-linked and acetalized using glutaraldehyde and

butyraldehyde, respectively), (**c**) PVA modified by butyraldehyde only, and (**d**) PVA modified by glutaraldehyde only. Hence, this analysis attempted to characterize the functionalization of PVA and to distinguish the chemical reactions occurring during PVA modification. The absorption peaks of the PVA spectrum (**a**) are mainly assignable to the following stretching vibrations of O−H at 3000−3600 cm^{-1}, overlapping symmetric and asymmetric C−H at 2850−2950 cm^{-1}, and C−O at 1170 cm^{-1}. For the PVB spectrum (**b**), which is related to cross-linking and acetalization of PVA to PVB, a decrease in the O−H peak intensity was observed, indicating conversion of PVA (polyol) to PVB (cyclic polyacetal), related to a diminution in the number of O−H groups (diminution of hydrogen bonding) and to a formation of acetal groups (*28*). Moreover, on acetalization, the O−H stretching vibration bands shifted toward higher frequencies due to the cleavage of the polymeric hydrogen bond chain (*29*). On the other hand, an increase in peak intensity was observed for C−H stretching, due to the alkyl groups of glutaraldehyde and butyraldehyde. The appearance of a strong peak at 1700 cm^{-1} is assigned to the C═O stretching vibration and can be explained by the presence of an aldehyde group from the butyraldehyde fraction that did not react with PVA. An increase in peak intensity was also observed for C−O stretching at 1170 cm^{-1} due to the formation of cyclic acetals resulting from the reactions between (i) PVA and glutaraldehyde (cross-linking) and (ii) PVA and butyraldehyde (acetalization) (*28*). As compared to the PVB spectrum (**b**), the spectra for the PVA reaction with butyraldehyde only (**c**) and with glutaraldehyde only (**d**) show that the degree of substitution of PVA with butyraldehyde is higher than that with glutaraldehyde. Indeed, spectrum **c** displays a weaker intensity of O−H vibration and a stronger intensity of C−H and C−O vibrations as compared to spectrum **d**. This suggests a higher reactivity between PVA and butyraldehyde in the formation of cyclic polyacetals, due most likely to an excess amount of butyraldehyde. As a consequence, it is interesting to note that the spectra (**b**) for PVB and (**c**) for PVA modified with butyraldehyde only are almost identical, suggesting a low quantity of glutaraldehyde that reacted with PVA as compared to butyraldehyde, which is clearly indicated by the weak bands assigned to C−H groups (2850−2950 cm^{-1}) and C−O groups (1170 cm^{-1}) in spectrum **d**, for PVA modified with glutaraldehyde only, as described above. Therefore, it can be assumed that the bands implied in glutaraldehyde cross-linking are overlapped with those implied in butyraldehyde functionalization, as observed in spectrum **b** for PVB characterization. The slight difference between spectra **b** and **c** concerns the ratio O−H intensity/C−H intensity that is weaker in spectrum **b** due to cross-linking via glutaraldehyde, hence suggesting a slight dehydration of the polymer.

WVTR of Coated Paperboard. *WVTR of Paperboard Coated with Preliminary Basic Coatings.* The WVTRs of preliminary basic coating formulations are presented in **Figure 2**. The abilities of the coating formulations to decrease the WVTRs of paperboard were in the following order: zein > WPI > PCL > Chi > control (uncoated paperboard) with respective WVTR values of 250, 272, 320, 380, and 513 g/m$^2 \cdot$24 h and significant differences between each formulation ($p \leq 0.05$). It is noteworthy that these formulations were not applied in a bilayer (e.g., absence of BW as a first layer), which explains the relatively high WVTR values after the application to paperboard. Chi is a hydrophilic polyaminoglucose saccharide that is obtained through the partial deacetylation of chitin (*30*). PCL is a hydrophobic polyester chemically synthesized from crude oil (*31*).

From the results, the zein-based surface coating produced a lower WVTR, due probably to its hydrophobic properties. Indeed, zein is insoluble in water due to high levels of apolar
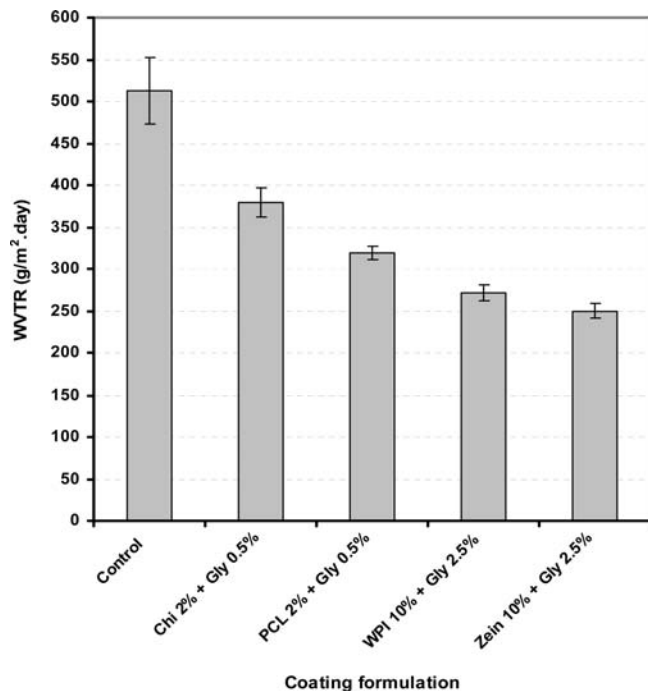
Article

J. Agric. Food Chem., Vol. 58, No. 5, 2010   **3129**

Figure 2. WVTRs of preliminary coating formulations applied to paperboard (at 30 °C and 90% RH). Control, uncoated paperboard.

Figure 3. WVTR of the BW-WPI/cellulose-based film bilayer system applied to paperboard (at 30 °C and 90% RH). Control, uncoated paperboard; BW-pressed film, free-standing film applied on BW layer under heating compression; and BW-pasted film, free-standing film applied on BW layer by pasting with starch-based glue under heating compression.

amino acids such as tryptophan (*32*). This stands in contrast to WPI, which when not denatured is readily soluble in water (*33*). According to other studies, the water barrier property of zein-based films was superior to other protein films (*34−36*). It was also reported that zein films coated with liquid vegetable oil exhibited a higher resistance to water vapor (*36, 37*). However, PCL showed a higher WVTR than zein, which could be due to adhesion of the film onto paperboard. Indeed, coating adhesiveness may influence the contact between paperboard and coating, resulting from polarity affinity and surface tension during process (*38*). These preliminary observations encouraged the development of WPI and zein-based coatings. WPI was selected for its low price and capacity to be cross-linked by chemical reagents via amino groups and by heating via disulfide bonding (*23*). Additionally, zein was selected for its compatibility with insoluble polymers.

WVTR of Paperboard Coated with BW-WPI/Cellulose-Based Film Bilayer System. The WVTRs of WPI/cellulose-based films used in a bilayer system on paperboard are presented in **Figure 3**. The abilities of the coating formulations to decrease the WVTR of paperboards were in the following order: BW-pasted film > BW-pressed film > BW > pasted film > pressed film > control (uncoated paperboard) with respective WVTR values of 41, 49, 54, 111, 195, and 513 g/m²·24 h and significant differences between each formulation ($p \leq 0.05$). It is noteworthy that the BW coating layer remarkably reduced the WVTR of paperboard. Moreover, the effect of adding BW as a prelayer reduced the WVTR by 75% for pressed film (from 195 to 49 g/m²·24 h) and by 63% for pasted film (from 111 to 41 g/m²·24 h). In general, a lipid-based coating layer like BW has a low affinity for water and low moisture permeability (*39*). Incorporation of hydrophobic agents with protein films has been shown to improve the water barrier property by decreasing the WVTR in the films (*40*). Concerning the WPI/cellulose-based film itself, the pasted film produced a 43% more decrease in WVTR than did the pressed film without glue, with values from 195 to 111 g/m²·24 h ($p \leq 0.05$). This result could be explained by the fact that the
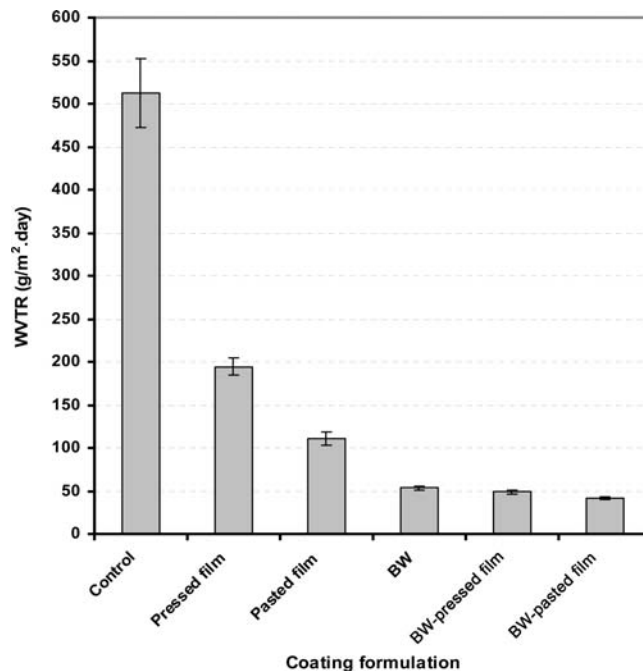
pasting process with starch-based glue as a sticking agent may have promoted starch gelatinization during heating compression, hence adding some barrier effect, and allowed reduction of the water vapor transfer through the film. Furthermore, a more efficient interfacial barrier could be accomplished by the adhesion of film onto paperboard in the presence of glue (starch-based sticking agent) under heating compression. Otherwise, these results showed that the addition of WPI/cellulose film on BW allowed improvement of the barrier properties of paperboard in lower proportions as compared to BW alone. Indeed, BW was more efficient since it decreased WVTR by 89% (from 513 to 54 g/m²·24 h), whereas WPI/cellulose films alone decreased WVTR by 78% (from 513 to 111 g/m²·24 h). However, it can be assessed that the bilayer system allowed us to obtain a decrease of WVTR by 92% (from 513 to 41 g/m²·24 h), which is a little improvement. Moreover, the BW-pasted film bilayer system allowed reduction of the WVTR of BW alone by 24%. Although WPI/cellulose-based films are insoluble due to protein fixation and regeneration of cellulose xanthate into cellulose (*41*), the hydrophobic nature of BW (approximately 80% ceryl myristate) is more dominant, which therefore causes its further hydrophobicity. As a result, the BW-pasted film was the most effective bilayer coating system by decreasing the WVTR of paperboard to 92% (from 513 to 41 g/m²·24 h). Relatively, it was reported that the application of a lipid layer significantly decreased the WVTR of bilayer films consisting of zein and plant wax, which was highly effective in improving water vapor barrier properties of protein-based films (*42, 43*).

WVTR of Paperboard Coated with BW-PVB/Zein-Based Film Bilayer System. The WVTRs of PVB/zein-based coatings used in a bilayer system on paperboard are presented in **Figure 4**. The abilities of the coating formulations to decrease the WVTR of paperboards were in the following order: BW-(PVB/zein) > BW-PVB > BW > PVB/zein > PVB > control (uncoated paperboard) with respective WVTR values of 24, 30, 54, 121, 190, and
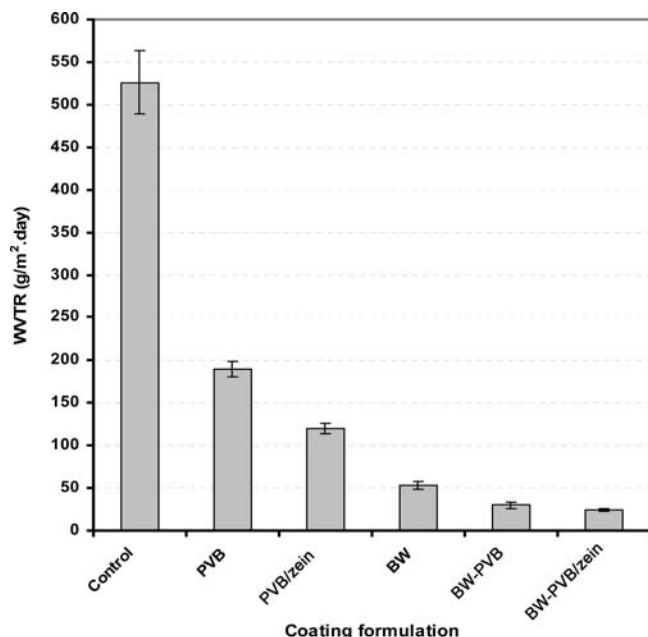
Figure 4. WVTR of the BW-PVB/zein bilayer system applied to paperboard (at 30 °C and 90% RH). Control, uncoated paperboard; and BW-PVB/zein, PVB containing entrapped zein and sprayed on BW layer.

526 g/m^2·24 h and significant differences between each formulation ($p \leq 0.05$). In the presence of BW as a prelayer, the PVB/zein coating induced a stronger reduction of WVTR as compared to WPI/cellulose films. Indeed, the effect of adding BW as a prelayer reduced the WVTR by 84% for the PVB coating treatment (from 190 to 30 g/m^2·24 h) and by 80% for the PVB/zein coating treatment (from 121 to 24 g/m^2·24 h). The addition of zein to the PVB-based coating formulation lowered the WVTR by 37% (from 190 to 121 g/m^2·24 h), enhancing the water barrier property by trapping zein into the PVB matrix. Moreover, the addition of the BW-PVB/zein bilayer allowed a decrease of the WVTR of BW to 55% (from 55 to 24 g/m^2·24 h). As reported for WPI/cellulose films, these results show that the addition of the PVB/zein coating on BW induced an improvement of the barrier properties in lower proportions as compared to BW alone. In the same evolution, the PVB/zein coating alone diminished the WVTR to 77% as compared to 89% for BW alone. However, it can be observed that the bilayer system allowed us to obtain a reduction of the WVTR to 95%, which is a little improvement. Therefore, the BW-PVB/zein coating formulation endowed hydrophilic paperboard with a increased water barrier efficiency by decreasing its WVTR to 95% (from 526 to 24 g/m^2·24 h). This remarkable property may be due to the insolubility of PVB resulting from the acetalization and cross-linking of PVA, along with its compatibility with zein. Generally, the hydrophobic characteristic and insulating property of acetals improve with the increase of degree of acetalization (*44*). BW also contributed with its highly hydrophobic chemical nature. Another processing parameter such as coating adhesion onto BW prelayer could result in better barrier properties of the PVB/zein coating due to a higher penetration of the coating into paperboard material. Indeed, the attraction force through the coating−substrate interface determines the adhesiveness between the two phases. This attraction may increase and consequently improve the contact between coating and paperboard in the function of physicochemical parameters such as the film formulation and its polarity, the solvent, the viscosity, the wettability of the surfaces by the coating

solution and the resulting surface tension, and the spreading process (*38*, *45*).

In conclusion, our results indicate the possibility of using two types of bilayer coating systems on paperboard as opposed to only secondary layers such as a free-standing WPI/cellulose film and PVB/zein coating. Results showed that the BW-PVB/zein bilayer system was more efficient than the BW-pasted WPI/cellulose film bilayer system ($p \leq 0.05$) with a strong reduction of WVTR to 95% as compared to uncoated paperboard. In both cases of study, a higher effect in reducing WVTR was noticed when BW was layered between paperboard and WPI/cellulose or PVB/zein formulations. These measurements allowed us to describe the capacity of biopolymer-based film and coating systems to improve the water vapor barrier as compared to a hydrophobic reference such as BW. From the WVTR evaluations, it can be concluded that (i) the coating formulations (WPI/cellulose and PVB/zein) allowed reduction of the WVTR by a range of approximately 80% (as compared to 90% for BW alone) and (ii) combining BW and coating formulations into a bilayer system does not have a high effect (only an improvement of barrier properties from 89 to 92−95%). Consequently, these surface-coating treatments can offer a good industrial perspective for the manufacture of paperboard-made containers in various applications. However, the formulations should be improved to approach a WVTR value of 10 g/m^2·24 h and to fulfill industrial requirements.

LITERATURE CITED

(1) Rhim, J.-W.; Kim, J.-H. Properties of poly(lactide)-coated paperboard for the use of 1-way paper cup. *J. Food Sci.* **2009**, *74*, E105–E111.

(2) Robertson, G. L. Paper and paper-based packaging materials. *Food Packaging, Principles and Practice*; Marcel Dekker Inc.: New York, 1993; pp 144−172.

(3) Andersson, C. New ways to enhance the functionality of paperboard by surface treatment—A review. *Packag. Technol. Sci.* **2008**, *21*, 339–373.

(4) Otway, P.; Johnson, D. C. Sizing in acid, neutral and alkaline conditions. In *Applications of Wet-End Paper Chemistry*; Au, C. O., Thorn, I., Eds.; Blackie Academic & Professional: London, United Kingdom, 1995; pp 142−171.

(5) Robson, N. C. Recycling practice and problems. In *International Symposium on Packaging, Economic Development, And the Environment*; Institute of Packaging Professionals: IL, 1993; pp 173−189.

(6) Han, J. H.; Krochta, J. M. Physical properties and oil absorption of whey-protein-coated paper. *J. Food Sci.* **2001**, *66*, 294–299.

(7) Lin, S. Y.; Krochta, J. M. Plasticizer effect on grease barrier and color properties of whey-protein coatings on paperboard. *J. Food Sci.* **2003**, *68*, 229–233.

(8) Park, H. J.; Kim, S. H.; Lim, S. T.; Shin, D. H.; Choi, S. Y.; Hwang, K. T. Grease resistance and mechanical properties of isolated soy protein-coated paper. *J. Am. Oil Chem. Soc.* **2000**, *77*, 269–273.

(9) Rhim, J. W.; Lee, J. H.; Hong, S. I. Water resistance and mechanical properties of biopolymer (alginate and soy protein) coated paperboards. *LWT−Food Sci. Technol.* **2006**, *39*, 806–813.

(10) Trezza, T. A.; Vergano, P. J. Grease resistance of corn zein coated paper. *J. Food Sci.* **1994**, *59*, 912–915.

(11) Shaw, N. B.; Monahan, F. J.; O'Riordan, E. D.; O'Sullvan, M. Physical properties of WPI films plasticized with glycerol, xylitol, or sorbitol. *J. Food Sci.* **2002**, *67*, 164–167.

(12) McHugh, T. H.; Aujard, J. F.; Krochta, J. M. Plasticized whey-protein edible films-water-vapor permeability properties. *J. Food Sci.* **1994**, *59*, 416–420.

(13) Atik, I. D.; Ozen, B.; Tihminlioglu, F. Water vapour barrier performance of corn-zein coated polypropylene (PP) packaging films. *J. Therm. Anal. Calorim.* **2008**, *94*, 687–693.

(14) Greener, I.; Fennema, O. Edible films and coatings: Characteristics, formation, definitions, and testing methods. In *Edible Coatings and Films to Improve Food Quality*; Krochta, J. M., Baldwin, E. A.,

Nisperos-Carriedo, M. O., Eds.; Technomic Publishing Company Inc.: Lancaster Basel, 1994; Chapter 1, pp 1−24.

(15) Laletin, A. I.; Gal'braikh, L. S.; Rogovin, Z. A. Synthesis of stable derivatives of cellulose xanthate by ester exchange. *Polym. Sci. U.S.S.R.* **1969**, *11*, 612–617.

(16) Petersen, K; Nielsen, P. V.; Bertelsen, G; Lawther, M; Olsen, M. B.; Nilssonk, N. H.; Mortenseny, G. Potential of biobased materials for food packaging. *Trends Food Sci. Technol.* **1999**, 1052–1068.

(17) Fernández, M. D.; Fernández, M. J.; Hoces, P. Synthesis of poly-(vinyl butyral)s in homogeneous phase and their thermal properties. *J. Appl. Polym. Sci.* **2006**, *102*, 5007–5017.

(18) Chetri, P.; Dass, N. N. Preparation of poly(vinyl butyral) with high acetalization rate. *J. Appl. Polym. Sci.* **2001**, *81*, 1182–1186.

(19) Shukla, R.; Cheryan, M. Zein: The industrial protein from corn. *Ind. Crops Prod.* **2001**, *13*, 171–192.

(20) Guilbert, S. Technology and application of edible protective films. In *Food Packaging and Preservation*; Mathlouthi, M., Ed.; Elsevier Applied Science: London, United Kingdom, 1986; pp 371−394.

(21) Krochta, J. M. Edible protein films and coatings. In *Food Proteins and Their Applications*; Damodaran, S., Ed.; Marcel Dekker: New York, 1997; pp 529−544.

(22) Cuq, B.; Gontrad, N.; Guilbert, S. Proteins as agricultural polymers for packaging production. *Cereal Chem.* **1998**, *75* (1), 1–9.

(23) Le Tien, C.; Letendre, M.; Ispas-Szabo, P.; Mateescu, M.-A.; Delmas-Patterson, G.; Yu, H.-L.; Lacroix, M. Development of biodegradable films from whey proteins by cross-linking and entrapment in cellulose. *J. Agric. Food Chem.* **2000**, *48*, 5566–5575.

(24) Kawahara, J.; Ishikawa, K.; Uchimaru, T.; Takaya, H. Chemical cross-linking by glutaraldehyde between amino groups: Its mechanism and effects. *Polymer Modification*; Plenum Press: New York, 1997; pp 119−131.

(25) Han, J.; Bourgeois, S.; Lacroix, M. Protein-based coatings on peanut to minimise oil migration. *Food Chem.* **2009**, *115*, 462–468.

(26) TAPPI. *Water Vapour Transmission Rate of Paper and Paperboard at High Temperature and Humidity*; Method T 464 om-95; TAPPI: Atlanta, 1995.

(27) Debeaufort, F.; Martin-Polo, M.; Voilley, A. Polarity homogeneity and structure affect water permeability of model edible films. *J. Food Sci.* **1993**, *58*, 426–429.

(28) Dos Reis, E. F.; Campos, F. S.; Lage, A. P.; Leite, R. C.; Heneine, L. G.; Vasconcelos, W. L.; Lobato, Z. I. P. Synthesis and characterization of poly(vinyl alcohol) hydrogels and hybrids for rMPB70 protein adsorption. *Mater. Res.* **2006**, *9*, 185–191.

(29) Kenney, J. F.; Willcockson, G. W. Structure-property relationships of poly(vinyl alcohol). III. Relationships between stereo-regularity, crystallinity, and water resistance in poly(vinyl alcohol). *J. Polym. Sci. Part A-1* **1966**, *4*, 679–698.

(30) Rinaudo, M.; Domard, A. Solution properties of chitosan. In *Chitin and Chitosan*; Skjak-Braek, G., Anthonsen, T., Sandford, P., Eds.; Elsevier: New York, 1989; pp 71−83.

(31) Yoshii, F.; Darwis, D.; Mitomo, H.; Keizo, M. Crosslinking of poly(ε-caprolactone) by radiation technique and its biodegradability. *Radiat. Phys. Chem.* **2000**, *57*, 417–420.

(32) Shukla, R.; Cheryan, M.; Devor, R. Solvent extraction of zein from dry-milled corn. *Cereal Chem.* **2000**, *77*, 724–730.

(33) Patocka, G.; Cervenkova, R.; Narine, S.; Jelen, P. Rheological behaviour of dairy products as affected by soluble whey protein isolate. *Int. Dairy J.* **2006**, *16*, 399–405.

(34) Guilbert, S. Technology and application of edible protective films. In *Food Packaging and Preservation: Theory and Practice*; Mathlouthi, M., Ed.; Elsevier Applied Science: London, 1986; pp 371−394.

(35) Wang, Q.; Padua, W. Properties of zein films coated with drying oils. *J. Agric. Food Chem.* **2005**, *53*, 3444–3448.

(36) Lai, H.-M.; Padua, G. W. Water vapor barrier properties of zein films plasticized with oleic acid. *Cereal Chem.* **1998**, *75*, 194–199.

(37) Rakotomirainy, A. M.; Padua, G. W. Effects of lamination and coating with drying oils on tensile and barrier properties of zein films. *J. Agric. Food Chem.* **2001**, *49*, 2860–2863.

(38) Lin, S.-Y. D.; Krochta, J. M. Whey protein coating efficiency on surfactant-modified hydrophobic surfaces. *J. Agric. Food Chem.* **2005**, *53*, 5018–5023.

(39) Lazari, M.; Chiantore, O. Drying and oxidative degradation of linseed oil. *Polym. Degrad. Stab.* **1999**, *65*, 303–313.

(40) Liu, L.; Kerry, J. F.; Kerry, J. P. Effect of food ingredients and selected lipids on the physical properties of extruded edible films/casing. *Int. J. Food Sci. Technol.* **2006**, *41*, 295–302.

(41) Gontard, N.; Guilbert, S.; Cuq, J.-L. Edible wheat gluten films: Influence of the main process variables on film properties using response surface methodology. *J. Food Sci.* **1992**, *57*, 190–195.

(42) Weller, C. L.; Gennadios, A; Saraiva, R. A. Edible bilayer films from zein and grain sorghum wax or carnauba wax. *LWT−Food Sci. Technol.* **1998**, *31*, 279–285.

(43) Lai, H.-M.; Padua, G. W.; Wei, L. S. Properties and microstructure of zein sheets plasticized with palmitic and stearic acids. *Cereal Chem.* **1997**, *74*, 83–90.

(44) Urbanski, J.; Czerwinski, W.; Janicka, K.; Majewska, F.; Zowall, H. *Handbook of Analysis of Synthetic Polymers and Plastics*; John Wiley & Sons, Inc.: Aberdeen, 1977; p 396.

(45) Hershko, V.; Nussinovitch, A. The behavior of hydrocolloid coatings on vegetative material. *Biotechnol. Prog.* **1998**, *14*, 756–765.