Respiration Rate of Cherry Tomatoes and Gas Permeability of Hydroxypropylmethyl Cellulose-Based Coating

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Abstract—The aim of this study was to measure the gas permeability of edible films using a homemade experimental apparatus and to determine the respiration rate of tomatoes (L. esculentum var. Cerasiforme) without (NC) and with (CC) edible coating at different temperatures. Permeability was determined using an experimental device according to the ASTM D1434 method and the apparatus was validated using permeability data from a synthetic film obtained using an Oxtran equipment. The coating applied to the tomatoes was based on hydroxypropyl methylcellulose (HPMC). Permeability values found to oxygen (O₂) for polyethylene/low-density polyethylene, polyamide/ polyethylene, and polyamide/ethylene vinyl alcohol-based synthetic film were 2.02x10⁻¹², 2.09x10⁻¹², and 4.81x10⁻¹¹ mol µm m⁻² s⁻¹ Pa⁻¹, respectively. These results were compared with permeability data obtained by the Oxtran equipment and no significant difference (p<0.05) was found. The permeability values of the coating used were 2.11x10⁻¹² and 2.19x10⁻¹² mol µm m⁻² s⁻¹ Pa⁻¹ for O₂ and carbon dioxide (CO₂), respectively. Regarding the respiration rate, the edible coating showed a significant difference (p<0.05) in O₂ consumption at temperatures of 10 °C, 15 °C, and 20 °C. However, the difference was not significant (p>0.05) for the production of CO₂ at all temperatures studied. The results showed that the homemade experimental unit was efficient to measure the permeability of edible films and the coating used decreased the respiration rate of cherry tomatoes as compared to the control.

Keywords—Gas permeability; respiration rate; coating.

I. INTRODUCTION

Tomato is a worldwide important agricultural commodity, with remarkably high concentrations of L-ascorbic acid and lycopene and is considered an important source of carotenoids in the human diet. However, this raw material is a perishable vegetable and has a very short shelf life of 2-3 weeks [1].

It is known that fruits and vegetables are living tissues after harvest and, thus, continue respiration. During postharvest, oxidation occurs as substrates of complex molecules normally present in the plant cells such as starch, sugar, and organic acids cleavage into simple molecules, which release energy, carbon dioxide, and water [2].

In this sense, edible coatings could be an alternative to preserve the quality of fresh cherries tomatoes after harvest. Edible coatings, in general, can improve the shelf life of foods because they act as semipermeable membranes, creating a modified atmosphere surrounding the product, decreasing the respiration rate and, hence, delaying ripening [3]. Coatings are made of biomolecules such as carbohydrates, proteins, and lipids and their function is to extend the shelf life of food products by controlling gas exchange and fermentative processes through low oxygen concentration [4]. Cellulose is the most abundant organic biomolecule and constitutes most of the terrestrial biomass [5]. Its derivatives, such as HPMC, are currently being studied since they have excellent properties for forming films, which are efficient barriers to oxygen permeation [6,7].

Successful applications of edible coatings have been reported in the cases of several fruits and vegetables. [4] evaluated the effect of two distinct edible coatings (alginate and zein) on parameters related to tomato ripening during nine days of postharvest storage at 20 °C and showed lower respiration rate and ethylene production for coated tomatoes than control. In addition, the onset of characteristics related to tomato quality losses, such as softening and color and mass loss, was significantly delayed (4–6 days on average) in coated tomatoes as compared to controls. [8] introduced additives such as antifungal ingredients into hydroxypropyl methylcellulose edible coatings applied onto cherry tomatoes and incubated at 20 °C and 90% RH. HPMC-lipid antifungal coatings successfully controlled black spotting caused by A. alternata.

Based on that, the aim of this study was to measure the gas permeability of edible films using a purpose-built experimental apparatus and to determine the respiration rate of tomatoes (L. esculentum var. Cerasiforme) coated with HPMC-based edible coating at different temperatures.
II. MATERIALS AND METHODS

A. Apparatus Assembled for Permeability Measurement

Figure 1 Homemade apparatus to measure the permeability of edible and synthetic films, (a) thermocouple, (b) pressure transducer, (c) sample, (d) thermostatic bath, (e) chamber gases, (f) micrometric valves, (g) block valves.

Figure 1 shows the apparatus assembled to measure permeability of polymeric films. The system was built of stainless steel and comprised two main chambers with total volume of 6.57 cm³ and transfer area of 6.88 cm². Each chamber contains a porous plate as support for the film with average pore size of 7.5 µm (±2.5 µm) and two rubber rings for sealing. Gas flow inside the chambers was controlled by four needle valves (Swagelok, Brazil) and the temperature was monitored by “J” thermocouples placed in both chambers. The system was jacketed for temperature control using a thermostatic bath (Quimis, Brazil). Pressure transducers with 0.01% accuracy and measurement range of 0-6 bar (Velki, São Paulo, Brazil) were used to monitor the pressure in the chambers.

B. Synthetic Film Permeability Measurement

The measurements were done using method D1434 of the American Society for Testing and Materials [9]. The sample was fixed in a gas-transmission cell to form a sealed semi-barrier between the two chambers. One chamber contained the test gas at high pressure while the other one, at a lower pressure, receiving the permeating gas. Either of the following procedures was used: 1) The lower pressure chamber was initially evacuated and the transmission of the gas through the film was indicated by an increase in pressure or 2) The high pressure chamber was kept near atmospheric pressure and the transmission of the gas through the film was indicated by a change in pressure.

C. Permeability Coefficient

The coefficient of permeability was obtained from a mass balance for O₂ and CO₂, in the chamber with lower pressure measured by the pressure transducer and using Eq. (1):

\[ P_{2(n+1)} = P_1 - \frac{(P_1 - P_2) \exp \left(-\left(A \cdot R \cdot T \cdot t \cdot P_e \right) \right)}{V \cdot l} \]  

Where: A is the permeable area (m²), V the chamber volume (m³), t the time (s), R the gas constant (m³ Pa K⁻¹ mol⁻¹), T the gas temperature inside the chamber (K), l the film thickness (µm), Pₑ the permeability (mol µm m⁻² s⁻¹ Pa⁻¹), P₂ the pressure at time (Pa), P₁ is the pressure for constant flow (Pa), and Pₑ is the pressure in the lower pressure chamber (Pa). The routine program used the software Matlab R2012a (Mathworks Inc., USA).

D. Experimental Permeability Apparatus

For accuracy, data obtained with the homemade apparatus, i.e., permeability to O₂ for polymeric films of low-density polyethylene/polyethylene (LDPE/PE), polyamide/polyethylene (PA/PE), and polyamide/ethylene vinyl alcohol (PA/EVOH) were measured and compared to data obtained by the Oxtran equipment (model 2/21 Mocon), a system which uses a patented colorimetric sensor (COULO ®). The test was carried out in the Package Technology Center- Food Technology Institute (CETEA-ITAL, Campinas, São Paulo, Brazil).

E. Plant Material

For this study, fresh cherry tomatoes (Solanum lycopersicum L. var. cerasiforme) were purchased in a local market from Florianópolis-SC (Brazil) and stored at 5 °C until use. The fruits were free from postharvest treatments. Before each experiment, cherry tomatoes were selected according to uniform size (diameter 20-30 mm), red color (more than 80 percent of the surface showing red color), on average 5.5 °Brix of total soluble solids, and physical integrity. Samples were washed in running water and sanitized in a 0.5 ppm ozonized solution for 1 min, then allowed to air-dry at room temperature.

F. Coating Formulation and Preparation

HPMC (Methocel E15) was purchased from Dow Chemical Com. (Midland, MI, USA) and beeswax (BW) (grade 1) was supplied by GM wax. (São Paulo, Brazil). Oleic acid and glycerol were obtained from Labsynth Laboratory Products Ltda (São Paulo, Brazil). HPMC-lipid edible composite emulsions were prepared by combining the hydrophilic phase (HPMC) and the hydrophobic phase (BW and oleic acid) suspended in water.
Glycerol and Tween 80 was used as plasticizer and emulsifier, respectively. Ratios of HPMC-glycerol (3:1) (dry basis, db) and BW-oleic acid (5:1) (db) were kept constant throughout the study. Tween 80 (Vetec Química Fina Ltda, Rio de Janeiro, Brazil) was also added to the formulations at a concentration of 1.5% (w/w) to improve wetting of the coating and adherence to the tomato fruit. Emulsions were prepared as described by [7].

G. Edible Coating Application

Tomatoes were immersed into the filmogenic solution at 25 °C and placed onto a stand for drying at ambient temperature. Next, samples were placed into the gas analyzer equipment to obtain the gas composition.

H. Gas Concentration and Respiration Rate from Tomatoes in the Non-permeable System

64±1.5 g of cherry tomatoes were placed into a stainless steel cylindrical recipient with total volume of 189.79 cm³, inner diameter of 4.9 cm, and height of 10 cm. After that, the chamber was closed and immersed in the thermostatic bath to control the temperature. The system was connected to a gas analyzer (CheckMate II PBI Dansensor) in a closed circuit, as shown by Figure 2 [10,11;12,13]. The gas concentration was measured at 5 °C, 10 °C, 15 °C, and 20 °C in triplicates. The Peleg model for humidity sorption, non-dependent on temperature and dependent on time, was used to fit the gas concentration data and is described by Equations (2), (3), (4), and (5) [14]:

\[
\frac{[O_2]}{t} = 0.21 - \frac{t}{(at + b)}
\]

\[
\frac{[CO_2]}{t} = \frac{b}{(at + b)}
\]

Deriving Equations (2) and (3) obtains:

\[
\frac{d[O_2]}{dt} = \frac{b}{(at + b)^2}
\]

\[
\frac{d[CO_2]}{dt} = \frac{b}{(at + b)^2}
\]

and replacing Equations (4) and (5) into Equations (6) and (7), the respiration rate is obtained from O₂ and CO₂ concentration data through the model proposed by [15], according to Equations (6) and (7). A computer program was developed using the MATLAB® software (Mathworks Inc., USA) to obtain the respiration rate values

\[
\tau_{O_2} = -\frac{V_t}{100W} \frac{d([O_2])}{dt}
\]

Where: \(\tau_{O_2}\) is the respiration rate as a function of O₂ consumption (mL kg⁻¹ h⁻¹), \(\tau_{CO_2}\) is the respiration rate as a function of CO₂ production (mL kg⁻¹ h⁻¹), \([O_2]\) and \([CO_2]\) are the concentrations of both gases, \(V_t\) is the free volume in the chamber (mL), and \(W\) is the weight of the tomatoes (kg).

I. Influence of Temperature on the Respiration Rate

The Arrhenius equation (Equation 8) was used to model the influence of temperature on the respiration rate.

\[
k(T) = k_o \exp\left(\frac{-Ea}{RT}\right)
\]

Where: \(k\) represents the respiration rate in mL kg⁻¹ h⁻¹, \(k_o\) is the pre-exponential constant in m kg⁻¹ h⁻¹, \(Ea\) is the activation energy in J mol⁻¹, \(R\) is the universal ideal gas constant in J mol⁻¹ K⁻¹, and \(T\) is the temperature in K.

J. Statistical Analysis

The results were evaluated using analysis of variance (ANOVA) by the software Statistic 6.0 (Stafsoft Inc., USA), and the factors showing significant difference (\(p<0.05\)) were submitted to Tukey’s test. The influence of the coating and the temperature were the dependent variables evaluated.
### III. RESULTS AND DISCUSSION

#### A. Set-up Validation

Table 1 shows the data for the permeability to \( \text{O}_2 \) obtained by the apparatus assembled in the laboratory and by the Oxtran equipment (COULO ®). A non-significant difference was observed for the permeability data obtained by both equipments. Thus, the apparatus is appropriate to obtain permeability data of films with the same reliability as Oxtran.

### Table 1

<table>
<thead>
<tr>
<th>Films</th>
<th>PEBD/PEx(10^{-12})</th>
<th>PA/PEx(10^{-11})</th>
<th>PA/EVOH(x10^{-12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CETEA-</td>
<td>1.92±0.065</td>
<td>4.66±0.182</td>
<td>2.27±0.145</td>
</tr>
<tr>
<td>Oxtran</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aparatus</td>
<td>2.02±0.146</td>
<td>4.81±0.24</td>
<td>2.09±0.254</td>
</tr>
</tbody>
</table>

PEDDB/PE- low density polyethylene and polyethylene. PA/PE- polyamide and polyethylene. PA/EVOH- polyamide and ethylene vinyl alcohol. Same lower case letters in columns indicate results do not differ, at a 5% probability level by Tukey test. The permeability data are expressed in mol.\(\mu\)m. m\(^{-2}\).s\(^{-1}\). Pa\(^{-1}\).

The advantage of building the equipment in the lab is that it is able to determine \( \text{O}_2 \), \( \text{CO}_2 \), and other non-toxic gases, while the Oxtran equipment measures only \( \text{O}_2 \) and at a different range. The price is another advantage of building this equipment compared with devices available on the market, such as GDP-C (Brugger Feinmechanik GmbH, Munich, Germany).

#### B. HPMC-based Film Permeability

Measured at 23 °C and 0% RH, permeabilities to \( \text{O}_2 \) and \( \text{CO}_2 \) of the HPMC-based edible films (film thickness of 0.205±0.03 mm) were 2.11x\(10^{-10}\) and 2.19x\(10^{-9}\) mol.\(\mu\)m. m\(^{-2}\). s\(^{-1}\). Pa\(^{-1}\), respectively. It was observed that \( \text{CO}_2 \) permeability was 10 times higher than \( \text{O}_2 \). The higher permeability to \( \text{CO}_2 \) was probably due to the its greater affinity with the films’ hydrophilic matrix since it is 35 times more soluble in water than \( \text{O}_2 \) [16]. This result matches [17], who reported a value of \( \text{CO}_2 \) permeability 36 times higher than to \( \text{O}_2 \) for chitosan films.

[18], while studying an HPMC film with the same concentration of solids but lower HPMC/glycerol ratio (2:1), obtained \( \text{O}_2 \) permeability of 1.6x\(10^{-10}\) mol.\(\mu\)m. m\(^{-2}\). s\(^{-1}\). Pa\(^{-1}\), a value lower than the one obtained in this study using an HPMC/glycerol ratio of 3:1. lower plasticizer content, and lower numbers of hydroxyl groups in the film, thus reducing the effect of hydrogen bonds and cohesive energy density, which facilitates the opening of the major polymer chains and allows the flow of permeate. The low permeability to \( \text{O}_2 \) of the film made in this study is appropriate to avoid lipid oxidation in food. Therefore, it could be used to package foods with high lipid content or fruits and vegetables under modified atmosphere. However, studies on vapor water permeability must be carried out. No \( \text{CO}_2 \) permeability data of HPMC films was found in the open literature with which to compare the results obtained in this study.

#### C. Gas Concentration and Respiration Rate of CC and NC tomatoes

Figure 3 (a to d) shows the gas composition profiles. \( \text{O}_2 \) and \( \text{CO}_2 \) concentrations inside the non-permeable system was evaluated for 60 hours until equilibrium was reached. A significant difference (p≤0.05) was observed for \( \text{O}_2 \) and \( \text{CO}_2 \) concentrations at the different temperatures. Higher gas concentration with higher temperature probably results in an acceleration of the metabolic process and higher consumption of substrate and, consequently, reduces the fruit’s shelf life. Similar results were found for banana [14], pear [19], apple [12], lychee [20], and mango [21].

The reduction in \( \text{O}_2 \) consumption for the coated fruits could be explained by the migration of gas in the following manner: Free diffusion through the pores of the skin, such as lenticels and stomata, or by barrier permeation, which consists of a gas dissolved in the side with high concentration diffusing into the solution with low concentration [22]. Thus, the reduction in gas concentration variation with the coatings indicates that they act as a barrier to block the free passage of gas through the pores of the fruit [3]. The Peleg model (Equations 3 and 4) and the model used to fit gas concentration experimental data showed a good fit with \( R^2>0.95 \) for all temperatures and both treatments.
For the CC samples, the respiration rate, as a function of CO₂, showed a significant difference (p<0.05) for all the temperatures studied. For the NC samples, there was a significant difference (p<0.05) between 5 °C and 10 °C compared to 15 °C and 20 °C.

[23] evaluated the effective application of the HPMC-based coating onto oranges stored at 9 °C and showed that there was a decrease in O₂ consumption and CO₂ production for the coated fruits, similar to the results obtained in this study.

Respiration rate was determined by experimental data of O₂ and CO₂ concentrations using Equations (4) and (5). Table 2 shows the influence of temperature on the respiration rate as a function of O₂ consumption and CO₂ production. For both NC and CC samples, as a function of O₂, there was a significant difference (p<0.05) between temperatures of 5 °C and 10 °C compared to 15 °C and 20 °C.

For the CC samples, the respiration rate, as a function of CO₂, showed a significant difference (p<0.05) for all the temperatures studied. For the NC samples, there was a significant difference (p<0.05) between 5 °C and 10 °C compared to 15 °C and 20 °C.

When the respiration rate of the samples, as a function of O₂ consumption, was analyzed between the treatments (CC and NC) at the same temperatures, only samples conditioned at 5 °C did not show a significant difference (p<0.05). For CO₂, the respiration rate had no significant difference between the CC and NC samples. This behavior probably occurred due to the film's high permeability to CO₂. On the other hand, the film has low permeability to O₂ as shown by the results for the respiration rate at 10 °C for CC samples, which were a little above the ones for NC samples stored at 5 °C.

[24], when using HPMC- and chitosan-based edible coatings on grapes stored at 1-2 °C for 12 d, showed a reduction in the respiration rate for the CC samples. Similar results were obtained in this study for tomatoes with HPMC-based coating.

The respiration rate of O₂ for the samples with an edible coating was lower in all cases, even with no differences among the temperatures, thus they could be applied in modified atmosphere synergism.
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Table 2. Respiration rate (mL O₂ or CO₂ kg⁻¹ h⁻¹) for CC and NC tomatoes.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-RR_O₂</td>
<td>2.42³±0.20</td>
<td>2.80³±0.04</td>
<td>5.05³±0.15</td>
<td>6.12³±0.26</td>
</tr>
<tr>
<td>CC-RR_O₂</td>
<td>1.55³±0.06</td>
<td>1.89³±0.03</td>
<td>3.25³±0.18</td>
<td>3.88³±0.41</td>
</tr>
<tr>
<td>NC-RR_CO₂</td>
<td>1.74³±0.12</td>
<td>2.17³±0.13</td>
<td>4.53³±0.37</td>
<td>5.56³±0.10</td>
</tr>
<tr>
<td>CC-RR_CO₂</td>
<td>1.36³±0.01</td>
<td>2.16³±0.02</td>
<td>3.46³±0.04</td>
<td>5.86³±1.37</td>
</tr>
</tbody>
</table>

NC-RR: respiration rate for non-coated samples, CC-RR: respiration rate for coated samples. Same lower case letters in the lines and same capital letters in columns indicate results do not differ, at a 5% probability level by Tukey test.

D. Influence of Temperature on Respiration rate

An Arrhenius-type equation was applied to the experimental respiration rate data to quantify the influence of temperature on respiration. Figure 4 (a and b) shows the curves plotted to determine $E_a$ from the calculation of the angular coefficient of the linearized curve of the Arrhenius equation for CC and NC tomatoes, respectively.

The Arrhenius model showed a good fit to the respiration rate data as a function of O₂ and CO₂, $R^2_{O₂}$ of 0.939 and 0.956, for CC and NC samples, respectively, and $R^2_{CO₂}$ of 0.941 and 0.997 for the samples CC and NC, respectively, were obtained. The activation energy for O₂ was 45.76 kJ mol⁻¹ and 44.60 kJ mol⁻¹, respectively. For CO₂, $E_a$ values were 56.90 kJ mol⁻¹ for coated samples and 65.50 kJ mol⁻¹ for NC ones. The results obtained for the activation energy in the two treatments were close and there was no significant (p ≥ 0.05) effect with the film application.

[25] obtained $E_a$ values for organic carrot of 50.59 kJ mol⁻¹ for samples with gelatin coating and 51.88 kJ mol⁻¹ for NC samples. The activation energy for fruits and vegetables vary in the range of 29 to 92 kJ mol⁻¹ [26], noting that the values found in this study are in accordance with the range presented in the literature.

IV. Conclusions

The homemade experimental apparatus built to measure the permeability of synthetic and edible films showed satisfactory results when compared to data obtained for polymeric films. The highest O₂ consumption and CO₂ production were found at 20 °C and the lowest, at 5 °C. The use of HPMC-based coating on the tomatoes decreased the metabolic process and delayed senescence due to the lower respiration rate.

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