

Effect of Plasticizer Type and Amount on Hydroxypropyl Methylcellulose–Beeswax Edible Film Properties and Postharvest Quality of Coated Plums (Cv. Angeleno)

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The effect of the composition of hydroxypropyl methylcellulose (HPMC)–beeswax (BW) edible coatings on stand-alone film properties and on postharvest quality of coated 'Angeleno' plums was studied. Glycerol (G) and mannitol (M) were tested as plasticizers at two different plasticizer/HPMC ratios (100:1 and 300:1 molar basis). BW content was 20 or 40% (dry basis). An increase in G content increased film flexibility and vapor permeability (WVP), whereas an increase in M content enhanced film brittleness without affecting WVP. An increase in BW content reduced film flexibility and reduced WVP of only G-plasticized films. Coatings reduced plum softening and bleeding, but were not effective in reducing plum weight loss. At low plasticizer content, coatings reduced texture loss effectively. Low BW also lowered plum bleeding. Plasticizer type affected only ethanol and acetaldehyde contents without affecting the remaining quality parameters. Therefore, HPMC–BW coatings have the potential to extend the shelf life of plums. However, this effect depends on coating composition. Differences between coating and film performance indicate that data from stand-alone films may be used as a preliminary screening, but coating performance should be analyzed on coated fruit.

KEYWORDS: Edible films and coatings; hydroxypropyl methylcellulose; plasticizer; postharvest quality; plum

INTRODUCTION

Plums are climateric fruits, which are suitable for cold storage for a short period depending on the susceptibility to internal breakdown and loss in texture. Some cultivars have shown an improvement in postharvest life by the use of edible coatings (1, 2). Application of edible coatings is a simple technology by which fruits and vegetables can be physically protected and have their respiration and, in some cases, ripening regulated as a passive modified atmosphere packaging (3, 4). Edible coatings can also offer a barrier to moisture transfer, reducing weight loss of the coated fruit (5).

Development of edible films and coatings has been focused upon barriers containing proteins, polysaccharides, lipids, or their combination. Proteins and polysaccharides are good film-forming materials, but they are poor moisture barriers. Lipids, on the other hand, provide a better moisture barrier, but they form brittle films (6). Therefore, most of the developed edible

films and coatings are combinations of a polymer matrix and a hydrophobic component.

The functionality of edible coatings depends on many factors, and it has been usually predicted by using stand-alone films as a model. Factors affecting edible film performance have been extensively studied (6–9). Many of these studies elucidated how composition, preparation, and storage conditions affected film barrier and mechanical properties. These works have shown the importance of polymer cohesion on film properties and the role of different components on polymer cohesion.

It has been shown that film polymer cohesion, as a result of polymer chain to chain interactions, affects film barrier and mechanical properties and can result in undesirable mechanical properties. To overcome this limitation, food-grade plasticizers are added to the film formulation. Plasticizers reduce polymer chain to chain interactions, increasing the mobility of the polymer chains and, therefore, improving film flexibility, elongation, and toughness (10). However, reduction of polymer–polymer interaction results in an increase in gas, water vapor, and solute permeability, affecting film functionality (10, 11).

Plasticizer chemical structure, size, and shape influence its ability to disrupt polymer–chain bonding, including its ability

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to attract water to the plasticized-polymer system. Plasticizer selection is normally based on compatibility between plasticizer and polymer, permanence in the formed film, and efficiency in terms of the amount necessary to plasticize films (12, 13). Good compatibility results from the plasticizer and polymer having a similar chemical structure (10, 14). Therefore, different polymers require different plasticizers. For polysaccharide-based edible films, hydrophilic plasticizers containing hydroxyl groups, which form hydrogen bonds with polysaccharides, are the best suited for this use. Plasticizers used for polysaccharide-based films are glycerol, sorbitol, xylitol, mannitol, polyethylene glycol, ethylene glycol, and propylene glycol (13).

Even though stand-alone films are usually used to determine the effect of coating composition on moisture barrier and mechanical properties, coating performance should be also analyzed when they are applied on the fruit, because additional factors, such as skin morphology and physiology of the fruit commodity, are also important controlling mass transfer of coated fruit. Not many works studying simultaneously the effect of the composition on stand-alone films and postharvest quality of a coated fruit have been done.

The objective of this work was to study the effect of plasticizer type and amount of hydroxypropyl methylcellulose (HPMC)—beeswax (BW) coatings on postharvest quality of coated 'Angeleno' plums and to relate the results with the barrier and mechanical properties of stand-alone films.

MATERIALS AND METHODS

Materials. Hydroxypropyl methylcellulose (HPMC) (Methocel E15) was supplied by Dow Chemical Co. (Midland, MI). Refined beeswax (BW) (grade 1) was supplied by Brilllocera, S.A. (Valencia, Spain). Stearic acid, glycerol (G), and mannitol (M) were purchased from Panreac Química, S.A. (Barcelona, Spain).

Emulsion Film and Coating Formulation. To prepare the formulations, a 7% HPMC solution was dispersed in hot water at 90 ± 2 °C. After dispersion, cooling to 20 °C was achieved for HPMC hydration. Next, BW was added at two BW contents (20 and 40%, dry basis). Stearic acid was added as emulsifier at a BW/stearic acid ratio of 5 parts BW to 1 part fatty acid (w/w), and this ratio was kept constant for all formulations. G or M was added as plasticizer at two different plasticizer/HPMC ratios (100:1 and 300:1 molar basis). Molar basis was used for comparing the plasticizer effect according to Cuq et al. (15). They concluded that at the same mass basis, lower molecular weight (M_w) plasticizers produced more film plasticization than higher M_w plasticizers because of the greater molar content, suggesting that plasticizer effect should be normalized to a molar basis. Water was added to bring the emulsions to a final solid content of 7% for stand-alone films and 4% solid content for coating solutions. To melt the BW, the solutions were heated at 90 ± 2 °C. Once the wax was melted, samples were homogenized with a high-shear probe mixer UltraTurrax (model T25 basic; IKA-Werke GmbH & Co. KG, Staufen, Germany) for 1 min at 13000 rpm, plus 3 min at 22000 rpm. Further cooling was achieved by placing the emulsions in an ice bath to lower the temperature to $<20 \pm 2$ °C. Agitation was continued for approximately 45 min after this temperature had been reached to ensure complete hydration of the HPMC. Emulsion film and coating compositions are shown in Table 1.

Film Preparation. The film-forming solution was degassed and applied onto a 15 cm internal diameter smooth high-density polyethylene casting plate at 3 g of total solids per plate to minimize thickness variations between formulations. The plates containing the film-forming solution were placed on a leveled surface and dried at room conditions until films could be peeled from the casting surface. Three replications were prepared for each formulation.

Tensile Property Measurement. Film mechanical properties were measured according to method DS882-97 of the American Society of Testing and Materials Standard (ASTM, 1997). Films were conditioned for 24 h at 23 ± 2 °C and $50 \pm 1\%$ relative humidity (RH), cut into

Table 1. Emulsion Film and Coating Composition (Percent Dry Basis)

formulation ^a	HPMC ^b	BW	G	M	SA ^c
20% BW–100 G	65.9	20.0	10.1		4.0
40% BW–100 G	45.1	40.0	6.9		8.0
20% BW–300 G	52.0	20.0	24.0		4.0
40% BW–300 G	35.6	40.0	16.4		8.0
20% BW–100 M	58.3	20.0		17.7	4.0
40% BW–100 M	39.9	40.0		12.1	8.0
20% BW–300 M	39.8	20.0		36.2	4.0
40% BW–300 M	27.2	40.0		24.8	8.0

^a Formulation name represents BW content (percent dry basis) and plasticizer molar content. Plasticizer/HPMC ratios were 100:1 and 300:1 molar basis. BW, beeswax; G, glycerol; M, mannitol. Solid contents were 7 and 4% for stand-alone films and coating formulations applied to plums, respectively. ^b HPMC, hydroxypropyl methylcellulose. ^c SA, stearic acid.

50 mm × 8 mm rectangular strips, and tested for tension analysis using an Instron Universal Machine (model 3343; Instron Corp., Canton, MA). Load cell and cross-head speed were 0.3 kN and 5 mm/min, respectively. Testing conditions were held constant at 23 ± 2 °C and $50 \pm 1\%$ RH throughout the analysis. Maximum tensile stress (TS), elongation at break (%E), elastic modulus (EM), and toughness (T) were calculated from the plot of stress versus strain, considering a rectangular cross-sectional area and using the average film thickness, measured at nine random positions. Twelve specimens from each replicate of each formulation were analyzed.

Water Vapor Permeability (WVP) Measurement. A modification of the ASTM E96-80 gravimetric method for measuring WVP (ASTM, 1980) was used (16). Upon drying, films were chosen on the basis of lack of physical defects such as cracks, bubbles, or pinholes. Two specimens from each replicate of each formulation were cut and mounted on polymethacrylate test cups containing 6 mL of distilled water. The specimens were analyzed with the film surface that had been exposed to air during drying facing either the low RH environment ("facing up") or the high RH environment ("facing down"), allowing detection of any phase separation within the film. The cups were placed in a pre-equilibrated desiccator cabinet fitted with a variable-speed fan. The environment within the cabinet was held constant at 23 ± 2 °C and $40 \pm 1\%$ RH using anhydrous potassium carbonate. Weights taken periodically after steady state was achieved and the average film thickness measured at six random positions were used to calculate the resulting WVP.

Film Thickness Measurement. Film thickness was measured using a Mitutoyo digital micrometer (model Quickmike Series 293-IP-54; Mitutoyo Corp., Kanagawa, Japan), taking measurements at random positions on the film.

Fruit Sample Preparation and Coating Application. 'Angeleno' plums from a local grove in Alicante (Spain) were selected for size, color, and absence of physical damage. Plums were randomly divided into 10 groups, which corresponded to eight coating treatments, one water-dipped treatment, and one uncoated—untreated control treatment. Plums were immersed in either water or the coating solutions for 1.5 min and drained of excess coating. Coated, water-dipped, and uncoated—untreated plums were dried in a tunnel at 50 – 55 °C for 2.2 min.

After drying, plums were stored for up to 8 weeks at 1 °C and $85 \pm 5\%$ RH (simulating storage conditions at packinghouses), followed by 1 week at 5 °C and $85 \pm 5\%$ RH (simulating transport conditions), and 1 or 2 additional weeks at 20 °C and $90 \pm 5\%$ RH (simulating retail handling conditions).

Fruit Weight Loss. Lots of 30 plums per treatment were used to measure weight loss. The same plums were weighed at the beginning of the experiment and at the end of each storage period. The results were expressed as the percentage loss of initial weight.

Ethanol and Acetaldehyde Contents. Ethanol and acetaldehyde concentrations in juice were determined by headspace gas chromatography. Three replicates per treatment of 10 plums each were juiced with an industrial juicer (LOMI model 4, Barcelona, Spain) and analyzed. Five milliliters of juice was transferred to 10 mL vials with crimp-top caps and TFE/silicone septum seals and frozen until analysis.

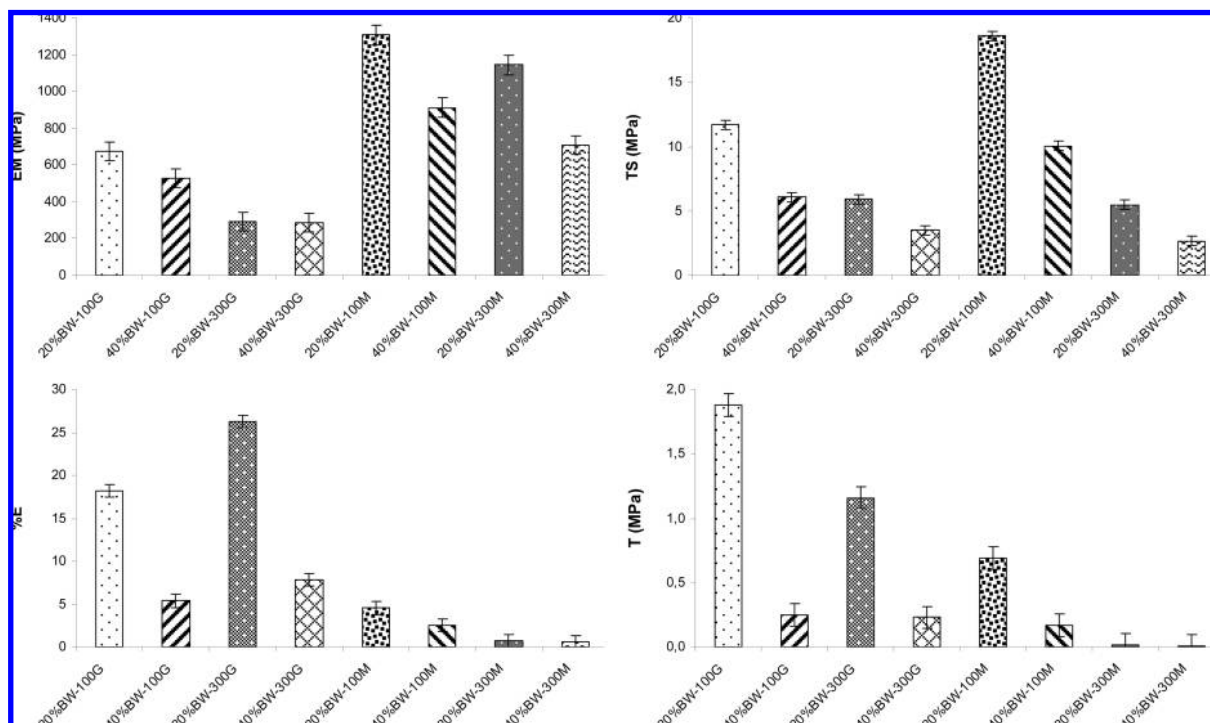


Figure 1. Mechanical properties of HPMC-based stand-alone edible films. EM, elastic modulus; TS, maximum tensile stress; *E*, elongation at break; *T*, toughness. Bars represent LSD values ($p < 0.05$).

Ethanol and acetaldehyde contents were analyzed in a gas chromatograph (Thermo Fisher Scientific, Inc., Waltham, MA) with an autosampler, a flame ionization detector (FID), and a 1.2×0.32 cm (i.d.) Poropak QS 80/100 column. A 1 mL sample of the headspace was withdrawn from vials previously equilibrated in the autosampler incubation chamber for 10 min at 60 °C. The injector, column, and detector temperatures were set at 175, 150, and 200 °C, respectively. Helium was used as carrier gas at 28 mL/min velocity. Ethanol and acetaldehyde contents were identified by comparison of retention times with standard solutions. Results were expressed as milligrams per 100 mL of juice.

Fruit Firmness. Plum firmness was determined as the maximum force in newtons (N) required to penetrate the fruit flesh. Lots of 20 plums per treatment were analyzed using an Instron Universal Testing Machine (model 3343) with a plunger of 8 mm diameter. Two tests per fruit were made, one on each of the opposite cheeks. Prior to the measurement, a disk of the skin of about 2 cm in diameter was removed to measure the plum firmness on the flesh.

Physiological Disorders. Physiological disorders affecting plum flesh (browning, translucency, lack of juiciness due to mealiness or leatheriness, and bleeding) were evaluated as described by Crisosto et al. (17). According to this method, fruits were cut in half and visually analyzed on the mesocarp and the area around the pit. The different degrees of flesh browning and translucency were rated as 1 = none, 2 = very slight, 3 = slight, 4 = moderate on <50%; 5 = severe on 50–75%; 6 = extreme on most of the flesh. Mealiness, leatheriness and bleeding were rated as 1 = none, 2 = moderate, 3 = severe. Forty fruits per treatment were inspected at the end of each storage period.

Statistical Analysis. A completely randomized experimental design was used to study the effect of BW content and plasticizer type and amount on the different film properties and plum quality parameters. STATGRAPHICS Plus 4.1 (Manugistics, Inc., Rockville, MD) was utilized to calculate analysis of variance (ANOVA). Significance between means was determined by least significant difference (LSD) at $p \leq 0.05$. Pearson's correlation was performed by Statgraphics Plus 4.1 to study the linear relationship among plum quality parameters.

RESULTS AND DISCUSSION

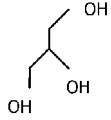
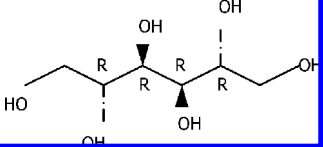
Film Mechanical Properties. Mechanical properties of stand-alone films were affected by BW content and plasticizer type

and content (**Figure 1**). M-plasticized films presented higher EM and lower %*E* and *T* at all plasticizer/HPMC ratios and higher TS at 100:1 mol of plasticizer/mol of HPMC ratio than G-plasticized films. Therefore, G-plasticized films were weaker and more stretchable, flexible, and durable than M-plasticized films. These results indicate that G was more effective by weakening the interactions among HPMC polymer chains and improving film mechanical properties than M.

Plasticizer physicochemical properties, such as chemical structure, shape, polarity, chain length, physical state, and number of active functional groups determine its ability to plasticize a polymer network (12, 15, 18, 19). The plasticizers studied in this work have similar chemical structures (**Table 2**). Both are straight-chain polyols with the ability to reduce polymer internal hydrogen bonding while increasing intermolecular spacing (18). Therefore, the chemical structure of both plasticizers should not be a reason for the different plasticizer behavior. Differences between both plasticizers are molecular weight (M_w), hygroscopic character, and physical state. Low plasticizer M_w has been related to good plasticizer diffusion into the polymer matrix (13). Thus, the lower M_w of G compared to M might explain its greater plasticizer ability. G also presents a high hygroscopic character, which tends to drive additional water into the matrix, increasing the plasticizer effect (20). In addition, several studies have shown greater efficiency of plasticizers at liquid state compared to plasticizers at solid state (21), which might be related to the lubricant effect of liquid plasticizers. Therefore, the liquid state of G at test conditions might improve its plasticizer ability compared to M, which is solid at test conditions.

The effect of both G and M on mechanical properties has been studied on highly carboxymethylated starch-based films (22). In this work, G-plasticized films showed higher %*E* than M-plasticized films. Other works show the greater plasticizer ability of G compared to sorbitol (S) in different polymer matrices such as whey protein (11) and β -lactoglobulin (12, 23). M is a stereoisomer of S with fairly similar physicochemical

Table 2. Physicochemical Properties of Selected Plasticizers

Plasticizer	Molecular weight	Melting temperature (°C)	Chemical formula	Chemical structure
Glycerol (G)	92	18	C ₃ H ₈ O ₃	
Mannitol (M)	182	167	C ₆ H ₁₄ O ₆	

properties, but lower solubility than S; therefore, their plasticization behaviors might be similar.

Plasticizer content had also an effect on film mechanical properties. Increasing either G or M content decreased film EM and TS. Higher G content increased film %E, whereas higher M content decreased film %E. Therefore, an increase in G content resulted in an improvement on film flexibility, whereas an increase in M content induced film brittleness. The increase in film flexibility as G content increased was previously observed in various protein films (11, 22, 24).

The increase in film brittleness as M content increased suggests an antiplasticizing effect of M (13). Antiplasticization of films has been attributed to several mechanisms, such as a reduction of polymer free volume, interaction between the polymer and plasticizer, and film stiffness due to the presence of rigid plasticizer molecules adjacent to the polar groups of the polymer (25). In our work, crystallization of M in the films was observed at both ratios of M/HPMC, which might confirm the antiplasticizer effect of M in the HPMC matrix.

Kim et al. (22) observed that M content did not affect the mechanical properties of starch-based films. It is possible that the range of M content studied in that work (from 0.1 to 0.3 g of mannitol per gram of hydrocolloid) was not large enough to see differences in mechanical properties compared to the range of M content studied in our work (0.3 and 0.91 g of mannitol per g of hydrocolloid). In addition, the different structure of the polymer matrix (HPMC vs starch) and the effect of the remaining ingredients in both film formulations could affect the behavior of M on film mechanical properties.

Generally, an increase in BW content from 20 to 40% (db) resulted in a decrease of all mechanical properties, which indicates an increase in film ductility and a decrease in film extensibility, toughness, and resistance to break. These results might be explained by three factors: (1) the BW effect disrupting the HPMC continuous matrix that becomes more evident as BW increased; (2) the loss of water affinity by BW incorporation, which reduces the water plasticizer effect on film mechanical properties; and (3) the reduction of the HPMC content (Table 2), which acts as film structural matrix (6). According to the literature, lipid addition to hydrocolloid-based films induces the development of a heterogeneous film structure, featuring discontinuities in the polymer network. These discontinuities, and also the lack of cohesive structural integrity of lipids, may enhance film brittleness, decreasing TS, %E, and T (26, 27). Additionally, lipids reduce film water affinity, reducing its plasticizer effect.

Film Water Vapor Permeability. Plasticizers are expected to decrease the intermolecular forces along polymer chains, increasing film flexibility while decreasing the film barrier properties (10, 11). Figure 2 shows the WVP of plasticized films. Films formulated with G showed higher WVP than films formulated with M. The greater ability of G to disrupt the polymer internal hydrogen bonds observed from the mechanical property data may explain the greater WVP of these films compared to the M-plasticized films.

Plasticizer content affected WVP of G-plasticized films without affecting WVP of M-plasticized films. An increase in G content increased WVP, which correlates with an improvement in film flexibility. The lack of effect of M content on WVP could be also correlated with film mechanical properties that were not improved at any of the M contents studied.

At similar plasticizer type and content, increasing BW content only reduced the WVP of G-plasticized films. The extent on WVP reduction depended on G content. At lower G content (G/HPMC ratio of 100:1), an increase in BW content from 20 to 40% decreased WVP around 10%, whereas WVP reduction was around 27% at higher G content (G/HPMC ratio of 300:1). In addition, film orientation during WVP measurements did not significantly affect WVP, except for films having 20% BW and higher G content. These results could be due to a lipid saturation above 20% BW content and/or a complete phase separation during drying. As explained, a critical lipid content beyond which moisture barrier was not further reduced (26) was

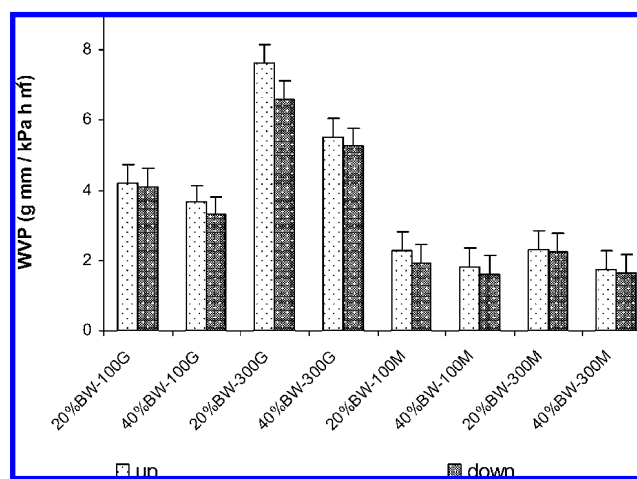


Figure 2. Water vapor permeability (WVP) of HPMC-based edible films. Bars within each film orientation represent LSD values ($p < 0.05$).

Table 3. Weight Loss of Coated and Control 'Angeleno' Plums after Cold Storage^a

treatment	storage conditions							
	weeks at 1 °C + 1 week at 5 °C + 1 week at 20 °C				weeks at 1 °C + 1 week at 5 °C + 2 weeks at 20 °C			
	2	4	6	8	2	4	6	8
20% BW-100 G	1.74de	2.60e	4.59f	5.64f	2.34b	3.21cd	5.73f	7.27d
40% BW-100 G	1.93fg	3.24g	4.11e	4.70de	2.91e	3.12c	5.11e	6.74c
20% BW-300 G	1.49ab	2.13ab	3.16b	4.45cd	2.02a	2.84ab	4.79cd	6.35bc
40% BW-300 G	1.43a	1.97a	3.48c	4.20bc	2.37bc	2.62a	4.09ab	6.54bc
20% BW-100 M	1.78e	2.36cd	3.46c	4.80e	3.04e	3.36de	4.53c	6.17b
40% BW-100 M	1.84ef	2.97f	3.97de	4.24bc	2.90e	3.84f	5.83f	6.30bc
20% BW-300 M	1.57bc	2.17b	3.75d	4.41cd	2.54cd	3.06bc	4.98de	6.26b
40% BW-300 M	1.56bc	2.28bc	2.87a	4.04b	2.96e	3.22c	4.23bc	5.39a
water dipped	1.99g	2.38c	2.65a	3.53a	2.88e	3.59e	3.84a	5.38a
uncoated	1.64 cd	2.48de	3.19b	3.33a	2.68d	3.25c	3.83a	5.19a

^a Means followed by the same letter within each storage time are not significantly different at $p < 0.05$.

attributed to a lipid saturation in the emulsion system and/or to a discontinuous distribution of lipid particles into hydrocolloid matrix (28). At higher G content, the increase in BW content reduced WVP of the films.

Plum Weight Loss. Table 3 shows weight loss of coated, water-dipped, and control plums after cold storage followed by 1 or 2 weeks of storage at 20 °C. No differences in weight loss were found between the uncoated and water-dipped plums, which indicated that the immersion in water was not enough to remove the natural waxes of 'Angeleno' plums. Increasing storage time increased weight loss, and the differences in weight loss between coated and control plums became more evident. These results indicate that coating application did not improve the natural moisture barrier of 'Angeleno' plums and even worsened it.

Plums are naturally covered by a continuous wax layer that provides high resistance to water movement across the cuticle. Coatings containing hydrophobic compounds deposited as an additional layer over the natural waxes should improve the moisture resistance of the fruit. However, the coatings in our study may partially remove the natural waxes resulting in no reduction in weight loss. Some works in the literature also reflect no effect of coating application on weight loss reduction of different fruits. Baldwin et al. (5) observed that the addition of soybean oil or carnauba wax to a hydroxypropyl cellulose coating did not reduce water loss of coated cherries or cucumbers compared to uncoated fruits. Bai et al. (29) reported no effect of carnauba-polysaccharide-based coating on weight loss reduction of 'Red Delicious' apples. Erbil and Mutfungil (30) also found higher weight loss of peaches coated with carboxymethyl cellulose-coconut oil based coatings compared to uncoated peaches stored at room temperature and 57–63% RH.

When coating treatment effect on weight loss was compared, no consistent effect was observed due to BW content and plasticizer type. Increasing plasticizer content decreased plum weight loss in G-plasticized coatings. This result contrasts with the behavior of stand-alone films, where an increase in G content significantly increased WVP of the films. These results show that performance of stand-alone films does not always correlate with coating performance on fruit commodity. Therefore, data from stand-alone films might be used as preliminary screening, but factors affecting coating performance should be analyzed when they are applied on the fruit. Coating performance is affected by coating distribution over the fruit surface, especially whether it forms a continuous layer or penetrates into pores (31). Fruit skin morphology (presence of hairs, thickness and type of cuticle, number of stomata, lenticels, and even cracks

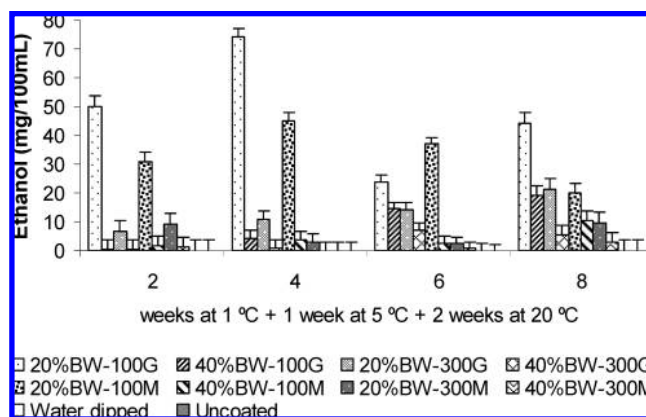


Figure 3. Ethanol content in juice of coated and control 'Angeleno' plums after cold storage plus 2 weeks at 20 °C. Bars within each storage time represent LSD values ($p < 0.05$).

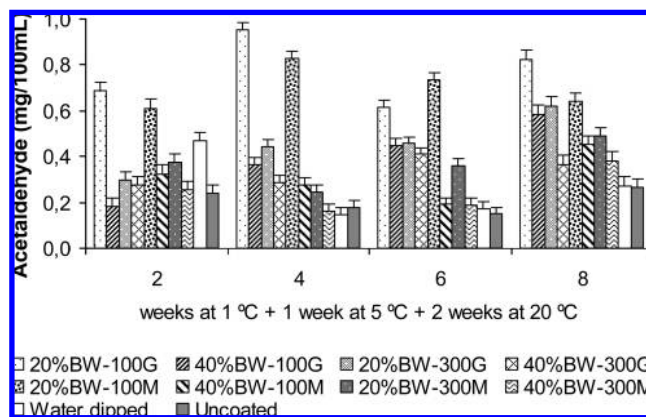


Figure 4. Acetaldehyde content in juice of coated and control 'Angeleno' plums after cold storage plus 2 weeks at 20 °C. Bars within each storage time represent LSD values ($p < 0.05$).

in the lenticels) and coating physical properties such as surface tension and viscosity strongly influence mass transfer of the coated fruit (31).

Ethanol and Acetaldehyde Content. Figures 3 and 4 show the ethanol and acetaldehyde contents of coated, water-dipped, and uncoated 'Angeleno' plums after cold storage followed by 2 weeks at 20 °C. Coated plums showed higher ethanol and acetaldehyde contents than water-dipped and uncoated fruit at the end of storage. This indicated that coatings provided an additional gas barrier to O₂ and CO₂, modifying the internal fruit atmosphere. Therefore, these coatings created a barrier to gas but not to water vapor. Ben-Yehoshua et al. (32) concluded that the resistance of citrus fruits to mass transport of water

vapor and gases occurred by different mechanisms: (a) gases diffuse mainly through the stomatal openings, and (b) water moves preferentially in a liquid aqueous phase in the cuticle. In addition, the resistance of fruit to water is less than to CO₂ and O₂ gases. Waxing partially or completely plugs stomatal pores, reducing gas exchange. However, the presence of cracks or lack of uniformity in the coating layer might not improve the final moisture barrier.

Ethanol and acetaldehyde contents were affected by coating composition. Decreasing BW content, which means an increase in HPMC content (Table 1), increased plum ethanol and acetaldehyde contents, which indicated an increase on coating gas barrier. This result could be related to (1) the low permeability to CO₂ and O₂ of hydrocolloid polymers such as HPMC (7), (2) the greater HPMC cohesion in films at low BW content as was observed in film mechanical properties (Figure 1), which may improve the coating integrity, and (3) the role of BW particles in O₂ diffusion. Han et al. (33) observed that beyond a critical BW content, the oxygen permeability of pea starch-based films increased. They assumed that O₂ molecules may penetrate through hydrophobic BW channels. Therefore, increasing BW content increased the pathway for O₂ transmission, which translated in higher film oxygen permeability. The increase in ethanol and acetaldehyde contents in HPMC-composite coatings as BW content decreased was previously observed in 'Autumn Giant' plums (1), 'Clemenules' tangerines (34), and 'Fortune' tangerines (35).

Plums coated with G-plasticized coatings showed higher ethanol and acetaldehyde contents than plums coated with M-plasticized coatings. The results could be related to the higher flexibility of G-plasticized films. Previous works have shown that G addition improved coating integrity, avoiding the formation of cracks and holes (36, 37). In our study, G addition increased flexibility of the HPMC-based film, which may improve coating integrity and adaptation to fruit surface, producing a higher gas barrier.

Plasticizer content affected ethanol and acetaldehyde contents for coatings containing 20% BW (i.e., coatings with greater content of HPMC), without affecting ethanol and acetaldehyde contents of coatings containing 40% BW. At 20% BW content, an increase in plasticizer content decreased ethanol and acetaldehyde contents of coated plums. In stand-alone edible films, oxygen permeability increases as plasticizer content increases (23). This increase in film permeability should translate in lower levels of ethanol and acetaldehyde when the coating formulations are applied to a fruit. The effect of plasticizer content on volatile components only for coatings containing 20% BW could indicate that there is an amount of HPMC beyond which the plasticizer-HPMC interaction is the main factor affecting coating gas permeability. Under this critical HPMC content, the effect of plasticizer content on coating gas permeability may be overwhelmed by BW content.

An increase in ethanol and acetaldehyde levels can develop off-flavor and poor quality of coated fruit if the gas barrier is high enough to induce anaerobic respiration. In our work, even though ethanol and acetaldehyde contents were affected by coating composition, these differences were not detected by a trained sensory panel, which did not find significant differences on plum flavor among treatments (data not shown). In all storage periods, all samples were evaluated above the limit of acceptability, indicating that ethanol and acetaldehyde levels were below the threshold to detect off-flavor.

Plum Firmness. Figure 5 shows flesh firmness of coated and uncoated 'Angeleno' plums. Coatings reduced texture loss

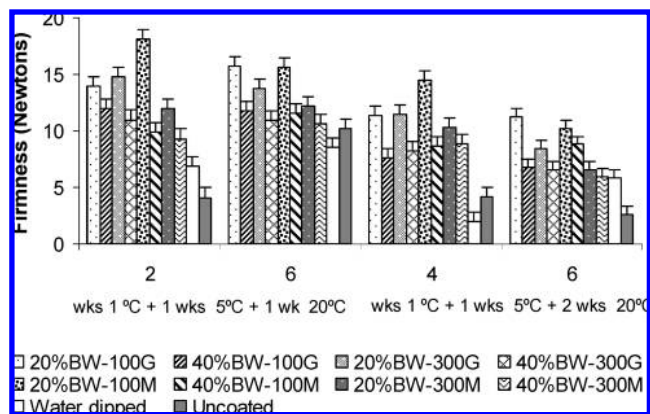


Figure 5. Firmness of coated and control 'Angeleno' plums. Bars within each storage time represent LSD values ($p < 0.05$).

Table 4. Pearson's Correlation among Acetaldehyde, Ethanol, Firmness, and Bleeding of Coated and Uncoated Plums

	acetaldehyde	ethanol	firmness	bleeding
acetaldehyde	1			
ethanol	0.894** ^a	1		
firmness	0.243**	0.245**	1	
bleeding	-0.517**	-0.505**	-0.471**	1

^a Correlation is significant at the 0.01 level (two-tailed).

up to 75% with respect to the control, depending on coating composition. Improvement on flesh firmness of coated fruit could be related with the ability of coatings modifying the internal atmosphere, which reduced the overall plum metabolism and, particularly, the cell wall degradation associated with fruit softening (38). The reduction in plum flesh softening under low O₂ atmosphere storage (38) and edible coating application (1, 2) has been previously reported.

Coatings with low BW content (i.e., high HPMC content) were more effective in reducing plum texture loss than coatings with high BW (i.e., low HPMC content). This result could be related with an improvement on coating gas barrier properties at low BW content, which produced a greater modification of the fruit internal atmosphere as reported by the higher ethanol and acetaldehyde contents (Figures 3 and 4). Similar results were observed in coated mangos with coatings that presented different gas permeabilities (39), and plums with coatings at different HPMC/lipid ratios (1, 2).

Plasticizer type did not affect plum firmness, but plasticizer content showed an effect on plum firmness. Generally, coatings with low plasticizer content were more effective maintaining plum firmness. The improvement on plum firmness by reducing the coating plasticizer content may be related with the improvement on HPMC polymer cohesion and gas barrier properties, as previously observed in ethanol and acetaldehyde results (Figures 3 and 4).

The correlation between volatile content and firmness was confirmed by Pearson's correlation test (Table 4). The test showed that an increase in both volatile content correlated with an increase in plum firmness ($p \leq 0.01$). The correlation coefficients for acetaldehyde and ethanol with plum firmness were 0.243 and 0.245, respectively, showing a weak linear relationship between these quality parameters.

Plum Internal Breakdown. The use of low temperature during storage extends plums market life (17). However, plums from some cultivars develop lack of juiciness with mealy or leathery texture, flesh browning, black cavity, flesh translucency, and red pigment accumulation (bleeding) after prolonged cold

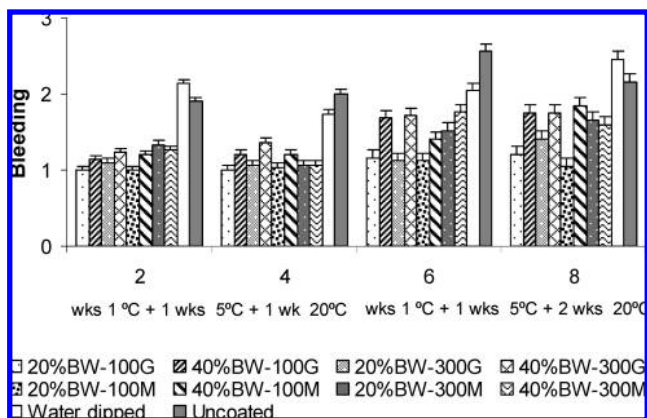


Figure 6. Bleeding of coated and control 'Angeleno' plums after cold storage plus 2 weeks at 20 °C. Bars within each storage time represent LSD values ($p < 0.05$).

storage and/or after ripening at room temperature. These disorders are known as forms of internal breakdown (IB). 'Angeleno' plum cultivars develop IB at storage temperatures of around 5 °C, whereas the optimum storage temperature is around 0 °C (17).

In our experiment, a short storage period at 5 °C was simulated after cold storage at 1 °C, because this temperature is very often reached during transportation. The main IB symptom observed in this experiment after storage was bleeding. Flesh bleeding is the result of anthocyanin diffusion from the cells surrounding the stone and the skin, where the pigments are initially located, to the overall plum flesh. This disorder may be a consequence of tissue senescence (40) or abnormal ripening (41) and can be prevented by controlled-atmosphere storage (42). Moreover, the cell wall degradation that produces plum flesh softening may enhance the diffusion of anthocyanins and bleeding incidence. **Figure 6** shows bleeding of coated and uncoated 'Angeleno' plums after cold storage and storage at 20 °C. Coatings were effective in reducing plum bleeding compared to control plums. This might be due to the internal atmosphere modification produced by coatings, which also translated on reduced plum softening.

BW content had an effect on plum flesh bleeding, whereas no consistent effect of coating plasticizer type and content was observed. Decreasing BW content decreased plum bleeding, which also correlated with higher ethanol and acetaldehyde in the plums (**Figures 3 and 4**) and higher plum firmness (**Figure 5**). These results were confirmed by Pearson's correlation test that showed a negative correlation between bleeding and volatile content, and bleeding and firmness at $p \leq 0.01$ (**Table 4**). When all of the correlations were compared, bleeding showed a higher correlation than firmness with acetaldehyde and ethanol content with $r = -0.517$ and $r = -0.505$, respectively.

The results show that coatings did not reduce plum weight loss, but modified the internal atmosphere of the fruit, reducing plum flesh softening and bleeding. BW content of coating formulations did not affect plum weight loss, but was the main factor affecting ethanol and acetaldehyde content, flesh firmness, and bleeding. Decreasing BW content (i.e., increasing HPMC content) retained plum firmness and reduced bleeding, which could be related to a greater atmosphere modification in the fruit. Above 20% BW, changes in plasticizer content did not affect volatile content. At this BW content, plums coated with G-plasticized films showed the highest levels of ethanol and acetaldehyde. This result could be related with a greater flexibility of this film that could improve coating integrity in

the fruit. WVP of stand-alone HPMC-based films did not correlate with plum weight loss. When plasticizer content was compared, plum weight loss decreased with increased plasticizer content, whereas WVP of films increased as G content increased or remained unaltered as M content increased. Differences between coating and film performance indicate that data from stand-alone films may be used as a preliminary screening, but coating performance should be analyzed on coated fruit. In general, formulations with 20% BW and G provided the best compromise in terms of maintaining fruit quality, because these coatings presented a better integrity, retained plum firmness, and reduced bleeding without affecting fruit flavor.

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