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Fatty Acid Effect on Hydroxypropyl Methylcellulose−Beeswax Edible Film Properties and Postharvest Quality of Coated 'Ortanique' Mandarins

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The objective of this work was to investigate the effect of fatty acid (FA) type and content on mechanical properties, water vapor permeability and oxygen permeability of hydroxypropyl methycellulose (HPMC)−beeswax (BW) stand-alone edible films. The effect of these films formed as coatings on the postharvest quality of 'Ortanique' mandarins was also studied. Selected FAs were stearic acid (SA), palmitic acid (PA), and oleic acid (OA), using BW/FA ratios of 1:0.5 and 1:0.2 (w/w). HPMC-BW coatings reduced weight and firmness loss of 'Ortanique' mandarins, without compromising flavor quality compared to uncoated mandarins. Coatings containing OA provided the best weight loss control at both concentrations tested; however, when the BW/OA ratio was 1:0.5, the coatings increased fruit internal CO_2, ethanol, and acetaldehyde contents of 'Ortanique' mandarins, therefore reducing flavor compared to the rest of the coatings studied. Although barrier and mechanical properties might be used to understand coating performance, differences observed between film oxygen permeability and coating permeability indicate that permeance should be measured on the coated fruit.

KEYWORDS: Edible films and coatings; hydroxypropyl methylcellulose; beeswax; fatty acids; postharvest quality; mandarins

INTRODUCTION

Edible films and coatings represent an environmentally friendly postharvest technique for fresh fruit preservation, because they are biodegradable and can be consumed with the coated fruit if desired, therefore avoiding waste disposal. Moreover, they are made of materials produced from renewable resources, in contrast to petroleum-based films and coatings, which are manufactured from a limited supply of fossil fuels (*1*).

Materials used in edible film and coating formulations include proteins, polysaccharides, and lipids (*2*), the combination of which affects physical properties and film performance. Edible films based on cellulose derivatives are very efficient barriers to oxygen and aroma compounds (*3, 4*), but are not a good barrier to water vapor due to their hydrophilic character. Thus, they are often combined with edible lipids to form composite coatings. Among edible hydrophobic components, waxes are more resistant to water vapor flux than most other lipid components (*5*).

Coating of citrus is a normal practice in the packinghouse industry, aimed at replacing natural waxes that are removed during washing. Coatings for citrus products must, therefore, provide a barrier to water loss and an adequate gas (CO_2 and O_2) exchange (*1*).

Hydroxypropyl methylcellulose (HPMC)−beeswax (BW) edible composite coatings have been shown to reduce weight loss and retain firmness of citrus fruits (*6, 7*). Formulations that provided the best weight loss control and gas exchange to CO_2 and O_2, and the lowest off-flavor, formed brittle coatings with low gloss, undesirable for citrus. To obtain high gloss, lipid particle size needs to be very small (*8*). For many fruit coatings containing waxes, fatty acids (FAs) such as stearic, palmitic, or oleic are often used as emulsifiers (*9*). Coating brittleness of cellulose-based films can be overcome with the addition of

Table 1. Emulsion Film and Coating Compositions (Percent Dry Basis)[a]

formulation	HPMC	BW	glycerol	FA
BW/FA (1:0.5)	26.7	40	13.3	20.0
BW/FA (1:0.2)	34.7	40	17.3	8.0

[a] HPMC, hydroxypropyl methylcellulose; BW, beeswax; FA, fatty acid. FA were stearic acid (SA), palmitic acid (PA), and oleic acid (OA). Solid contents were 10 and 4% for stand-alone films and coating formulations applied to mandarins, respectively.

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plasticizers, such as glycerol, to the coating formulation (*10*). Lipid plasticizers such as long-chain and saturated FAs also have been used in different cellulose-based films to improve moisture retention, besides reducing brittleness (*11*−*14*).

Considering that FAs can act as emulsifiers and plasticizers and also improve the moisture barrier of HPMC-BW films and coatings, our objectives were to study the effect of FA type and content on mechanical and barrier properties of HPMC-BW stand-alone edible films and evaluate their effect when formed as coatings on postharvest quality of 'Ortanique' mandarins.

MATERIALS AND METHODS

Materials. HPMC (Methocel E15) was supplied by Dow Chemical Co. (Midland, MI). Refined BW (grade 1) was purchased from Brillocera, S.A. (Valencia, Spain). Glycerol, stearic acid (SA), palmitic acid (PA), and oleic acid (OA) were from Panreac Química, S.A. (Barcelona, Spain).

Emulsion Film and Coating Formulation. HPMC (5%) was prepared by initial dispersion of the cellulose in hot water at 90 ± 2 °C and later hydration at 20 °C. Next, BW was added at 40% (dry basis). Glycerol was added as plasticizer at a HPMC/glycerol ratio of 2 parts HPMC to 1 part glycerol (w/w), which was kept constant for all formulations. SA, PA, or OA was added as emulsifier at two BW/FA ratios (1:0.5 and 1:0.2, w/w). Water was added to bring the mixtures to a final solid content of 10% for stand-alone films and 4% for coating formulations. Mixtures with all of the ingredients were heated at 90 ± 2 °C to melt the BW. They were then homogenized to form an emulsion with a high-shear probe mixer UltraTurrax (model T25 basic; IKA-Werke GmbH & Co. KG, Staufen, Germany) for 1 min at 13000 rpm followed by 3 min at 22000 rpm. After the emulsions had been cooled in an ice bath to <20 ± 2 °C, they were continuously agitated for approximately 45 min to ensure complete hydration of the HPMC. The compositions of emulsion films and coatings are shown in **Table 1**.

Film Preparation. The film-forming emulsions were degassed, and 3 g of total solids was applied to a smooth high-density polyethylene casting plate to minimize thickness variations among formulations. The plates were placed on a leveled surface and dried at room conditions until films could be removed from the casting surface. Three replications were prepared for each formulation.

Film Mechanical Properties. Film mechanical properties were measured according to American Society of Testing and Materials Standard method DS882-97 (*15*). Films were conditioned for 24 h at 23 ± 2 °C and 50 ± 1% relative humidity (RH), cut into 50 mm × 8 mm rectangular strips, and tested for tensile properties 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 ± 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.

Film Water Vapor Permeability. A modification of the ASTM E96-80 (*16*) gravimetric method for measuring water vapor permeability (WVP) was used (*17*). 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 ± 1% RH using anhydrous potassium carbonate. Weights were taken periodically until steady state was achieved, and the average film thickness measured at six random positions was used to calculate the resulting WVP.

Film Oxygen Permeability. Oxygen permeability (OP) of stand-alone films was measured at 23 °C and 50 ± 1% RH using an Ox-Tran 2/20 ML modular system (Modern Control, Inc., Minneapolis, MN) according to ASTM D3985-95 standard method (*18*). Films were placed on a stainless steel mask with an open testing area of 5 cm^2. Masked films were placed into a test cell and exposed to 98% N_2 + 2% H_2 flow on one side and pure O_2 flow on the other side. OP was calculated by dividing the oxygen transmission rate by the difference in oxygen partial pressure between both sides of the film (1 atm) and multiplying by the average film thickness, measured at four random positions. Three replicates of each film were evaluated.

Film Thickness Measurements. Film thickness was measured using a digital micrometer (Quickmike Series 293-IP-54, Mitutoyo Manufacturing Co., Ltd., Japan), taking measurements at random positions on the film.

Fruit Sample Preparation and Coating Application. 'Ortanique' mandarins from a local grove in Valencia (Spain) were selected for size, color, and absence of physical damage and then dipped for 1 min in 1000 ppm of imazalil solution, followed by air-drying. Mandarins were randomly divided into seven groups, which corresponded to six HPMC-BW coating treatments with various FA types and amount and one uncoated control. After washing, fruits were dip-coated by immersion in the coating emulsions for 1 min and drained of excess coating. Coated and uncoated mandarins were dried in a tunnel at 45−50 °C for 2.5 min.

After drying, mandarins were stored for 3 and 6 weeks at 5 °C and 80 ± 5% RH (simulating storage conditions at packinghouses), followed by 1 additional week at 20 °C and 85 ± 5% RH (simulating retail handling conditions). Another set of samples was stored for 1 and 2 weeks at 20 °C and 85 ± 5% RH, simulating retail handling conditions.

Fruit Weight Loss. Lots consisting of 30 fruits per treatment were used to measure weight loss. The same fruit was 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.

Fruit Texture. The firmness of 20 mandarins per treatment was determined at the end of each storage time using an Instron Universal Testing Machine (model 3343, Instron Corp.). The instrument gave the deformation (length) after application of a compressed load of 1 kg to the equatorial region of the fruit, at a rate of 5 mm·min^{-1}. Results were expressed as the percentage deformation related to the initial diameter.

Internal CO_2 and O_2 in the Fruit. Internal CO_2 and O_2 concentrations were measured with a gas chromatograph (Thermo Fisher Scientific, Inc., Waltham, MA) equipped with a thermal conductivity detector and fitted with a Poropak QS 80/100 column (1.2 m × 0.32 cm). Temperatures were 35, 125, and 180 °C, respectively, for the oven, injector, and detector. Helium was used as the carrier gas at a flow rate of 22 mL·min^{-1}. One milliliter of internal gas sample was withdrawn with a syringe while the fruit was submerged under water. O_2 and CO_2 concentrations were calculated using peak areas of the sample relative to the peak areas of standard gas mixtures. Ten fruits per treatment were analyzed.

Ethanol and Acetaldehyde Contents. Ethanol and acetaldehyde contents in juice were determined by headspace gas chromatography according to the method described by Ke and Kader (*19*). Ten fruits each in three replicates per treatment were analyzed. Five milliliter samples of juice were transferred to 10 mL vials with crimp-top caps and TFE/silicone septum seals and frozen until analysis. Ethanol and acetaldehyde were analyzed in a gas chromatograph (Thermo Fisher Scientific, Inc.) equipped with an autosampler and a flame ionization detector and fitted with a Poropak QS 80/100 column (1.2 m × 0.32 cm). Temperatures of the oven, injector, and detector were 150, 175, and 200 °C, respectively. Helium was used as the carrier gas at a flow rate of 28 mL·min^{-1}. A 1 mL sample of the headspace was withdrawn from each vial previously equilibrated in the autosampler incubation chamber for 10 min at 40 °C. Ethanol and acetaldehyde concentrations

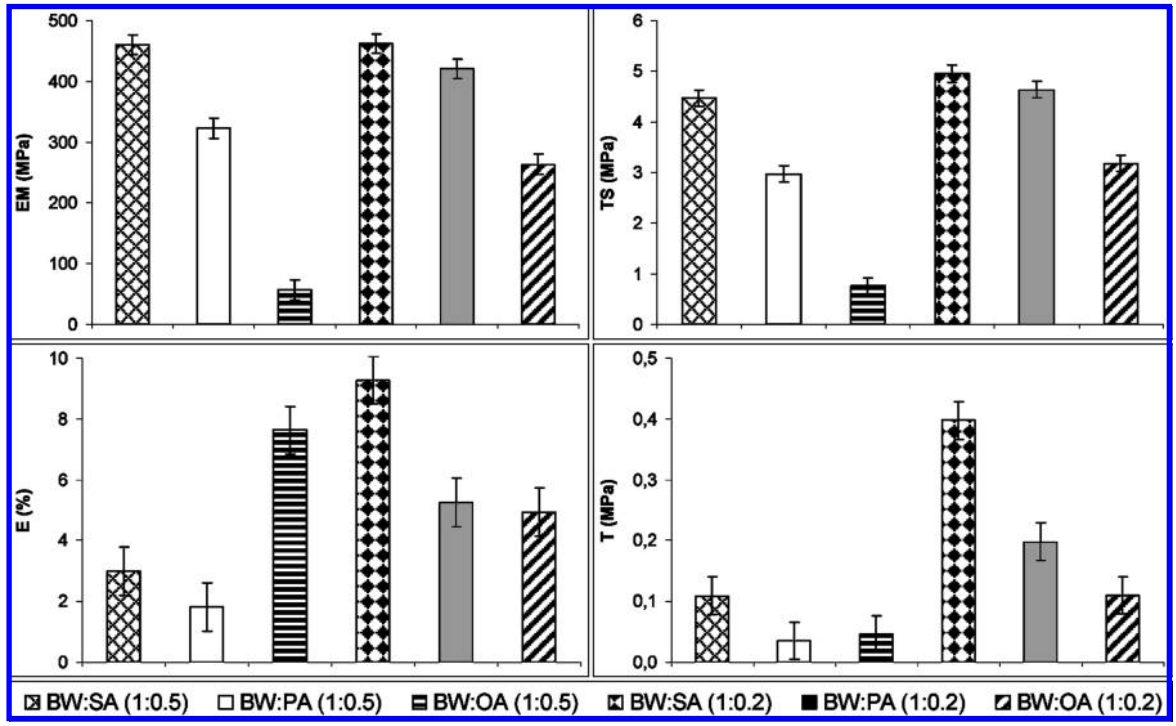

Figure 1. Mechanical properties of HPMC-BW edible films: effect of fatty acid type and amount. Bars indicate LSD values ($p < 0.05$). EM, elastic modulus; TS, maximum tensile stress; *E*, elongation at break; *T*, toughness; BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

were calculated using peak areas of the samples relative to the peak areas of standard solutions. Results were expressed as milligrams per 100 mL of juice.

Sensory Evaluation. Sensory evaluation was conducted by 10 trained judges. Panelists rated flavor on a 9-point scale, where 1−3 represented a range of nonacceptable quality with the presence of off-flavor, 4−5 represented a range of acceptable quality, and 7−9 represented a range of excellent quality. One sample consisted of whole segments taken from about six individual fruits. Samples were presented to the panelists in trays labeled with three-digit random codes and served at room temperature (25 ± 1). The judges had to taste several segments of each treatment to compensate, as far as possible, for biological variation of material. Mineral spring water was provided for rinsing between samples. The effect of the treatments on external quality (appearance) was also evaluated. One set of five fruits per treatment was presented to the panelists for appearance evaluation. Panelists rated the overall appearance of the fruit as 1 = bad, 2 = acceptable, and 3 = good.

Statistical Analysis. Statistical analysis was performed using Statgraphics Plus 4.1 (Manugistics, Inc., Rockville, MD). Significance between means was determined by least significant difference (LSD) at $p \leq 0.05$.

RESULTS AND DISCUSSION

Film Mechanical Properties. Mechanical properties are important for edible films and coatings, as they reflect the durability of films (*10*) and the ability of coatings to form and maintain a continuous layer over the coated product. Moreover, loss in film and coating mechanical integrity due to poor mechanical properties reduces their effectiveness as a barrier (*20*).

Figure 1 shows the effect of FA type and amount on mechanical properties of HPMC-BW edible films. With the same BW/FA ratio, films containing SA had the highest EM, TS, and *T* and were stronger and stiffer than films containing OA, which had the lowest values. Increasing SA content decreased *%E*, without modifying EM and TS, making the films more brittle. Increasing PA content decreased all mechanical parameters, forming weaker, more flexible, and less extendible films, whereas increasing OA content decreased EM and TS, but increased *%E*, forming weaker, more flexible and extendible films. Film *T* decreased as FA content increased, and this effect was more pronounced for films with SA. These results suggest that OA had a plasticizing effect on films, compared to SA or PA.

Table 2. Physicochemical Properties of Stearic Acid (SA), Palmitic Acid (PA), and Oleic Acid (OA)

FA	Molecular weight	Melting temperature (°C)	Chemical formula	Chemical structure
SA	284	69,6	$C_{18}H_{36}O_2$	
PA	256	82,9	$C_{16}H_{32}O_2$	
OA	282	15,3	$C_{18}H_{34}O_2$	

Lipids such as FAs have been used as plasticizers for different protein- and polysaccharide-based films (*12, 21*). Jongjareonrak et al. (*22*) observed that an increase in FA chain length increased TS of fish gelatin-based films. Similar results were observed by Rhim et al. (*23*) for soy protein-based films. Therefore, the greater chain length of SA compared to PA (**Table 2**) might explain why these films had the greatest EM and TS values.

One of the theories of plasticization suggests that plasticizers act like a lubricant to facilitate the movement of polymer chains over each other, thereby lowering resistance to deformation (*24*). Quezada-Gallo et al. (*25*) observed that oils induced such a lubrication effect in emulsified polysaccharide-based films, increasing *%E*. Therefore, the difference in melting temperature among fatty acids (**Table 2**) might explain why films containing OA, which is liquid at test conditions, showed greater flexibility than films containing either SA or PA, which are solids at test temperature. OA has been reported to increase elongation of soy protein, corn zein, and egg white films (*26*).

Our results suggest that coatings containing OA would possess a greater ability to form a continuous and flexible layer

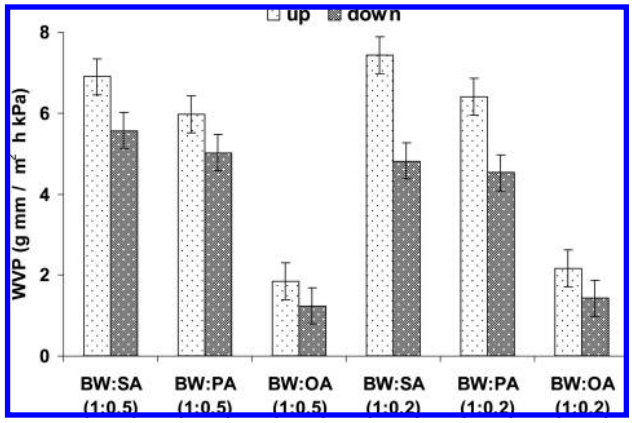

Figure 2. Water vapor permeability (WVP) of HPMC-BW edible films: effect of fatty acid type and amount. Bars indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid; up, film side exposed to air during drying faced to the lower RH during analysis; down, film side exposed to air during drying faced to the higher RH during analysis.

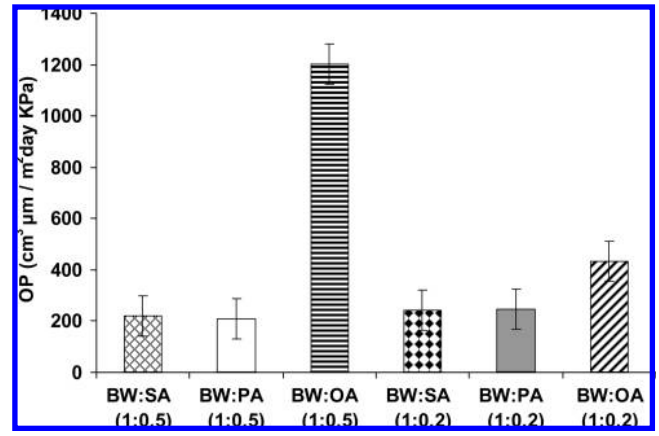

Figure 3. Oxygen permeability (OP) of HPMC-BW edible films: effect of fatty acid type and amount. Bars indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

over fruit surfaces than the remaining coatings, due to the OA plasticizing effect. However, coatings containing SA would offer a greater overall resistance to fruit handling, indicated by the greater T of the stand-alone films.

Film Water Vapor Permeability. The possibility of nonhomogeneous lipid distribution within the film was assessed by measuring WVP as a function of film orientation on the WVP test cup. Films with homogeneous lipid distribution throughout the film or with complete separation of lipid to form a bilayer would show no orientation effect. However, films with nonhomogeneous distribution of lipid throughout the film would show an orientation effect.

Films containing OA had the lowest WVP (**Figure 2**), with no orientation effect. An orientation effect on WVP for films containing SA or PA indicated nonhomogeneous distribution of lipids throughout these films. FA concentration did not affect WVP of HPMC-BW films.

Previous studies have shown that WVP of FA films decreases as the degree of saturation and chain length of the FAs increases (*14, 22, 27*−*29*). In our work, formulations contained BW as the main hydrophobic component, and FAs at low concentrations were added as emulsifiers. Therefore, the effect of adding different FAs could be related to their ability to form stable emulsions, which would affect the final lipid distribution in the film. Barrier efficiency of edible composite films depends on the polarity of the components and the uniformity of distribution of hydrophobic substances (*14, 30*). When the hydrophobic component was laminating the hydrophilic film, forming a bilayer, the barrier against water vapor transfer was higher than when an emulsion was formed (*14*). Kamper and Fennema (*14*) obtained a complete phase separation of HPMC-FA emulsions, leading to an apparent bilayer structure in the final film, which significantly reduced film WVP. In our work, lack of orientation effect for films containing OA indicated the formation of a bilayer with a lipid-enriched layer that was more homogeneous and continuous than films containing SA or PA.

In emulsion films, lipid particle size and distribution within the polymer matrix have been shown to affect the film moisture barrier, which was reflected by film orientation during WVP measurements (*31, 32*). When phase separation of hydrocolloid−lipid emulsion films occurs without forming a complete bilayer, the film WVP is lower when the lipid-enriched phase is exposed to the high relative humidity side during WVP measurements. In our work, only films containing SA or PA showed different WVP values depending on film orientation. Moreover, differences between "up" and "down" positions were more pronounced for lower FA content than for higher content, which could indicate improved emulsion stability as FA content increased (**Figure 2**). Perez-Gago and Krochta (*32*) showed that as lipid particle size increased, WVP of whey protein isolate−BW films increased, and differences in WVP due to film orientation were more pronounced. Films containing OA, however, showed no differences in WVP due to film orientation or FA content. This could be due to the complete lipid phase separation from the composite film, forming a continuous lipid layer (i.e., a bilayer film) that offered resistance to moisture transfer independently of the film orientation during WVP measurements.

Increasing FA content did not affect film WVP, even though the hydrophobic content was increased. It may be that BW acted as the main moisture barrier, and small changes in fatty acid content were not enough to modify film WVP. In addition, other works have shown that WVP did not decrease linearly as lipid content increased, and there was a threshold beyond which WVP did not further decrease (*31, 33*). Our formulations contained 40% BW (dry basis), which corresponds with the threshold found for whey protein isolate−BW composite films above which film WVP did not further decrease (*31*).

Film Oxygen Permeability. Films containing OA showed the greatest OP, and no differences in OP were found between films containing SA or PA (**Figure 3**). Moreover, increasing OA content increased film OP, whereas an increase in either SA or PA did not affect OP.

In general, polysaccharides and proteins show lower OP than lipid materials (*34*). WVP and film appearance suggested that the addition of OA formed a bilayer film. Because of the relatively large OP of lipids, complete separation of lipid into a bilayer would be no advantage. However, SA or PA addition formed films in which the lipid was dispersed within the HPMC matrix with some phase separation. Therefore, the higher barrier to oxygen of films containing SA or PA could be due to the higher barrier to oxygen transfer through the hydrophilic HPMC matrix when the lipid particles are dispersed. In such dispersed-phase emulsion films, the immobilization of the polymer chain at the lipid interface, with resulting formation of a more ordered and tightly cross-linked structure, might result in a greater oxygen barrier of the final film compared to a bilayer film.

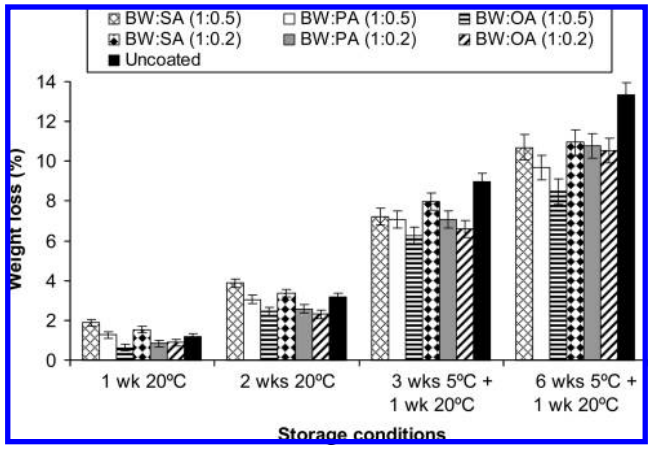

Figure 4. Weight loss of HPMC-BW coated and uncoated 'Ortanique' mandarins: effect of fatty acid type and amount. Bars within each storage time indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

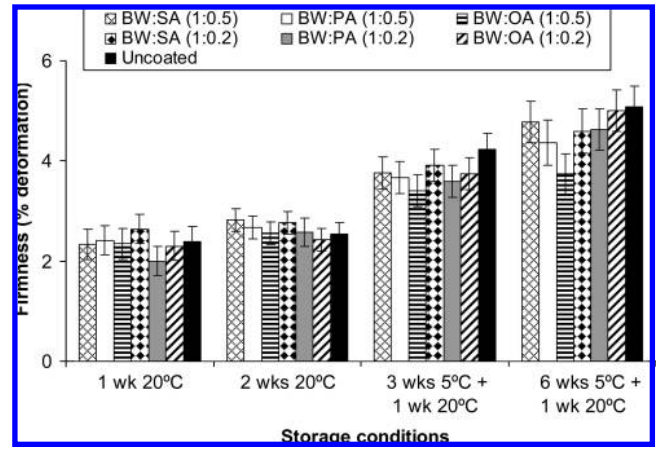

Figure 5. Firmness of HPMC-BW coated and uncoated 'Ortanique' mandarins (% deformation after compression): effect of fatty acid type and amount. Bars within each storage time indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

Optimization of polymer structure by increasing crystallinity, orientation, or cross-linking during film formation may result in further reductions in the oxygen permeability of the film (*34*).

Mandarin Weight Loss. Weight loss increased with storage time, increasing to nearly 13% after 6 weeks at 5 °C plus 1 week at 20 °C on uncoated samples (**Figure 4**). Compared to the control, HPMC-BW coatings reduced weight loss on fruit stored at 5 °C by up to 30% with some treatments after 7 weeks of storage. Effectiveness of the coatings at 20 °C in reducing weight loss of mandarins compared to uncoated samples was lower than when fruits were stored at 5 °C, indicating that storage temperature has an important effect on coating performance. Similar HPMC-BW coatings reduced weight loss of 'Fortune' mandarins about the same amount after 4 weeks of cold storage plus 1 week at 20 °C (*6*).

The most effective coatings for reducing mandarin weight loss were those formulated with OA, followed by those formulated with PA and SA. These results correlate with the lower film WVP of stand-alone films with OA. In addition, stand-alone films containing OA showed greater flexibility, which could suggest a better ability of the coating to adapt to surface changes as the fruit lost weight and volume. Formulations containing SA formed strong and stiff stand-alone films, and fruit coated with formulations containing SA showed higher weight loss than control samples when stored at 20 °C.

FA content effect on mandarin weight loss depended on storage conditions and FA type. In mandarins stored at 20 °C, a reduction in SA or PA contents in coating formulations resulted in slightly less mandarin weight loss reduction. When mandarins were stored at 5 °C followed by 1 week at 20 °C, changes in SA and PA contents did not affect fruit weight loss. OA content did not affect mandarin weight loss at any storage period, except after 6 weeks of storage at 5 °C, when fruit weight loss increased as OA content decreased. This could be due to handling of the fruit, which might have altered coating permeability. The results could be correlated with WVP of stand-alone films, for which no effect of FA content on WVP was found.

Mandarin Texture. During storage at 20 °C, no differences were found between the textures of coated and uncoated mandarins (**Figure 5**). Under prolonged storage at 5 °C, coatings containing OA at a BW/OA ratio of 1:0.5 were the most effective at reducing texture loss compared to the control. All other coatings had no effect on reducing texture loss, even though all reduced weight loss. The effect of OA coatings maintaining mandarin firmness could be related to its best weight loss control (**Figure 4**). Some investigators have observed a correlation between citrus fruit weight loss and firmness (*35, 36*), whereas others have found no correlation (*6, 37*). Contrasting results might indicate that in order to see an effect on fruit texture due to coating application, the coatings should provide sufficient weight loss. Moreover, fruit cultivar could be a factor for the observed differences.

Internal Gas Composition in the Fruit. Coating application to 'Ortanique' mandarins increased internal CO_2 and decreased O_2 contents compared to uncoated fruit, which indicates the creation of an internal modified atmosphere (**Figure 6**). Levels of internal gas composition as affected by FA type fluctuated with storage time, possibly due to handling of the fruit altering coating permeability. Nevertheless, some conclusions can be drawn from the results.

In general, coated fruit reached an internal gas composition around 6% O_2 and 12% CO_2 at the end of the storage, whereas control fruit had an internal gas composition around 15% O_2 and 6% CO_2. With a BW/FA ratio of 1:0.5, coatings with OA modified the mandarin internal atmosphere more than those containing PA and SA. In contrast, when the BW/FA ratio was 1:0.2, FA type affected mandarin internal atmosphere only when fruits were stored at 20 °C, showing a similar behavior. A decrease in SA or PA content in the coating formulation increased mandarin internal CO_2 content and decreased O_2 content.

Coating performance in fruit internal atmosphere contrasted with OP of stand-alone films, where films containing OA showed the highest OP. In addition, OP of stand-alone films was not affected by SA or PA content (**Figure 3**). Differences could be due to factors that affect coating performance on the fruit surface. In contrast with stand-alone films, the coating barrier is affected by coating distribution over the surface of the fruit (*38*). Fruit peel morphology (i.e., thickness and type of cuticle, number of stomates, lenticels, and presence of cracks in the lenticels) (*39*) and coating formulation physical properties such as surface tension and viscosity, which affect the coating's ability to block pores (*38*), strongly influence mass transfer of the coated fruit. Chen and Nussinovich (*40*) also observed discordance between stand-alone film gas permeability and the concentration of gases in coated citrus fruit. They indicated that

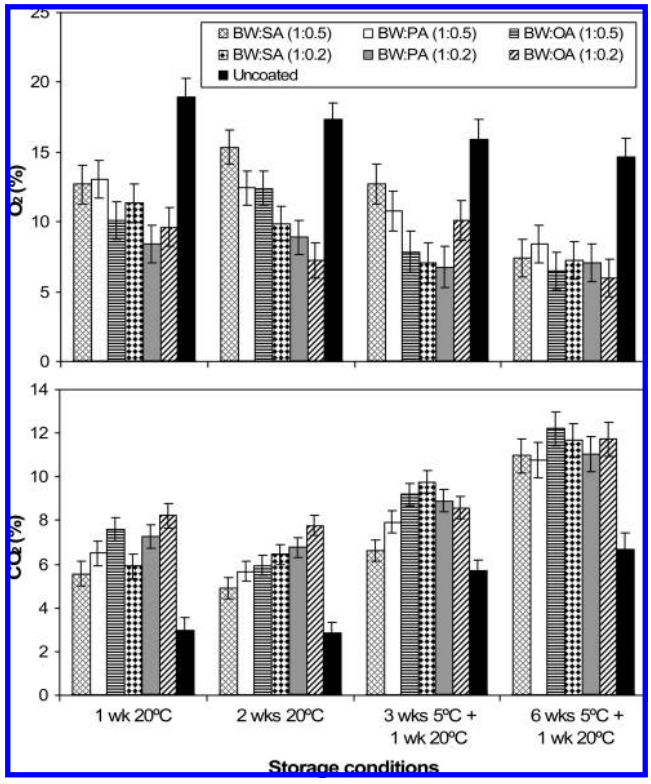

Figure 6. Internal gas concentration of HPMC-BW coated and uncoated 'Ortanique' mandarins: effect of fatty acid type and amount. Bars within each storage time indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

coatings on fruit behave differently from stand-alone films. Therefore, not only must the permeability of the film-coating material be considered, but the nature of the fruit peel as well. Moreover, coating flexibility or the ability to adapt to the fruit surface affects the mass transfer of the coated fruit. Therefore, the greater CO_2 and O_2 barrier of coatings containing OA could be related to their greater flexibility or ability to adapt to fruit surface, related to mechanical properties of stand-alone films (**Figure 1**).

Ethanol and Acetaldehyde Contents. Ethanol and acetaldehyde accumulation in waxed citrus fruits have been related to anaerobic conditions (relatively low O_2 and high CO_2) within the fruit (*38, 41*). **Figure 7** shows the ethanol levels in coated and uncoated mandarins with storage time. Acetaldehyde level followed a similar behavior, and data are not shown. Coatings increased both ethanol and acetaldehyde levels in mandarins compared to uncoated fruit. This correlates with changes in the internal gas composition. Differences in ethanol levels due to FA type were observed when the coatings were formulated at a BW/FA ratio of 1:0.5. At this concentration, coatings with OA increased ethanol levels to a greater extent compared to the other FAs. When mandarins were stored at 5 °C, a decrease in either SA or PA content increased ethanol level, whereas the content of OA in the coatings did not affect volatile levels.

Sensory Evaluation. The flavor of 'Ortanique' mandarins decreased with storage time, but it was considered within the range of acceptability for all treatments after storage, including 6 weeks at 5 °C followed by 1 week at 20 °C (**Figure 8**). In general, mandarins coated with coatings containing OA were evaluated with the lowest flavor, reaching the lowest score when the BW/OA ratio was 1:0.5. This result can be correlated with the highest ethanol level of this treatment. Restriction of gas

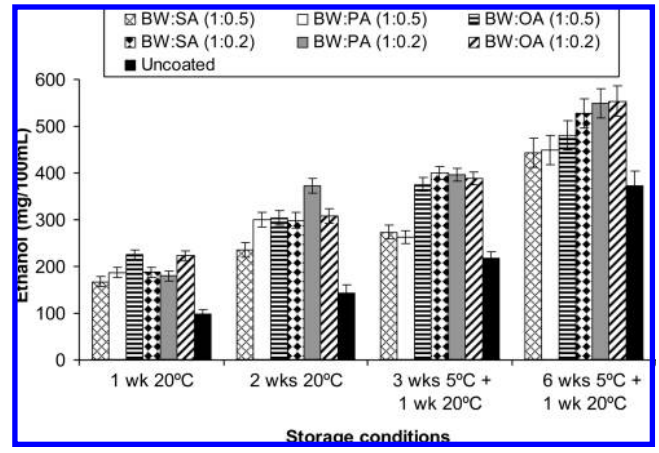

Figure 7. Ethanol content in juice of HPMC-BW coated and uncoated 'Ortanique' mandarins: effect of fatty acid type and amount. Bars within each storage time indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

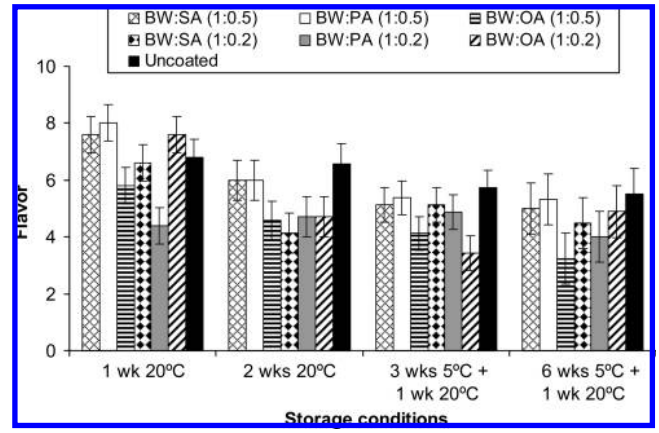

Figure 8. Flavor of HPMC-BW coated and uncoated 'Ortanique' mandarins: effect of fatty acid type and amount. Bars within each storage time indicate LSD values ($p < 0.05$). BW, beeswax; SA, stearic acid; PA, palmitic acid; OA, oleic acid.

exchange and the resulting creation of a modified internal atmosphere by coatings may affect fruit metabolism and volatile compound synthesis (*41*), as well as adversely affect citrus flavor (*38, 42*).

Flavor was assessed to be within the range of acceptability after 7 weeks of storage, even though ethanol levels reached values between 400 and 500 mg/100 mL. Other reports have shown that ethanol content in citrus fruits depends on cultivar. Ke and Kader (*19*) established the minimum ethanol content associated with off-flavor in 'Valencia' oranges to be 200 mg/100 mL. Perez-Gago et al. (*6*) found flavor degradation in mandarin 'Fortune' at an ethanol content above 300 mg/100 mL. Navarro-Tarazaga and Perez-Gago (*7*) found that an ethanol content of 100 mg/100 mL reduced the flavor quality of 'Clemenules' mandarins. Differences among off-flavor perception for the different cultivars might be due to the global contribution of other volatile components. Baldwin et al. (*41*) observed that ethanol content was not the only volatile contributing to off-flavor, but when ethanol was high, other compounds such as acetaldehyde and ethyl acetate may contribute to off-flavor.

Our results indicate 'Ortanique' mandarins showed low sensitivity to off-flavor development. Care must be taken for further applications of these coatings for cultivars with high

off-flavor sensitivity and/or for different storage conditions (i.e., increase of storage time and/or temperature).

Mandarins' external appearance was rated either as good or acceptable. No consistent effect of coating application and/or coating composition on external appearance was observed (data not shown).

Compared to untreated fruit, HPMC-BW-based coatings improved posthavest quality of 'Ortanique' mandarins by reducing weight and firmness loss, without compromising flavor quality. Coating performance could be optimized by adjusting adequate FA type and content. Coatings containing OA provided the best control of weight loss at both concentrations tested; however, when the BW/OA ratio was 1:0.5, fruit internal atmosphere and volatile content increased, thereby reducing flavor.

Evaluation of stand-alone films suggested that both barrier and mechanical properties could be used preliminarily to predict and understand coating performance when applied to citrus fruit. Nevertheless, differences observed between film OP and coating permeability to gases indicate that coating performance should be evaluated on the fruit.

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LITERATURE CITED

(1) Baldwin, E. A. Edible coatings for fresh fruits and vegetables: past, present and future. In *Edible Coatings and Films to Improve Food Quality*; Krochta, J. M., Baldwin, E. A., Nisperos-Carriedo, M. O., Eds.; Technomic Publishing: Lancaster, PA, 1994; pp 25−64.

(2) Kester, J. J.; Fennema, O. R. Edible films and coatings: a review. *Food Technol.* **1986**, *40*, 47–59.

(3) Greener-Donhowe, I. K.; Fennema, O. R. The effects of solution composition and drying temperature on crystalinity, permeability and mechanical properties of methylcellulose films. *J. Food Process. Preserv.* **1993**, *17*, 231–246.

(4) Debeaufort, F.; Voilley, A. Aroma compound and water vapor permeability of edible films and polymeric packagings. *J. Agric. Food Chem.* **1994**, *42*, 2871–2876.

(5) Callegarin, F.; Quezada-Gallo, J. A.; Debeaufort, F.; Voilley, A. Lipids and biopackaging. *J. Am. Oil Chem. Soc.* **1997**, *74*, 1183–1192.

(6) Perez-Gago, M. B.; Rojas, C.; Del Río, M. A. Effect of lipid type and amount of edible hydroxypropyl methylcellulose-lipid composite coatings used to protect postharvest quality of mandarins cv. Fortune. *J. Food Sci.* **2002**, *67*, 2903–2909.

(7) Navarro-Tarazaga, M. Ll.; Pérez-Gago, M. B. Effect of edible coatings on quality of mandarins cv. Clemenules. *Proc. Fla. Hortic. Soc.* **2006**, *119*, 350–352.

(8) Hagenmaier, R. D. Wax microemulsion formulations used as fruit coatings. *Proc. Fla. State Hortic. Soc.* **1998**, *111*, 251–255.

(9) Baldwin, E. A.; Nisperos-Carriedo, M. O.; Hagenmaier, R. D.; Baker, R. A. Use of lipids in coatings for food products. *Food Technol.* **1997**, *51*, 56–62.

(10) Sothornvit, R.; Krochta, J. M. Plasticizers in edible films and coatings. In *Innovations in Food Packaging*, Han, J. H., Ed.; Elsevier Publishers: New York, 2005; pp 403−433.

(11) Kester, J. J.; Fennema, O. R. An edible film of lipids and cellulose ethers: barrier properties to moisture vapor transmission and structural evaluation. *J. Food Sci.* **1989**, *54*, 1383–1389.

(12) Rico-Pena, D. C.; Torres, J. A. Sorbic acid and potassium sorbate permeability of an edible methylcellulose−palmitic acid film: water activity and pH effects. *J. Food Sci.* **1991**, *56*, 497–499.

(13) Park, J. W.; Testin, R. F.; Park, H. J.; Vergano, P. J.; Wellwer, C. L. Fatty acid concentration effect on tensile strength, elongation, and water vapor permeability of laminated edible films. *J. Food Sci.* **1994**, *59*, 916–919.

(14) Kamper, S. L.; Fennema, O. Water vapor permeability of an edible, fatty acid, bilayer film. *J. Food Sci.* **1984**, *49*, 1482–1485.

(15) ASTM. Standard test method for tensile properties of thin plastic sheeting. Standard Designation D882-97. In *Annual Book of American Standard Testing Methods*; ASTM: Philadelphia, PA, 1997; pp 162−170.

(16) ASTM. Standard test methods for water vapor transmission of materials. Standard Designation E96-80. In *Annual Book of American Standard Testing Methods*; ASTM: Philadelphia, PA, 1980; pp 771−778.

(17) McHugh, T. H.; Avena-Bustillos, R.; Krochta, J. M. Hydrophilic edible films: modified procedure for water vapor permeability and explanation of thickness effects. *J. Food Sci.* **1993**, *58*, 899–903.

(18) ASTM. Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulimetric sensor. Standard Designation D3985-95. In *Annual Book of American Standard Testing Methods*; ASTM: Philadelphia, PA, 1995; pp 532−537.

(19) Ke, D.; Kader, A. A. Tolerance of 'Valencia' oranges to controlled atmospheres as determined by physiological responses and quality attributes. *J. Am. Soc. Hortic. Sci.* **1990**, *115*, 779–783.

(20) Bravin, B.; Peressini, D.; Sensidoni, A. Influence of emulsifier type and content on functional properties of polysaccharide lipid-based edible films. *J. Agric. Food Chem.* **2004**, *52*, 6448–6455.

(21) Sherwin, C. P.; Smith, D. E.; Fulcher, R. G. Effect of fatty acid type on dispersed particle size distribution in emulsion edible films. *J. Agric. Food Chem.* **1998**, *46*, 4534–4538.

(22) Jongjareonrak, A.; Benjakul, S.; Visessanguan, W.; Tanaka, M. Fatty acids and their sucrose esters affect the properties of fish gelatin-based film. *Eur. Food Res. Technol.* **2006**, *222*, 650–657.

(23) Rhim, J. W.; Wu, Y.; Weller, C. L.; Schnepf, M. Physical characteristics of emulsified soy protein−fatty acid composite films. *Sci. Aliments* **1999**, *19*, 57–71.

(24) Sears, J. K.; Darby, J. R. Mechanism of plasticizer action. In *The Technology of Plasticizers*; Sears, J. K., Darby, J. R., Eds.; Wiley: New York, 1982; pp 35−77.

(25) Quezada-Gallo, J. A.; Debeaufort, F.; Callegarin, F.; Voilley, A. Lipid hydrophobicity, physical state and distribution effects on the properties of emulsion-based films. *J. Membr. Sci.* **2000**, *180*, 37–46.

(26) Handa, A.; Gennadios, A.; Hanna, M. A.; Weller, C. L.; Kuroda, N. Physical and molecular properties of egg-white lipid films. *J. Food Sci.* **1999**, *64*, 860–864.

(27) Schultz, T. H.; Miers, J. C.; Owens, H. S.; Maclay, W. D. Permeability of pectinate films to water vapor. *J. Phys. Colloid Chem.* **1949**, *53*, 1320–1330.

(28) Koelsch, C. M.; Labuza, T. P. Functional, physical and morphological properties of methyl cellulose and fatty acid-based edible barriers. *Lebensm. Wiss. Technol.* **1992**, *25*, 404–411.

(29) McHugh, T. H.; Krochta, J. M. Water vapor permeability properties of edible whey protein−lipid emulsion films. *J. Am. Oil Chem. Soc.* **1994**, *71*, 307–311.

(30) Debeaufort, F.; Quezada-Gallo, J. A.; Voilley, A. Polarity, homogenity and structure affect water vapor permeability of model edible films. *J. Food Sci* **1993**, *58*, 426–429.

(31) Shellhammer, T. H.; Krochta, J. M. Whey protein emulsion film performance as affected by lipid type and amount. *J. Food Sci.* **1997**, *62*, 390–394.

(32) Perez-Gago, M. B.; Krochta, J. M. Lipid particle size effect on water vapor permeability and mechanical properties of whey protein−beeswax emulsion films. *J. Agric. Food Chem.* **2001**, *49*, 996–1002.

(33) Hagenmaier, R. D.; Shaw, P. E. Moisture permeability of edible films made with fatty acids and hydroxypropyl methylcellulose. *J. Agric. Food Chem.* **1990**, *38*, 1799–1803.

(34) Miller, K. S.; Krochta, J. M. Oxygen and aroma barrier properties of edible films: A review. *Trends Food Sci. Technol.* **1997**, *8*, 228–237.

(35) Ben-Yehoshua, S. Individual seal-packaging of fruits and vegetables in plastic film - a new postharvest technique. *HortSci.* **1985**, *20*, 32–37.
(36) Pozzan, M. A.; Cuquerella, J.; Navarro, P. Efecto de diferentes recubrimientos en la comercialización directa de naranjas 'Navelina'. *Actas Hortic. Soc. Española Cienc. Hortic.* **1993**, *9*, 614–619.
(37) Hagenmaier, R. D. Evaluation of a polyethylene−candelilla coating for 'Valencia' oranges. *Postharvest Biol. Technol.* **2000**, *19*, 147–154.
(38) Hagenmaier, R. D.; Baker, R. A. Reduction in gas exchange of citrus fruit by wax coatings. *J. Agric. Food Chem.* **1993**, *41*, 283–287.
(39) Claypool, L. L.; King, J. R. Fruit waxing in relation to character of cover. *Proc. Am. Soc. Hortic. Sci.* **1941**, *38*, 261–265.
(40) Chen, S.; Nussinovitch, A. Permeability and roughness determinations of wax-hydrocolloid coatings, and their limitations in determining citrus fruit overall quality. *Food Hydrocolloids* **2001**, *15*, 127–137.
(41) Baldwin, E. A.; Nisperos-Carriedo, M. O.; Shaw, P. E.; Burns, J. K. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees brix, and ascorbic acid levels. *J. Agric. Food Chem.* **1995**, *43*, 1321–1331.
(42) Cohen, E.; Shalom, Y.; Rosenberg, I. Postharvest ethanol buildup and off-flavor in 'Murcot' tangerine fruits. *J. Am. Hortic. Soc.* **1990**, *115*, 775–778.

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