Dependence of Coating Thickness on Viscosity of Coating Solution Applied to Fruits and Vegetables by Dipping Method

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ABSTRACT: Hydroxypropyl methylcellulose solutions were used as coating systems in this study and solution concentrations, viscosity, densities, and surface tensions were characterized. Fuji apples were coated by dipping and stored for 4 days at room temperature, after which the internal oxygen and carbon dioxide were measured. Results indicated that coating thickness varied with viscosity, concentration, density, and draining time of the biopolymer solution. Coating thickness relates to the square root of viscosity and the inverse square root of draining time, which agrees with the theoretical approach for flat plate dip-coating in low-capillary-number Newtonian liquids. These results indicate the possibility of controlling coating thickness and internal gas composition based on coating solution properties.

Keywords: coating thickness, viscosity, fruits, vegetables, modified atmosphere

Introduction

The use of biopolymer coatings to modify internal atmospheres of fruits and vegetables has been studied extensively during the past 20 years. However, research in this area has been mostly empirical, providing unpredictable results and diverse conclusions.

Internal atmosphere modification seems to depend on elements such as coating permeability, thickness, and surface coverage by the film. However, little is known of the factors that may influence these elements. Thus, we believe that knowledge of the physical-chemical properties of the coating solutions and coating interactions with the surface of different commodities will allow a more predictable coating performance (Cisneros-Zevallos and others 1994a).

Film thickness is considered to influence coating response by defining the distance through which the gas permeant has to diffuse (Ben-Yehoshua 1967; Meheriuk and Lai 1988; Hagenmeier and Shaw 1992; Hagenmeier and Baker 1994; Park and others 1994a). The internal gas modification in coated fruits has been indirectly related to coating thickness through coating gas resistance parameters (Trout and others 1953; Banks and others 1993; Hagenmeier and Baker 1993), and through the solid concentration of coating solutions (Park and others 1994a, 1994b).

Studies on plate dip-coating have shown that the thickness of deposited liquid film coatings depends on the coating solution properties such as density, viscosity, and surface tension, as well as surface withdrawal speed from the coating solution. Different theoretical approaches have been used to estimate the film thickness from these properties (Levich 1962; Groenveld 1970; Scriven 1988; Derjaguin 1993). It has been reported that thickness, \( h \), relates to withdrawal speed, \( U \), by \( h = U^{1/2} \), and under certain conditions \( h = U^{2/3} \). For viscosity, \( \eta \), the relation is \( h = \eta^{1/2} \) or \( h = \eta^{2/3} \).

The following equations have been proposed to describe the thickness of coatings:

\[
h = 0.944Ca^{1/6}(\eta U/m g)^{1/2}
\]

and

\[
h = K(\eta U/m g)^{1/2}
\]

Eq. 1, proposed by Landau and Levich (1942), is used in the case where thickness is defined by a 3-sided force competition between the viscosity, surface tension, and gravity. Eq. 1 holds for low capillary numbers (\( Ca < 10^{-3} \)). Eq. 2 defines thickness as a competition between viscous and gravity forces, with surface tension forces being overshadowed by the first 2. Eq. 2 was derived by solving the flow equation for a liquid film of constant thickness, in the case of Newtonian fluids where the capillary number is \( < 10^{-3} \). However, it has also been used for high capillary numbers (\( Ca > 1 \)). In both cases, the proportionality constant \( K \) can be experimentally determined (Groenveld 1970; Scriven 1988; Guglielmi and Zenezini 1990; Guglielmi and others 1992).

The same approach can be applied to problems of liquid coating plate withdrawal and drainage. A plate that is pulled out of the bath in a very short time and then left to drain is considered a draining plate. The transformation of withdrawal speed (\( U \)) to draining time is given as (Groenveld 1970; Toledo 1991):

\[
U = z/t
\]

The objective of our study was to apply the physical principles of the dip coating process to apple fruits and to define the relationship between the coating thickness, the properties of coating solution and the internal gas modification of fruits.

Material and Methods

Fruit material

Fuji apples used in this study were harvested at commercial maturity stage from the experimental orchard of the Pomology Dept., Univ. California, Davis (Davis, Calif., U.S.A.). All fruits were carefully hand harvested leaving stems attached to the fruit and avoiding touching the surface, then stored at 2.5 °C until use.

Coating solutions

Hydroxypropyl methylcellulose (HPMC) (Methocel, Dow Chemical Co., Midland, Mich., U.S.A.) aqueous solutions were used for
coatings. HPMC of 2 different molecular weights, E-5 (about 30000) and E-50 (about 90000) were prepared at concentrations of 1, 2, 3, and 4% by weight. The initial mixture of HPMC and water was heated to 80 to 90 °C on a stirring plate. Afterwards, the temperature was dropped to 5 to 10 °C by placing the mixture on a crushed ice bath for more than 20 min. The viscosity of cellulose solutions was measured using a Rotovisco RV-20 from Haake Mess-Technik GmbH Co. (Karlsruhe, Germany). Surface tension measurements were done using a Fisher surface tensiomat® model 21 tensiometer (Fisher Scientific Co., Pittsburgh, Pa., U.S.A.) based on the DuNouy-ring method. HPMC solution densities of 1, 2, 3, and 4% solid concentration were 1.00117, 1.00372, 1.00667, and 1.00911 g/cm³, respectively (Methodol, Dow Chemical Co.). Densities of dried films were obtained by measuring the volume and weight of cast films dried overnight on high-density polyethylene (HDPE) plates at ~20 °C and 50% RH.

Coating procedure

Fuji apples were held at 20 °C and 50% RH for 24 h to equilibrate with the temperature. Without touching the surface, the fruits were thoroughly washed with running water (deionized water) to eliminate any visible contaminants and then allowed to dry at room temperature.

Coating application was done by dipping. The method involved holding the apples by the stems using clips. The fruits were dipped by hand into a solution for 30 to 60 s for complete equilibrium (Guglielmi and Zenenzi 1990) and then withdrawn quickly and allowed to drain over the glass vessel containing the HPMC solution. The glass vessel was on top of a Mettler PM2500 DeltaRange® analytical balance (Mettler Instrument Corp., Hightstown, N.J., U.S.A.), allowing recording of the HPMC solution weight over time. The amount of coating on the fruit at any time was the difference between the initial weight of the HPMC solution in the glass vessel and the weight recorded at the respective draining time. After the dipping and withdrawal process, the apples were allowed to drain for 2.5 min and then they were dried at 20 °C and 50% RH using a fan with air velocity of 180 m/min. Measurements of relative humidity and air velocity were done with a Solomat hygrometer (Solomat Corp., Stamford, Conn., U.S.A.).

Internal gas composition

Coated apples were held at 20 °C and 50% RH for 4 days before measuring the internal oxygen and carbon dioxide concentration. Gas sampling was performed with a 5-mL syringe having a side-hole needle. The apples were sampled under water to avoid external gas contamination (Saltveit 1982). The needle was introduced through the blossom end until reaching the seed cavity. Once the gas was withdrawn, the needle was removed and a rubber stopper was used to seal the syringe under water. The syringes were then sealed syringes were transferred to 1-mL syringes by introducing the needles through the rubber stopper. The end of the 5-mL syringe was pushed, exerting pressure and thus filling the 1-mL syringe with the gas sample. By using this positive pressure, contamination was avoided. Approximately 2-mL samples were obtained from each fruit. A PIR-2000 infrared CO₂ gas analyzer (IRGA) (Horiba Instruments, Irvine, CA) and a Model S-3A electrochemical O₂ analyzer (Applied Electrochemistry, Inc.) were used for gas measurements. These instruments were connected one after the other to obtain readings of both CO₂ and O₂ from one injection (Saltveit and Strike 1989). For each treatment, 4 to 5 fruits were used.

Statistics

Statview 4.0 was used for statistical analysis (Abacus Concepts, Berkeley, Calif., U.S.A.). Analysis of variance and Fisher PLSD multiple-comparison tests were performed. Curve fitting, linear and non-linear regression analysis was performed using MacCurvefit (Kevin Rainer Software, Mt. Waverly, Victoria, Australia).

Model system and theoretical approach

Mathematical solutions are proposed for determining the amount of coating adhered to a fruit surface in a dipping coating process. The coating process consists of 2 steps: (1) dipping the fruit into the coating solution and (2) withdrawing the fruit and draining the coating solution covering the fruit over time. It is assumed that evaporation of the solvent does not take place during the process, which is a very short time. Thus, properties such as viscosity, surface tension, and density of the solution remain constant. The coating solution is assumed to be a Newtonian fluid.

Calculation of amount of coating adhering to the fruit surface. From Eq. 2 and 3, we describe how coating film thickness varies with fruit height. Thus, for the calculation of total amount of coating solution adhering to the fruit surface, it will be necessary to integrate the quantity of fluid adhering at different positions over the height of a given fruit. We will analyze a cylindrical and spherical geometry for this purpose.

Cylindrical geometry. At any given time, t, the increment volume of fluid, dq, over an increment of height, dz, will be:

\[
dq = h dA = h 2\pi r dz
\]

The total volume of coating film, q, covering the cylinder height, Z, can be determined by replacing h with Eq. 2 and 3. Thus, integrating Eq. 4 over height z, for a given time:

\[
q = \frac{2\pi r K(\eta/\rho g t)^{1/2}} {0} Z^{3/2} dz = 2\pi r K(\eta/\rho g t)^{1/2}(Z/3)^{3/2}
\]

Since q is coating volume we can define an average liquid film thickness \(h_{avg}\) as \(q/A_{fruit}\). Where \(A_{fruit}\) is defined as 2 π r Z

\[
h_{avg} = q/A_{fruit} = (2/3)K(\eta/\rho g t)^{1/2}
\]

Spherical geometry. For fruits with spherical geometry, Eq. 1 and 2 will apply if the radius of curvature, r, is much larger than the capillary constant \((\gamma/\rho g)^{1/2}\) (Levich 1962). The curvature over which the fluid will drain is given by z (Eq. 3). We define the total height-curvature for a sphere as \(Z = \pi r\) (half perimeter).

Using the equation for the surface area of a spherical cap of radius r and height L (Spiegel and Liu 1999): \(A = 2\pi r L\), we can define the increment volume of fluid, dq, over an increment of height L as follows:

\[
dq = h dA = h 2\pi r dL
\]

Defining h by Eq. 2 and 3, the height-curvature, z, as \(z = r\), the height of the spherical cap as \(L = r - r \cos \theta\), and \(dL = r \sin \theta d\theta\), we obtain the following relationship for dq at any given time:

\[
dq = 2\pi K(\eta/\rho g t)^{1/2} r \sin \theta d\theta
\]

The total volume of coating film (q) covering the sphere of height–curvature z can be determined by integrating Eq. 8 over angle \(\theta\), for a given time.
Coating thickness of fruits and vegetables...

Table 1—Physico-chemical properties of HPMC biopolymer solutions at 20ºC

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Concentration (%w/w)</th>
<th>Viscosity (mPa.s)</th>
<th>Surface Tension (mN.m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC E-50</td>
<td>1</td>
<td>8.96</td>
<td>47.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16.26</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>47.3</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>47.3</td>
<td>49.3</td>
</tr>
<tr>
<td>HPMC E-5</td>
<td>1</td>
<td>2.32</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.78</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.31</td>
<td>46.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>15.05</td>
<td>46.5</td>
</tr>
</tbody>
</table>

Table 2—Dimensionless K factors and capillary number range for HPMC solutions at different solid concentrations at 20ºC.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Concentration (%w/w)</th>
<th>K</th>
<th>*Ca range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC E-50</td>
<td>1</td>
<td>0.890 ± 0.064</td>
<td>0.0000014 – 0.00013</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.685 ± 0.003</td>
<td>0.0024 – 0.037</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.691 ± 0.016</td>
<td>0.000114 – 0.00037</td>
</tr>
<tr>
<td></td>
<td>Avg</td>
<td>0.772 ± 0.005</td>
<td>0.00016 – 0.00017</td>
</tr>
<tr>
<td>HPMC E-5</td>
<td>1</td>
<td>0.890 ± 0.004</td>
<td>0.000036 – 0.000041</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.745 ± 0.071</td>
<td>0.000091 – 0.0001</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.772 ± 0.055</td>
<td>0.00016 – 0.00017</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.798 ± 0.020</td>
<td>0.000022 – 0.00022</td>
</tr>
<tr>
<td></td>
<td>Avg</td>
<td>0.772 ± 0.022</td>
<td>0.000036 – 0.00022</td>
</tr>
</tbody>
</table>

* Capillary number calculated as (πZ/γt), where Z is half perimeter of a sphere (πr)

Results and Discussion

Principles of dipping-draining method applied to fruit coating

Viscosity and surface tension of HPMC solutions are given in Table 1. The HPMC solutions can be considered as Newtonian fluids. These solutions are surface active, reducing water surface tension from 72 mPa.s to a range of 46 to 49 mPa.s.

The apples, dipped into the HPMC solution and then quickly withdrawn, had a certain amount of liquid remaining in the conical shape area of the stem end during the draining process. Initially, we tried to correlate this conical volume to the fruit weight, but this was not successful. The idea was to eliminate this factor when evaluating amount of coating, q, remaining on the fruit surface. However, we followed a second approach, by which liquid thickness on the amount of coating, q, remaining on the fruit surface. However, not successful. We calculated capillary numbers for our fruit systems using (πZ/γt), where Z would be the half perimeter of a sphere (πr). Calculated Ca for the coating solutions were in the range of 10⁻³ to 10⁻⁵ (Table 2), indicating that thickness may relate to the square root of viscosity and inverse square root of draining time. Since we measured the amount of adhered coating instead of coating thickness, we decided to use the theoretical solution approach for the total amount of coating adhering to a fruit surface (with Z = πr) as a function of time (Eq. 11).

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The apples, dipped into the HPMC solution and then quickly withdrawn, had a certain amount of liquid remaining in the conical shape area of the stem end during the draining process. Initially, we wanted to eliminate this factor when evaluating the amount of coating, q, remaining on the fruit surface. However, we followed a second approach, by which liquid thickness on the amount of coating, q, remaining on the fruit surface. However, we found that liquid thickness on dipped plates relate to [math]10^{1/2}\text{ and } U^{1/2}\text{ (for low and high Ca)}\text{ or to }\eta^{2/3}\text{ and } U^{1/3}\text{ (for low Ca)}\text{. We calculated capillary numbers for our fruit systems using }\left(\eta Z/\gamma t\right),\text{ where }Z\text{ would be the half perimeter of a sphere }\left(\pi r\right)\text{. Calculated Ca for the coating solutions were in the range of }10^{1/3}\text{ to }10^{-5}\text{ (Table 2), indicating that thickness may relate to the square root of viscosity and inverse square root of draining time. Since we measured the amount of adhered coating instead of coating thickness, we decided to use the theoretical solution approach for the total amount of coating adhering to a fruit surface (with }Z = \pi r\text{) as a function of time (Eq. 11).}

Total liquid weight adhered to the apple divided by fruit area and liquid density (W/A fruit), and plotted against (πZ/γt)^{1/2} (see Eq. 11) yields a straight line (Figure 1). Thus, each fruit sample was fitted to a power function curve, such as:

\[ (W/A_{\text{fruit}}) = H_c + k'(\eta Z/\gamma t)^{1/2} \]  

(13)

From Eq. 13, the average liquid film thickness, h avg (see Eq. 11), is defined as

\[ h_{\text{avg}} = (W/A_{\text{fruit}})/(\pi Z/\gamma t)^{1/2} \]  

(14)

The regression coefficient, r², is over 0.99 in all cases (Figure 1). The intersection, H c, gives the value describing the amount of coating corresponding to the conical stem end of the apple, which does not change with time throughout the whole draining process. The amount of liquid coating on each sample was corrected by using Eq. 14.

Figure 2A and B shows the average corrected liquid film thickness as a function of draining time and viscosity of the biopolymer solution. The slope is the dimensionless flow, k’, determined as 0.69 ± 0.022 for HPMC-E50 and 0.77 ± 0.016 for HPMC-E5 solutions, when *Ca is calculated as (πZ/γt), where Z is half perimeter of a sphere (πr)
Coating thickness of fruits and vegetables...

Coating Fuji apples (Table 2). In general, fruits with cylindrical and spherical shapes would have k' values of (2/3)K and (1)K, respectively (Eq. 6 and 11), which could be considered characteristic geometric shape factors. The K constant was apparently not influenced by the range of solids used in the HPMC solutions. However, at 1% solid concentration and low capillary numbers there was a slight increase (Table 2). Constant K values have been described as dependent on the type of solution and surface used (Guglielmi and others 1992). K values have been reported to be in the order of 0.8 (Scrivens 1988), 0.66 (Groenveld 1970) and 1.0 (Jeffrey 1930, Derjaguin 1993) for high capillary numbers (for example, Ca > 1).

Our results indicate that the average liquid film thickness (and the amount of liquid coating adhered to the surface) on coated apples is a function of viscosity, draining time and density of the biopolymer solutions. The physical principle applicable to draining plates can be applied to describe a fruit dip-coating process. This is possible because, according to Levich (1962), the same principles can be applied to any shape, provided that the radius of curvature is much larger than the capillary constant (γ/ρg)^1/2. In this study, fruits had a radius of curvature equal to the radius of a sphere, which we assumed to describe the shape of our fruit system. Fruit radii ranged from 3.5 to 4 cm compared with the capillary constant (γ/ρg)^1/2 which ranged from 0.3 to 0.35 cm.

However, Michalski and others (1998, 1999) indicate that when the capillary constant (~3 × 10^3 µm in this study) is larger than the liquid film thickness formed on plates (~10 to 100 µm in this study), then the surface tension effects from liquids and solids may play a major role. They suggest that residual adhesion of liquids on hydrophobic surfaces (low surface energy) will depend on surface tension forces, while for medium hydrophilicity and medium surface energy solids, the dependence will be on rheological and surface tension factors. However, for solids with high hydrophilicity and high surface energy, liquid spreading proceeds and residual adhesion depends on rheological effects. They also indicate that specific factors such as surface roughness may also influence the liquid residual adhesion.

Most likely the draining coating process in our study seemed to follow a purely mechanical model because many of the parameters mentioned by Michalski and others (1998, 1999) remained constant, such as the fruit surface energy (26 mN/m for Fuji apples, Cisneros-Zevallos and others 1994b), the liquid surface tension (Table 1) and the surface roughness. This may be reflected in the constant values obtained for the K factors (Table 2). This K factor will be equivalent to the correction factor introduced by Michalski and others (1998) to the purely mechanical model describing draining plates when using different solids, oils and emulsion fluids. Their correction factor included solid surface energy, liquid surface tension and roughness effects. According to this, we propose that the K factor in Eq. 6 and 11 will depend on differing surface energy of fruits, surface tension of liquids and fruit surface roughness.

Coating solution properties and fruit coating thickness

Viscosity effects on liquid film thickness and dry coating load. Liquid film thickness (h_avg) decreases as draining time increases, and increases with solution viscosity for both HPMC polymers (Figure 3) in a power law relationship, according to Eq. 14. After a 150-
Coating thickness of fruits and vegetables...

s draining time, there was no apparent change ($P > 0.05$) in the amount of liquid adhered to the surface (liquid coating load = mg liquid coating/cm$^2$). This time, $t_f$, was used to define the maximum amount of coating load on the fruit surface after the draining process.

Plotting liquid film thickness ($h_{avg}$) as compared with viscosity at a given draining time (for example, 150 s) shows the dependence of thickness on $\eta^{1/2}$ (Figure 4a). For both HPMC solutions, experimental points fit curves of the type $y = ax^b$ and seem to overlap. Once the liquid film dries, the final dry coating load will depend on the initial concentration of the HPMC solution used (Figure 4b). The dry coating load can be linearly related to liquid film thickness as follows:

$$D_c = h_{avg} \rho c 1000$$  \hspace{1cm} (15)

Thus, for a given viscosity and draining time these two HPMC solutions would have similar liquid film thickness, but the amount of dry coating load will depend on the initial solid solution concentration. This observation has important implications, since it is common to compare performance of coating materials based on solid content of the coating solutions and not considering viscosity as a factor. Thus, when comparing different coating materials with distinct viscosity at a similar solid level, it is possible that different dry coating loads are being compared without knowing it. The relationship between dry coating load and coating solution properties is as follows:

$$D_c = \rho c 1000 k' (\eta Z / \rho g t_f)^{1/2}$$  \hspace{1cm} (16)

Solution solid concentration effects on dry film thickness. Studies on coating systems are usually based on solution solid concentration (Smith and others 1987; Meheriuk and Lau 1988; El Ghaouth and others 1992). Thus, it is necessary to determine the relationship between solid concentration and dry coating load or dry film thickness. Dry coating load can be linearly related to dry film thickness as follows:

$$D_{avg} = C_{avg} / (1000 \rho g)$$  \hspace{1cm} (17)

The film density will have a direct effect on the final dry film thickness, according to Eq. 17. The dry film density may differ depending on the type of coating material being used. For example, the densities for HPMC, methyl cellulose and whey protein films (film with protein/glycerol ratio = 2/1) are about 1.29, 1.39, and 1.38 g/cm$^3$, respectively.

Calculated, average dry film thickness in our study, were in the range of 0.15 to 2.1 $\mu$m and 0.08 to 0.92 $\mu$m for HPMC E-50 and HPMC E-5, respectively. Coating thickness has been reported to be in the range of 1 to 5 $\mu$m (Trout and others 1953; Brusewitz and Singh 1985; Elson and Hayes 1985; Hagenmeier and Shaw 1992) and 4.5 to 13 $\mu$m (Park and others 1994b).

Plotting dry coating load (or dry film thickness) as compared with solution solid concentration gives a power law relationship (Figure 5) with an increasing dry coating load as solution solid content increases. The effect is more dramatic for the higher viscosity HPMC solutions. The curve is convex with respect to the X axes, therefore, a small change in solid content will give a larger change in dry coating load. The power law behavior observed depends on the relationship between solid concentration and viscosity. For example, viscosity has been related to solid concentration (Figure 6) with an empirical expression as (Sakka and others 1984):

$$\eta = \eta_{solv} + a c^b$$  \hspace{1cm} (18)
Coating thickness of fruits and vegetables...

and for concentration:
\[ c = \left( \frac{\eta - \eta_{solv}}{a} \right)^{1/b} \]  
(19)

Where constants a and b of the power function, might be related to the molecular weight of the polymer. Thus, dry film thickness would relate to solution concentration as follows:
\[ H_{\text{avg}} = k' \left( \frac{Z_{m}}{\rho_{solv} g t_{2}^{1/2}(\eta_{solv} c^{d} + a c^{b})} \right)^{1/2} \]  
(20)

If \( \eta_{solv} \) is small, as for high viscosity solutions, then \( \eta_{solv} \ll a c^{b} \). This would indicate that the final relationship between dry film thickness and solid concentration will be largely influenced or conditioned by the relationship between viscosity and coating solution solid concentration through the power factor b:
\[ H_{\text{avg}} = k' \left( \frac{Z_{m}}{\rho_{solv} g t_{2}^{1/2} c^{1+b/2}} \right) \]  
(21)

HPMC solution systems in water have a power factor b > 1 (Figure 6), while HPMC in other polar solvents, such as ethanol-water mixtures may have power factors b < 1 (Methocel, Dow Chemical Co., Midland, Mich., U.S.A.). This means that the polymer type and the solvent-polymer interaction have important effects on the final dry film thickness.

Park and others (1994b) also obtained similar experimental trends between dry film thickness and coating solution solid concentration applied to apples by a dipping method. Their results can be explained by a power law relationship described by Eq. 21.

Source of thickness variation. For a given solution solid concentration, we observed thickness differences. These differences could be due to factors such as the initial amount of liquid coating adhering on the fruit during the quick withdrawal operation and before the draining process. Differences could also be due to the drying rate of the coating solution, which will depend on the position of the fruit with respect to the fan. Fruit size may as well affect thickness according to Eq. 11, since larger fruits can hold larger amounts of coating at a given draining time. In addition to this, factors such as surface energy, liquid surface tension and surface roughness may be a source of thickness variation (Michalski and others 1998). Thus, any fruit surface treatment has the potential to affect coating thickness.

The above factors may also explain thickness differences between different coating processes such as, spray or brush coating assuming that once the coating solution is applied to the fruit surface by these methods, the same physical principles of draining plates will proceed.

Internal modified atmosphere of coated fruits

Film thickness effects. Internal gas modification of coated fruits will depend on factors such as gas exchange rate, gas resistance, and internal gas concentrations. In our study, fruit skin gas exchange rate, J, can be described using Fick's law. For oxygen gas exchange:
\[ I_{O_2} = A_{\text{fruit}}(p_{O_2}^i - p_{O_2}^o)/W_{\text{fruit}} R_{O_2} \text{total} \]  
(22)

and for carbon dioxide gas exchange:
\[ I_{CO_2} = A_{\text{fruit}}(p_{CO_2}^i - p_{CO_2}^o)/W_{\text{fruit}} R_{CO_2} \text{total} \]  
(23)

while internal oxygen consumption, \( r_{O_2} \), can be described with a Michaelis-Menten type relationship:
\[ r_{O_2} = V_{m}(p_{O_2}^i/(k_{m} + p_{O_2}^i)) \]  
(24)

Internal gas modification was modeled using a loosely adhering coating (lac) model described by Banks and others (1993). In this model, the coating loosely covers a fruit allowing for an exchange of gases in the space between the fruit surface and the coating, similar to an individual fruit plastic wrapping. The gas coating film resistance (\( R_{\text{coat}} \)) and gas fruit skin resistance (\( R_{\text{fruit}} \)) are added in series, giving the total gas resistance (\( R_{\text{total}} \)). Thus,
\[ R_{\text{total}} = R_{\text{fruit}} + R_{\text{coat}} \]  
(25)

where \( R_{\text{coat}} \) is defined as \( H_{\text{avg}}/P_{\text{coat}} \). The \( R_{\text{fruit}} \) is the addition of the effective gas resistances that occur in parallel of pores (\( R_{\text{pores}} \)) and cuticles (\( R_{\text{cut}} \)):
\[ 1/R_{\text{fruit}} = 1/R_{\text{pores}} + 1/R_{\text{cut}} \]  
(26)

In the specific case that gas exchange of both gases is mainly through pores, then total gas resistance would be the addition of the effective pore resistance and the coating resistance.

At steady-state conditions, skin gas transfer and gas consumption can be equated (Eq. 22 and 24). Solving for \( p_{O_2}^i \) gives a relationship between internal oxygen pressure and coating thickness, which we call the oxygen/thickness model:
\[ p_{O_2}^i/r_{O_2} = \left( \frac{R_{\text{total}}}{A_{\text{fruit}}} \right)^{2} \]  
(27)

To find a relationship between \( p_{CO_2}^i \) and \( H_{\text{avg}} \), we first equate Eq. 23 and 24 by the relationship \( I_{CO_2}/I_{O_2} = R_{Q} \). The \( R_{\text{total}} \) for oxygen and carbon dioxide is replaced by Eq. 25. Thereby yielding the following equation:
\[ p_{CO_2}^i = \frac{R_{Q}(p_{O_2}^i - p_{O_2}^o)(p_{CO_2}^o - p_{CO_2}^i)H_{\text{avg}}^{2}}{(R_{O_2} \text{fruit} + R_{CO_2} \text{coat})H_{\text{avg}}^{2}} \]  
(28)
The \( p_{O_2} \) can be replaced by Eq. 27, providing a relationship between internal carbon dioxide partial pressure and coating thickness, which we call the carbon dioxide/thickness model.

The oxygen/thickness model (Eq. 27) and the carbon dioxide/thickness model (Eq. 28) were fitted to the experimental data for HPMC E-50 and HPMC E-5 coated fruits (Figures 7 and 8). The gas composition of individual fruits was plotted against the calculated average dry film thickness, according to Eq. 17.

With a \( V_m = 10 \text{ cm}^3/\text{kg h} \), \( A_{\text{fruit}} = 176 \text{ cm}^2 \), \( W_{\text{fruit}} = 0.177 \text{ kg} \), \( p_{O_2} = 0.21 \text{ atm} \), \( R_{O_2,\text{fruit}} = 10000 \text{ atm cm/s} \), \( R_{CO_2,\text{fruit}} = 10000 \text{ atm cm/s} \), \( R_Q = 1 \) and \( k_m = 0.015 \text{ atm} \) (Cisneros-Zevallos and others 1994a), we obtained oxygen and carbon dioxide permeability values for both biopolymer coatings. The carbon dioxide/thickness model will only hold for aerobic respiration of a fruit, since \( R_Q \) is assumed to be constant in this analysis.

The \( P_{O_2,\text{coat}} \) and \( P_{CO_2,\text{coat}} \) obtained for HPMC E-50 films were \( 1.159 \times 10^{-9} \text{ cm}^2/\text{atm s} \) (or \( 98.85 \text{ cm}^3/\text{m/m}^2 \text{ d kPa} \)) and \( 1.480 \times 10^{-9} \text{ cm}^2/\text{atm s} \) (or \( 126.25 \text{ cm}^3/\text{m/m}^2 \text{ d kPa} \)), respectively. While the \( P_{O_2,\text{coat}} \) and \( P_{CO_2,\text{coat}} \) obtained for HPMC E-5 films were \( 1.702 \times 10^{-9} \text{ cm}^2/\text{atm s} \) (or \( 145.14 \text{ cm}^3/\text{m/m}^2 \text{ d kPa} \)), and \( 2.060 \times 10^{-9} \text{ cm}^2/\text{atm s} \) (or \( 175.70 \text{ cm}^3/\text{m/m}^2 \text{ d kPa} \)), respectively. The \( a \) values for both films were \( 1.2 \).

Figures 7A and 7B show how internal oxygen decreases and carbon dioxide increases in individual apple fruits, with an increasing amount of dry coating load. According to the fitted model, this is due to an increase of dry film thickness that reduces gas film permeance (or increases film gas resistance).

The form and fitting of the curve (\( r^2 = 0.96 \) to 0.91 for HPMC E-50, and \( r^2 = 0.68 \) to 0.55 for HPMC E-5) and the permeability values obtained would indicate that a lac model may explain the possible mechanism of gas transfer for coated fruits. These results could also satisfy a specific case of complete surface coverage and gas exchange through pores. According to this, film permeability and film thickness would play an important role in internal gas modification.

**Conclusions**

The same physical principles applied to dip-plate coatings can be applied to fruit coating systems. During dip coating of a fruit of a given size, liquid film thickness is defined by coating solution properties such as viscosity and density and by the process draining time of the coating solution. When the liquid film dries, the dry film thickness is defined by the same solution properties and by the solid concentration of the original solution. Thus, it is not appropriate to compare coating performance based only on percent of solids of the coating solutions used without considering the factors studied here. Additionally, internal gas measurements showed that oxygen and carbon dioxide concentrations varied according to the amount of dry coating load or film thickness, thus giving the possibility of modifying internal gases by controlling coating solution properties.

**Notation**

- A: area, \( \text{cm}^2 \)
- \( a, b \): constants of the power function
- c: concentration of solids in solution, \( \text{g/g} \)
- Ca: capillary number (\( \eta U/p \))
- Dc: dry coating load, \( \text{mg dry coating/cm}^2 \)
- \( g \): gravity acceleration, \( \text{cm/s}^2 \)
- h: liquid film thickness, \( \text{cm} \)
- h_avg: average liquid film thickness, \( \text{cm} \)
- h_avg: final average liquid film thickness at time \( t_f \) (\( t_f = 150 \text{ s} \)), \( \text{cm} \)
- H_avg: dry film thickness, \( \text{cm} \)
- Hc: \( \text{H}_c \) (liquid weight on stem end)/(\( A_{\text{fruit}} \)), \( \text{cm} \)
- J: fruit skin gas exchange rate, \( \text{cm}^3/\text{kg-s} \)
- k: dimensionless constant
- k_m: Michaelis-Menten constant, \( \text{atm} \)
- K: dimensionless flow constant
- L: height of a spherical cap, \( \text{cm} \)
- p: partial pressure, \( \text{atm} \)
- P: coating permeability, \( \text{cm}^2/\text{atm s} \)
- q: coating volume, \( \text{cm}^3 \)
- r: radius, \( \text{cm} \)
- \( r_{O_2} \): fruit oxygen consumption, \( \text{cm}^3/\text{kg-s} \)
- R: gas resistances, \( \text{atm cm/s} \)
- RQ: respiration quotient
- t: draining time, \( \text{s} \)
- t_f: final draining time at 150 \( \text{s} \)
- U: withdrawal speed, \( \text{cm/s} \)
- \( V_{\text{fruit}} \): fruit volume, \( \text{cm}^3 \)
Coating thickness of fruits and vegetables...

V_m maximum respiration rate when oxygen is non-limiting, cm^3/kg-s
W coating weight adhered to the surface, kg
W_fruit fruit weight, kg
Z distance from the top of a draining plate, a cylinder, or a sphere height-curvature, cm
Z_f total height of a draining plate, a cylinder or the total height-curvature of a sphere (Z=π r), cm

Greek symbols
β ratio of CO_2 to O_2 permeability (P_{CO_2}^{coat}/P_{O_2}^{coat})
γ surface tension of the liquid, mN.m^{-1}
η viscosity, mP.a.s
η_{sol} solvent viscosity, mP.a.s
θ angle subtended at the center of the circle by the arc or height-curvature, z, (z = r θ)
ρ liquid density, g/cm^3
ρ_{fr} dry film density, g /cm^3
ρ_{fruit} fruit density, g /cm^3

Subscript
CO_2, CO_2 in reference to oxygen and carbon dioxide, respectively.
fruit in reference to fruit.

Superscript
r in reference to external and internal pores cut, in reference to the terms total, film coating, fruit skin, pores and cuticle, respectively.

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