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# A New Composite Coating Containing HPMC, Beeswax, and Shellac for 'Valencia' Oranges and 'Marisol' Tangerines

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**Commercial coatings used for citrus fruit include carnauba and shellac waxes or resins, which provide an attractive shine to the fruit, but are not necessarily made of 100% food-grade ingredients. A new food-grade formulation based on beeswax (BW), shellac resin (Sh), hydroxypropylmethylcellulose (HPMC), and glycerol (Gly) was tested, along with an experimental polyethylene–candelilla (PE) wax emulsion, and two commercial citrus coatings (shellac and carnauba based). 'Valencia' oranges from a local grove were washed, hand-coated, dried, and stored 2 weeks at 23 to 25 °C. The PE and carnauba coatings provided the best weight loss control, and were preferred for appearance by a sensory taste panel. The HPMC–BW–Sh-based coating exhibited the least shine, and was rated similar to the control for appearance. On the contrary, shellac-coated fruit were the shiniest, but had intermediate appearance preference ratings. Shellac-coated fruit had high levels of $CO_2$, followed by HPMC–BW–Sh-coated fruit. Volatiles analysis showed that ethanol, methanol, ethyl actetae, and hexanal were high in shellac-coated fruit, while uncoated oranges had higher levels of volatile compounds that characterize fresh citrus flavor. The HPMC-containing coating was modified to increase permeability to $O_2$ and $CO_2$ and four formulations were tested on 'Marisol' tangerines from Spain, and stored at 23 °C for 1, 2, and 3 weeks. A reduction of the HPMC : glycerol ratio from 18% : 11% to 11% : 18% improved gas permeability and sensory quality of tangerine stored 1 and 2 weeks at 24 °C. Increasing solid content (SC) in the composite coating from 5% to 8% reduced weight loss. Therefore, the HPMC : BW:Sh-containing formulation with HPMC : glycerol ratio of 11% : 18% and at 8% SC could be considered an edible coating appropriate for tangerines.**

Coatings are commonly used on citrus fruit because washing removes much of the natural wax from the peel, thereby increasing shriveling and fruit drying (Wills et al., 1998). Coatings can decrease weight loss and slow down fruit shriveling by minimizing water losses, and they can create a microcontrolled atmosphere in the fruit, thereby modifying gas exchange with the surrounding air. However, a high gas barrier can induce anaerobic conditions and off-flavor development in the fruit (Baldwin, 1994). Formulations vary depending on the usage, commodity, and qualities that they impart to the commodity. While lipid coatings, such as those containing carnauba or beeswax, and resin coatings (containing shellac or wood rosin) have the advantage of reducing water exchange, resin coatings may induce anaerobiosis (absence of oxygen) by limiting gas exchange (Baldwin and Baker, 2002). Polysaccharide or protein do not offer the high water loss reduction that lipid coatings do, but their gas exchange characteristics may be advantageous to delaying fruit ripening without inducing anaerobiosis (Baldwin, 1994; Baldwin and Baker, 2002). A coating based on candelilla wax was improved by adding gelatin (a protein) or hydroxypropyl methylcellulose (HPMC, a polysaccharide): fruit gloss was increased and internal $O_2$ was decreased without leading to anaerobiosis (Hagenmaier and Baker, 1996).

Recently, there has been an increased interest by consumers in all-natural and organic foods (Plotto and Narciso, 2006). While ingredients in a commercial coating are approved by the US Food and Drug Administration (21 CFR 172.235), some of these ingredients, for example morpholine, cannot be used in a coating made in Europe (Hagenmaier, 2004). Developing composite coatings made with all food-grade ingredients has been one objective of the Instituto Valenciano de Investigacions Agrarias (Valencia, Spain). The characteristics of a HPMC:beeswax (BW) edible coating were evaluated on 'Clemenules' tangerines (Navarro-Tarazaga and Pérez-Gago, 2006). Increasing the coating solid content (SC) increased tangerine internal $CO_2$, ethanol, and off-flavor, but weight loss and texture were not affected. Increasing the BW content reduced weight loss, internal $CO_2$, ethanol, and off-flavor, but appearance was worsened. Shellac is used in virtually all high-gloss fruit coatings (Dreier, 1991; Groves, 1977). Therefore, it was hypothesized that by adding shellac (a resin) to the formulation, appearance (as measured by gloss) would be improved.

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Coating performance is usually evaluated by the characteristics it imparts to the commodity on which it is applied. Permeability to gases such as water and $CO_2$ are measures of weight loss control and anaerobiosis prevention, respectively. High internal $CO_2$ has been related to high ethanol content and to off-flavor in citrus (Hagenmaier, 2000). However, other volatile compounds may be responsible for off-flavor, and only a complete volatile profile can explain sensory evaluation results.

The present work reports the performance of a composite coating made with HPMC, BW, shellac, and glycerol, in comparison with two commercial carnauba- and shellac-based coatings, and one experimental coating previously developed at the USDA–Citrus and Subtropical Products Laboratory, made with polyethylene and candelilla wax (Hagenmaier, 2000) on 'Valencia' oranges. Coating performance was evaluated using weight loss, internal gases ($O_2$, $CO_2$), appearance, volatile composition, and sensory evaluation. This study also reports the optimization of the composite coating for use on 'Marisol' tangerines.

## Materials and Methods

**Fruit handling and coating application.** 'Valencia' oranges were harvested from a local grove in Lake Alfred , FL, on 8 May 2006. 'Marisol' tangerines were obtained from a local packing house in Museros, Valencia, Spain on 14 Sept. 2006. Fruit were immediately washed in a 10% commercial fruit detergent (Fruit & Vegetable Kleen 241, Decco Cerexagri Inc., Monrovia, CA), brushed, and dried 9 min at 25 °C (tangerines) or 29 °C (oranges) on a pilot fruit washer and drier. The next day, fruit were individually hand coated with about 0.3 g of coating, and dried at 45 to 50 °C for 2 min 25 s. Uncoated fruit were also exposed to the same drying conditions. Storage was at room temperature (23 to 25 °C, 50% to 60% RH), 1 week for 'Valencia' oranges, and 1, 2, and 3 weeks for 'Marisol' tangerines.

**Coatings.** Commercial coatings applied on 'Valencia' oranges were carnauba- and shellac-based waxes. A polyethylene : candelilla (PE) emulsion was made in a 2-L stirred pressure cell (Parr Instrument Co., Moline, IL) as described by Hagenmaier (2004). Coating composition on a dry basis (d.b.) was: 62% oxidized polyethylenes homopolymers (CAS #68441-17-8) grade 673-P (Honeywell Specialty Chemicals, Morristown, NJ), 21% candelilla wax, grade S.P. 75 (Strahl & Pitsh Inc., W. Babylon, NY), 12% oleic acid (Industrene® 106, from Chemtura, Middlebury, CT), 4% myristic acid (Hystrene® 9014, Chemtura), 1% of 29% ammonium hydroxide (JT Baker, Phillipsburg, NJ), and two drops of antifoam (Silicone Antifoam emulsion of polydimethylsiloxane, FG-1510, Dow Corning, Midland, MI). Water was added to a final mixture of 25% solid content (SC). The composite edible coating formulation (HPMC : BW : Sh-based coating) on a d.b. was: 19% HPMC (grade E-15, from Dow Chemicals, Midland, MI), 42% BW (grade A, from Brillocera S.A., Valencia, Spain), 14% dewaxed shellac 152 (Renshel, West Bengal, India), 12% oleic acid (Industrene® 106, Chemtura), 10% glycerol (JT Baker), and 3% of 29% ammonium hydroxide (JT Baker). For emulsion preparation, 2% shellac was dispersed in water at 45 °C and ammonium hydroxide was added to solubilize the resin. At the same time, 5% HPMC was dispersed in hot water, and BW, oleic acid, glycerol, the shellac solution, and water were added to bring the final mixture to 6% SC. The mixture was heated to 10 to 20 °C above the melting point of the BW (80 °C) and homogenized with a high-shear probe mixer (PolyTron, Model PT 2100; Kinematica AG Inc., Lucerne, Switzerland) for 4 min at 30,000 rpm. Further cooling was achieved by placing the emulsion in an ice bath to bring it to less than 20 °C. Agitation was continued for approximately 45 min after reaching this temperature to ensure complete hydration of the HPMC.

For 'Marisol' tangerines, four composite edible coating formulations were made in a 2-L stirred pressure cell (Parr Instrument Co., Molline, IL). Coating composition on a d.b. was: 28% BW (grade A, from Brillocera S.A.), 28% dewaxed shellac 152 (Renshel), 9% oleic acid (Panreac Química, S.A., Barcelona, Spain), 6% of 29% ammonium hydroxide (Panreac Química), HPMC (grade E-15, from Dow Chemicals) and glycerol (Panreac Química, S.A.). The amount of HPMC and glycerol varied to obtain a ratio of HPMC : glycerol of 18% : 11% or 11% : 18% d.b., respectively. Water was added to a final SC of 5% or 8%. Table 1 shows the coating formulations as applied to 'Marisol' tangerines.

**Quality parameters.** Weight loss, gloss, internal $O_2$ and $CO_2$, internal ethanol, and volatile content were measured on 'Valencia' oranges. Weight loss, and internal $O_2$ and $CO_2$ were measured on 'Marisol' tangerines. Sensory evaluation was performed on both cultivars.

Thirty fruit per treatment were used to measure weight loss. The same fruit were weighed at the beginning of the experiment and at the end of each storage period. The results were expressed as the percent loss of initial weight.

Gloss was measured with a reflectometer (Micro-TRI-gloss, BYK Gardner, Columbia, MD) calibrated on the standard surface supplied with the instrument. Measurements were made using a shield having an 18-mm-diameter hole to block out stray light, and at an angle 60° to a line normal to the fruit surface. Ten measurements were made on the equatorial section of each orange, and 30 fruit per treatment were measured.

For 'Valencia' oranges, internal $CO_2$ was measured with a Hewlett Packard 5890 (Agilent Technologies, Palo Alto, CA) gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and fitted with a CTR 1 column (1.8 m × 0.32 cm) packed with porous polymer mixture (Alltech Associates Inc., Deerfield, IL). Conditions of the run were isothermal (70 °C), helium flow at 110 $mL \cdot min^{-1}$, injection was via a 167-µL loop, and detector temperature was 120 °C. Gas samples were withdrawn with a 3-mL syringe from fruits submerged in water. The $CO_2$ concentration was calculated using peak area of the sample relative to the peak area of a 2.5% $CO_2$ standard. Ten fruit were analyzed per treatment.

For 'Marisol' tangerines, internal $O_2$ and $CO_2$ was measured with a Thermo Trace (Thermo Fisher Scientific, Inc., Waltham, MA) gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and fitted with a Poropak QS 80/100 column (1.2 m × 0.32 cm). Conditions of the run were isothermal (35 °C), helium flow at 22 $mL \cdot min^{-1}$, injector and detector temperature were 125 and 180 °C, respectively. Gas samples were withdrawn with a 1-mL syringe from fruits submerged in water. The $O_2$ and

Table 1. Coating treatments for 'Marisol' tangerines.

| HPMC : Glycerol (%)[z] | Solid content (%) | Viscosity (cP) |
|---|---|---|
| 18:11 | 8 | 30.8 |
| 18:11 | 5 | 12.2 |
| 11:18 | 8 | 10.5 |
| 11:18 | 5 | 10.7 |

[z]Percentage expressed on a dry basis.

$CO_2$ concentration was calculated using peak area of the sample relative to the peak area of a 15.0 : 2.5% $O_2 : CO_2$ standard. Ten fruits were analyzed per treatment.

Ethanol was measured with a Perkin Elmer AutoSystem GC (Perkin Elmer Corp., Norwalk, CT) equipped with a flame ionization detector (FID) and fitted with a FFAP (crosslinked FFAP, Agilent Technologies) 50 m × 0.32 mm, 0.52-µm film thickness capillary column (Agilent Technologies). Column flow was 7 $mL \cdot min^{-1}$ injector and detector temperatures were 200 and 250 °C, respectively. Oven temperature was the following: initial 55 °C for 0.1 min, then increased to 66 °C at 3 $°C \cdot min^{-1}$, then to 95 °C at 10 $°C \cdot min^{-1}$. Ethanol content was determined from a composite juice sample from 10 fruits, replicated 3 times. The juice was spiked with 1000 $mg \cdot L^{-1}$ n-propanol as an internal standard, centrifuged, and 1 µL of the supernatant was directly injected in the GC, with a split ratio of 1:29. Ethanol concentration in the sample was calculated from the area ratio of ethanol and n-propanol, calibrated from the same ratio from a 1000 $mg \cdot L^{-1}$ of both n-propanol and ethanol as external standard.

Volatile content was analyzed from the headspace of juice from 'Valencia' oranges using a Perkin Elmer AutoSystem XL GC (Perkin Elmer Corp.) equipped with a 30 m × 0.53 mm, 1.0-mm film thickness, non-polar VF-5ms column (Varian, Lake Forest, CA), a flame ionization detector (FID), and a Gerstel MPS2 autosampler (Gerstel, Baltimore). Thirty fruit were juiced for volatile analysis, with three composite samples of 10 fruits as three replications. Vials (10 mL) containing 3 mL of juice were heated to 40 °C for 15 min; then 1 mL of the headspace was injected in a splitless mode. The conditions of the run were: initial temperature 40 °C for 5 min, then to 200 °C at 5 $°C \cdot min^{-1}$, raised again to 280 ºC at 15 °C $min^{-1}$ and held at 280 °C for 15 min. Column flow was 6 $mL \cdot min^{-1}$. Injector and detector temperatures were 200 and 290 °C, respectively. Volatiles were quantified using calibration curves obtained from deodorized orange juice where volatiles are removed by rotary evaporation, then spiked with five levels of authentic standards (Sigma-Aldrich, St. Louis) (Baldwin et al., 1995).

Twenty (for 'Valencia') and 10 (for 'Marisol') panelists, laboratory staff accustomed to taste citrus products, evaluated 'Valencia' or 'Marisol' fruit. Flavor evaluation was performed in isolated booths under red lighting to mask possible differences due to coating shininess on the peel. For 'Valencia' sensory evaluation, each fruit was divided into eight slices and two slices from a different fruit were served per treatment to each panelist in a random order, with a 3-digit random code. Panelists were asked to rank the slices in decreasing order of flavor preference, then indicate "yes/no" to the presence of off-flavor. For 'Marisol', each fruit was divided into eight slices, and each slice was then divided in two halves. A plate containing the five treatments arranged in a random order for each panelist was presented for each question. In a first serving, panelists were asked to rank the half slices by decreasing order of flavor preference. In the second serving, they were asked to rate off-flavor on a 6-point category scale, where the panelist had to choose from "none," "barely perceivable," "slight," "moderate," "strong," and "very strong." In the two servings, the half slices were from the same fruit, and a total of two slices was presented per treatment. The two servings were done to avoid biasing the response from one question to the next one. For both 'Valencia' and 'Marisol', after tasting, panelists were asked to rate visual appearance of coated fruits displayed in a room with natural lighting. They were asked to rank the fruit shine by decreasing order of intensity, and to rank the fruits by decreasing order of preference for appearance. Also, for 'Valencia', they were asked to rate shine intensity on a 3-point "just-right" scale ("not shiny enough," "just right," "too shiny").

**Statistical analyses.** For 'Valencia', instrumental data were analyzed by analysis of variance (ANOVA) with the SAS statistical software (SAS System Software V.9.1, 1999). Mean separation within each storage period was performed using Duncan's multiple range test, with $\alpha = 0.05$. Volatile data were additionally examined with factor analysis (FA), using the principal component method on the data correlation matrix to account for differences in peak scaling (Johnson and Wichern, 1992; SAS, 1999). Two factors were extracted from the principal components initial analysis, and rotated with the Varimax method (SAS, 1999). The orthogonal rotation Varimax maximizes high and minimizes low correlations, and maximizes the variance explained by the new factors (Tabachnick and Fidel, 1989). It was performed to determine how volatile compounds correlated with each other. The plots of coating treatments in the two-factor coordinate system allowed determination of the variation due to volatile concentration. Off-flavor perception (yes/no) and "just-right" shininess were analyzed with the chi-square test, using the Marascuilo procedure for pairwise comparisons between proportions (XLStats, Addinsoft, Paris). For 'Marisol', instrumental data and sensory evaluation of off-flavor were analyzed by ANOVA with Statgraphics statistical software Plus 4.1 (Manugistics, Inc., Rockville, MD). Mean separation within each storage period was performed using the LSD test, with $\alpha = 0.5$. For both 'Valencia' and 'Marisol', ranked sensory data were analyzed using the Friedman test (Meilgaard et al., 1999).

## Results and Discussion

**'Valencia' oranges.** All coating types reduced weight loss after 2 weeks at 24 °C (Table 2). Polyethylene (PE) coating had the best weight loss control, followed by commercial carnauba wax. Shellac and HPMC : BW:Sh coatings performed similarly, and only reduced weight loss by 25%. Fruit gloss was highest with shellac coating, and lowest with HPMC : BW : Sh coating (Table 2). Even though shellac imparted the most shine to the fruit, PE ranked highest for appearance acceptance, with 79% "just right" shine (Table 3). Shellac-coated fruit were ranked third for appearance, and were rated as too shiny (74% of ratings, data not shown), while fruit coated with the HPMC : BW : Sh formulation or uncoated fruit had the lowest appearance ratings and were qualified as "not enough shine" (95% and 84% of ratings for HPMC : BW : Sh and control, respectively, data not shown). In

Table 2. Weight loss, fruit gloss, internal $CO_2$, ethanol content (%) of 'Valencia' oranges coated with commercial carnauba and shellac waxes, and two experimental coatings: polyethylene : candellila wax (PE) and HPMC : BW : shellac (HPMC) after 1 week at 24 °C.[z]

| Treatment | Wt loss (%) | Fruit gloss (G.U.) | Internal $CO_2$ (%) | Internal ethanol (mg·kg) |
|---|---|---|---|---|
| Uncoated control | 5.1 a | 3.5 d | 6.9 c | 595 b |
| Carnauba | 2.8 c | 5.1 b | 7.9 c | 590 b |
| Shellac | 3.8 b | 5.4 a | 17.5 a | 964 a |
| PE | 2.0 d | 4.7 c | 9.1 bc | 654 b |
| HPMC | 3.7 b | 2.6 e | 11.5 b | 734 b |

[z]Mean followed by the same letter are not significantly different by the Duncan test at 5% confidence level.

Table 3. Sensory analysis, appearance preference, shininess, flavor preference, and off-flavor of 'Valencia' oranges coated with commercial carnauba and shellac waxes, and two experimental coatings: polyethylene : candellila wax (PE) and HPMC : BW : shellac (HPMC) after 1 week at 24 °C.[z]

| Treatment | Appearance (mean rank) | Just-right shine (%) | Flavor preference (mean rank) | Off-flavor (%) |
|---|---|---|---|---|
| Uncoated control | 4.0 a | 15.8 bc | 2.1 b | 8.3 b |
| Carnauba | 2.5 bc | 47.4 ab | 3.1 a | 20.8 ab |
| Shellac | 2.7 b | 26.3 bc | 3.2 a | 41.7 a |
| PE | 1.5 c | 78.9 a | 3.3 a | 12.5 ab |
| HPMC | 4.3 a | 5.20 c | 3.4 a | 20.8 ab |

[z]Mean ranks for appearance and flavor preferences followed by the same letter were not significantly different by the Friedman test ($\alpha = 0.05$). Percentage of "just-right shine" and "off-flavor" followed by the same letter were not significantly different by the Marascuilo test.

[y]Ranks were 1 = ranked first (i.e. preferred), to 5 = ranked last (rated worst).

addition, even if it were more desirable commercially, the higher gloss imparted by shellac may not persist in longer storage, as it was shown that there was a direct correlation between weight loss and decrease in gloss in 'Valencia' oranges (Hagenmaier, 2000).

Fruit internal $CO_2$ and ethanol were highest when coated with shellac (Table 2). Shellac has been known to reduce gas exchange, creating an anaerobic/fermentative environment in the fruit (Baldwin et al., 1995; Hagenmaier, 2000; Hagenmaier and Baker, 1994). High ethanol has directly been linked to off-flavor (Baldwin et al., 1995; Hagenmaier, 2000; Hagenmaier and Goodner, 2002; Ke and Kader, 1990) and indeed, shellac-coated fruit had the highest off-flavor level (Table 3), even though flavor preference was not different from other coated fruit. Fruit coated with HPMC:BW:Sh also had relatively high $CO_2$ content but not as high as shellac-coated fruit. Ethanol content was not different from uncoated fruit for HPMC, PE, and carnauba coated fruit.

Methanol, ethanol, and ethyl acetate were highest in the juice headspace of 'Valencia' oranges coated with shellac (Table 4). These volatile compounds are often associated with fermentative reactions, an indication of anaerobic environment in that case. Ethyl acetate was the lowest in carnauba-waxed oranges. Hexanal was lowest in carnauba-coated fruit, followed by the uncoated control, and octanal was only seen in uncoated control fruit (Table 4). Only volatiles that were significantly different due to treatment effect are presented in Table 4, while Figure 1 shows how the samples are mapped in the multivariate space determined by the volatile compounds, each represented as vectors in the first two factors' dimensional space. Uncoated control fruit had a high score on factor 1 (27% of the variation), with high loading values for limonene, myrcene, $\alpha$-pinene, $\gamma$-terpinene, valencene, decanal, linalool, methyl butyrate, and octanal. These volatile compounds are usually known to be contributors of fresh orange juice flavor (Moshonas and Shaw, 1994; Shaw, 1991), and this would explains why uncoated fruit were preferred for flavor (Table 3). On the other hand, shellac coated fruit had a high positive score on factor 2 (23% of the variation), with high loading for ethyl acetate, ethanol, methanol, confirming Table 4 results, and also hexanal. The high level of these compounds in combination may explain higher off-flavor in shellac-coated fruit, more than the level of ethanol alone, as assumed earlier (Baldwin et al., 1995; Hagenmaier, 2000; Ke and Kader, 1990). PE-coated fruit was on the negative side of factor 1, and carnauba-coated fruit was on negative side of factor 2, indicating the volatile content of these fruits was low in the orange characteristic and the fermentative volatiles, respectively. Carnauba-coated fruit were higher in hexanol, linalool, octanal, and methyl butyrate, characterized as fruity (methyl butyrate), floral (linalool), and citrus (octanal) (Buettner and Schieberle, 2001; Plotto et al., 2004). HPMC : BW : Sh coated fruit was near zero for factors 1 and 2, most likely with an average content of all the volatiles. In conclusion, the relative distribution of volatile compounds in the different treatments may explain flavor preferences and the cause of off-flavor in the different treatments.

**'Marisol' tangerines.** Coatings reduced weight loss of 'Marisol' tangerines 1, 2, and 3 weeks in 23 °C storage (Fig. 2). The control weight loss was high after 3 weeks, indicating that this specific fruit might have been stored beyond commercial limit. Formulations with 8% SC were more effective than those with 5% SC at reducing weight loss after 3 weeks. This result contradicts earlier work, which showed that SC did not affect fruit weight loss (Navarro-Tarazaga and Pérez-Gago, 2006). In the earlier work, coating composition was different and the emulsion presented a milky appearance and was not stable after a long storage period, which indicated that the lipids were dispersed in the aqueous phase as macroemulsion. In the present work, coating composition and preparation formed a translucent and stable emulsion, which indicates that globule particle size was smaller than in the previous work, approaching a microemulsion (characterized by low turbidity and high stability). These differences in particle size could have some effect on the different behavior observed in the coatings. In the macroemulsion, the lipid particles (BW) remain interspersed in the HPMC matrix, allowing water to travel through the HPMC matrix. Therefore, SC, which is related to coating thickness (Cisneros-Zevallos and Krochta, 2003), might not affect the water barrier property of the coating. In contrast, as lipid particle size gets smaller, they may form an organized structure within the HPMC matrix, forming a greater water barrier. In this case coating SC, and therefore coating thickness, might become a factor affecting water barrier. McHugh and Krochta (1994), and Pérez-Gago and Krochta (2001) reported that in edible composite films based on lipid and whey protein, a reduction in lipid particle

Table 4. Volatile content (ppm) of 'Valencia' oranges coated with commercial carnauba and shellac waxes, and two experimental coatings: polyethylene : candellila wax (PE) and HPMC : BW : shellac (HPMC) after 1 week at 24 °C.[z]

| Treatment | Methanol | Ethanol | Ethyl acetate | Hexanal | Octanal |
|---|---|---|---|---|---|
| Uncoated control | 88.1 b | 1031 b | 0.670 bc | 0.920 ab | 0.117 a |
| Carnauba | 85.7 b | 1078 b | 0.177 c | 0.470 b | 0.000 b |
| Shellac | 125.8 a | 1684 a | 1.643 a | 1.383 a | 0.000 b |
| PE | 84.0 b | 1051 b | 0.710 bc | 1.047 a | 0.000 b |
| HPMC | 89.9 b | 1102 b | 0.833 b | 1.040 a | 0.000 b |

[z]Only those volatiles that were significantly different between treatments are shown. Mean followed by the same letter are not significantly different by the Duncan multiple range test ($\alpha = 0.05$).

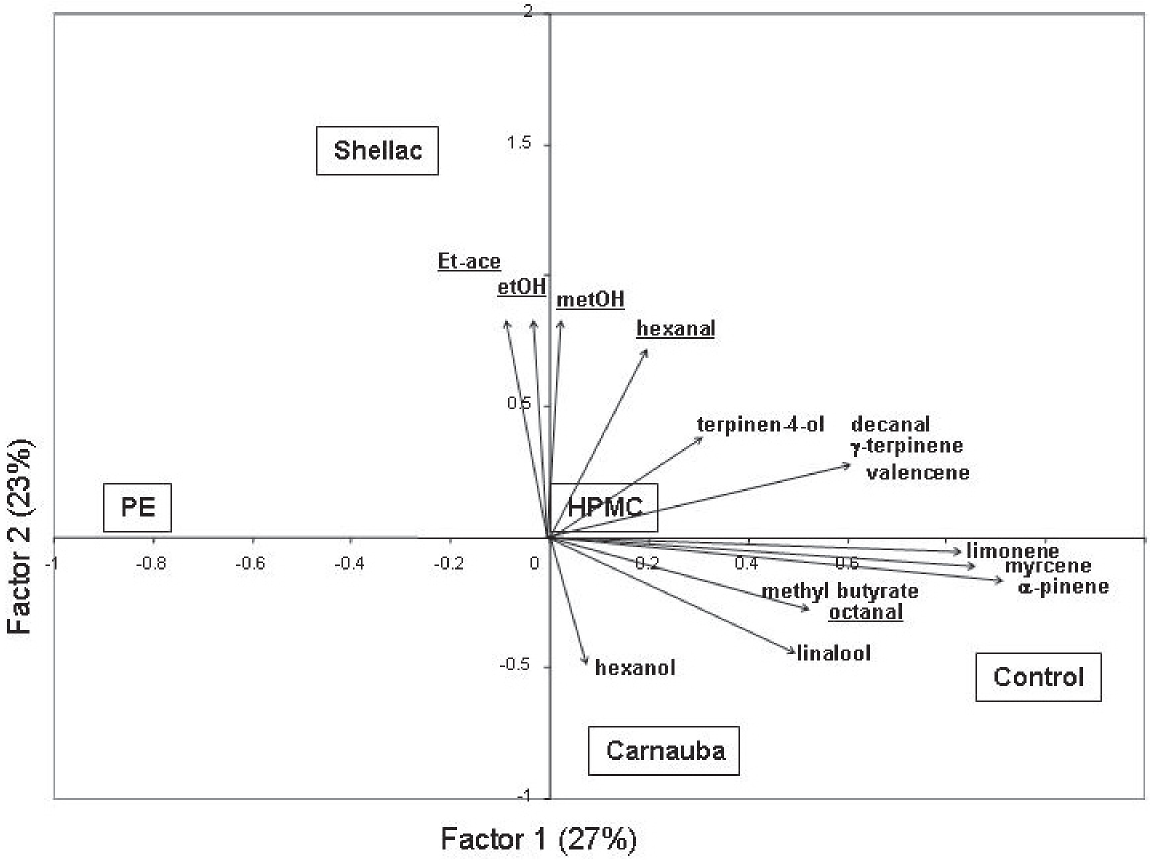


Fig. 1. Factor analysis of the volatiles of 'Valencia' oranges coated with carnauba and shellac waxes, a polyethylene–candelilla wax (PE), a HPMC : BW : shellac formulation (HPMC), and uncoated fruit (control) after 2 weeks at 24 °C. Arrows indicate the direction and weight of the vectors (volatile compounds) in the first two-dimensional factor space.

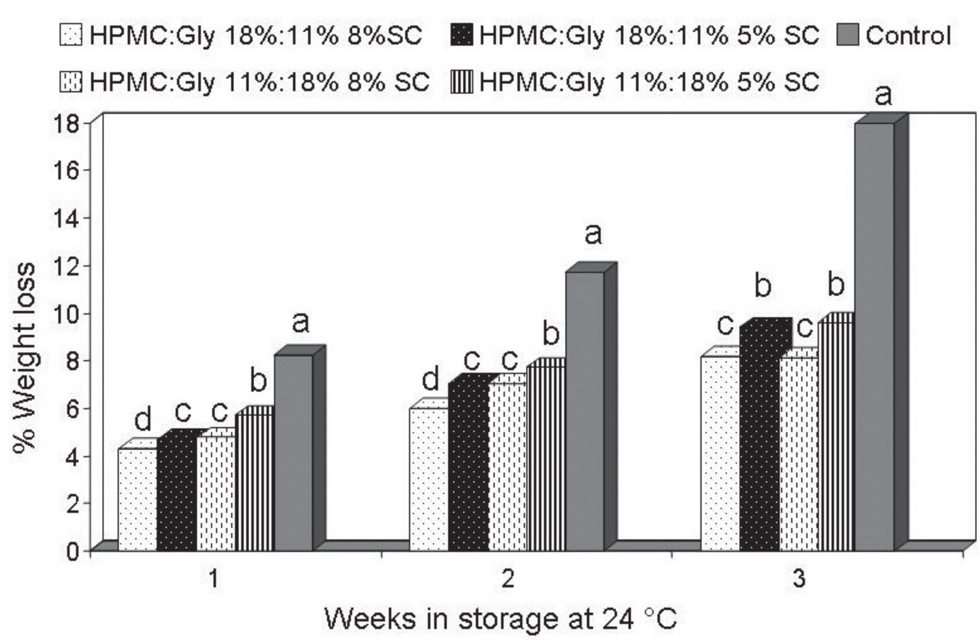


Fig. 2. Weight loss of 'Marisol' tangerines coated with an HPMC : BW : shellac composite coating. The ratio of HPMC to glycerol was 18% : 11% or 11% : 18%, and the total solids content (%SC) was 5% or 8%. Means within each storage time with the same letter are not significantly different by LSD ($\alpha = 0.05$).

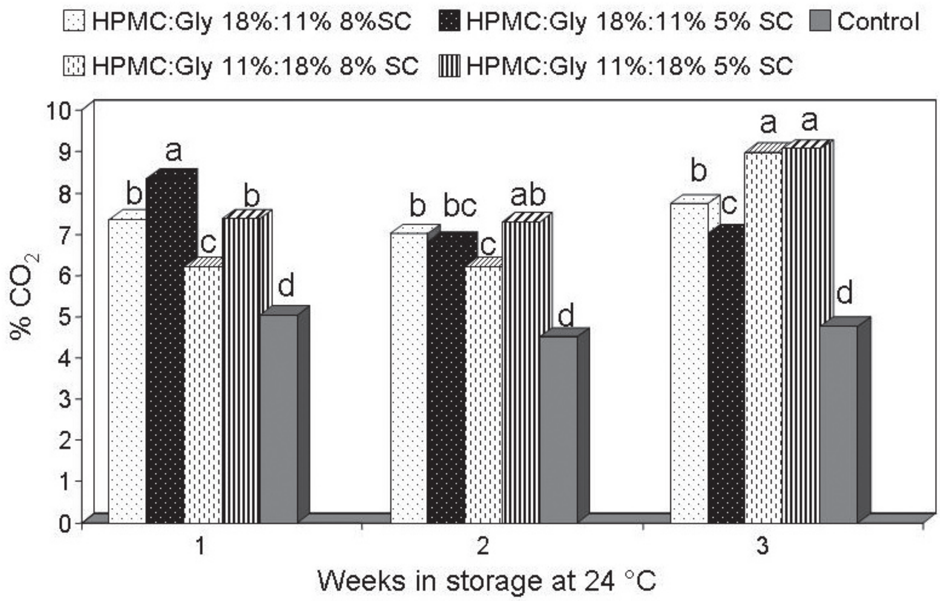


Fig. 3. Internal $CO_2$ content of 'Marisol' tangerines coated with an HPMC : BW : shellac composite coating. The ratio of HPMC to glycerol was 18% : 11% or 11% : 18%, and the total solids content (%SC) was 5% or 8%. Means within each storage time with the same letter are not significantly different by LSD ($\alpha = 0.05$).

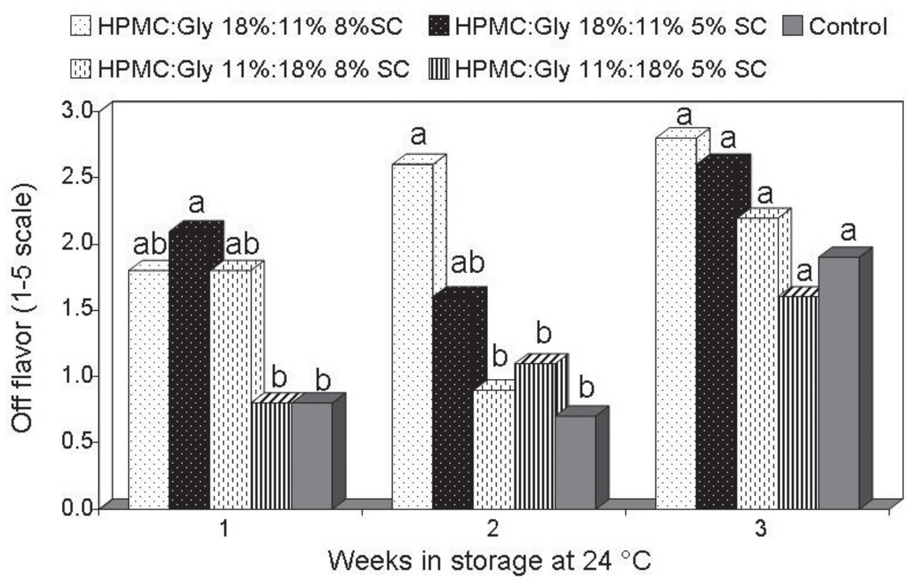


Fig. 4. Off-flavor of 'Marisol' tangerines coated with an HPMC : BW : shellac composite coating. The ratio of HPMC to glycerol was 18% : 11% or 11% : 18%, and the total solids content (%SC) was 5% or 8%. Means within each storage time with the same letter are not significantly different by LSD ($\alpha = 0.05$).

size made possible the formation of an interconnected lipid-whey protein structure that improves film water barrier. In addition, the glycerol content also had an effect on weight loss control: coatings containing the lowest glycerol content (HPMC : Gly 18% : 11%) with 8% SC provided the least weight loss across storage. In studies made with stand-alone films, it was reported that hydrophilic plasticizers, such as glycerol, increase film water vapor permeability (Sothornvit and Krochta, 2005), which would explain the results observed in our experiment.

All formulations of HPMC : BW : Sh decreased internal $O_2$ and increased internal $CO_2$ as compared to uncoated fruit (Fig. 3, data not shown for $O_2$). After 1 and 2 weeks at room temperature, the low HPMC content (HPMC : Gly 11% : 18%) with 8% SC had lower internal $CO_2$ than the other formulations, but differences can be considered small. SC did not affect internal $O_2$ (data not shown) or $CO_2$ of tangerines, but there was not a clear tendency (i.e., formulations that had the least effect on $CO_2$ accumulation at week 1 resulted in the highest amount of internal $CO_2$ by week 3) (Fig. 3). This result is in contradiction to previous work, where an increase in formulation SC resulted in an increase in internal $CO_2$ (Navarro-Tarazaga and Pérez-Gago, 2006). A possible explanation for this difference could be, as above, the effect of the globule particle size on gas barrier. The HPMC matrix, which is the main component in the composite coating system that provide the gas barrier to $O_2$ and $CO_2$, is more disrupted when the globule particle size decreases, therefore, microemulsions may provide more permeability to $O_2$ and $CO_2$ than macroemulsions in composite coatings. Han et al. (2006) hypothesized that in films made with starch and BW, $O_2$ may penetrate through the BW/starch interface. Therefore, the coating structure (or lipid distribution) might overcome the effect of SC on $O_2$ and $CO_2$ permeability in the present experiment.

Coatings with 8% SC and/or lower levels of plasticizer (glycerol) resulted in more off-flavor after 1 week of storage. By 2 weeks of storage, only the higher level of HPMC (HPMC : Gly ratio of 18% : 11%) increased off-flavor, regardless of SC content (Fig. 4). By 3 weeks, there were no differences; off-flavor was high for all fruits, indicating end of shelf-life. Flavor preference tended to be higher for uncoated fruit, but there were no consistent differences between coated fruit (data not shown). The coating with HPMC : Gly ratio of 18% : 11% and 8% was the least preferred after 2 and 3 weeks at room temperature, which could be explained by the higher perceived off-flavor (Fig. 4). The formulation with 11% : 18% HPMC : Gly and 8% SC had the lowest preference rating on the first week, but was similar to the other formulations after 2 and 3 weeks (data not shown). After 3 weeks, the HPMC : Gly ratio of 11% : 18% with 5% SC was ranked similarly to the control, which was preferred. Overall, all coatings increased shine in comparison with the control, especially the HPMC : Gly 18% : 11% at 5% SC (data not shown). This result is in contrast with the result observed in 'Valencia' oranges, for which the HPMC-containing coating decreased shine. Differences in the skin texture and properties between 'Valencia' oranges and 'Marisol' tangerines could account for the differences in coating appearance.

## Conclusion

Adding shellac to a HPMC : BW coating improved shine without, however, reaching the quality of a commercial coating. A reduction in the HPMC : Gly ratio from 18% : 11% (in the 'Valencia' experiment) to 11% : 18% improved gas permeability and sensory quality for tangerines stored 1 and 2 weeks at 24 °C. The SC did not affect gas permeability, but affected water permeability. Increasing SC from 5% to 8% decreased fruit weight loss after 3 weeks at room temperature. Therefore, overall, the formulation with 11%:18% HPMC : Gly ratio and 8% SC might provide a coating made with all food-grade ingredients for tangerines.

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