BIODEGRADABLE AND COMPOSTABLE FILM AND MODIFIED ATMOSPHERE PACKAGING IN POSTHARVEST SUPPLY CHAIN OF RASPBERRY FRUITS (CV. GRANDEUR)

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ABSTRACT

In this study, noncommercial biodegradable and compostable nonperforated films (F2, F3, F4) were evaluated for modified atmosphere packaging storage for 5 days at 1 ± 1°C and 7 days at 20 ± 1°C of raspberries cv. Grandeur. After measuring the CO₂ (PeCO₂) and the O₂ (PeO₂) permeability of new films at different temperatures, the most important qualitative traits and nutraceutical components of fruits were analyzed and compared with those of unwrapped raspberries and macroperforated film (F1). As the temperature increased, the F2 and F3 were the only films to allow storage of the fruits up to 12 days, but the F3 film (5.7 kPa O₂ and values of 31.6 kPa CO₂) was the best for maintaining the color parameter (L 29.0, chroma 36.4) close to the value observed at harvest because of a similar ratio between the PeCO₂ and the PeO₂ (4.2 and 4.1, respectively) at both low and high temperatures.

PRACTICAL APPLICATIONS

This study of the permeability of new films from renewable sources for packaging raspberries in a temperature range that can simulate the postharvest supply chain could indicate that storing these perishable fruits under modified atmospheric packaging could increase environmental sustainability.

INTRODUCTION

The raspberry industry has recently undergone significant changes due to increasing customer quality requirements, health and lifestyle (sustainable consumption) concerns, and the need to stock fresh raspberries in supermarkets year-round (Paraušić et al. 2010; Girgenti et al. 2013). Such changes require producers and traders to develop new strategies to reduce soft fruit losses and improve shelf life, and access to new varieties and innovation in packaging technology could play a key role in improving the postharvest quality during storage. Genetically improved varieties have led to the cv. Grandeur, a new everbearing variety of red raspberry (Rubus idaeus L.) that is of particular interest to the European market because of its good resistance to climate stresses, long picking period, large size, high pulp consistency and the bright color of the epidermis (Ackerman and Adams 2009).

Because raspberries provide an important source of chemical compounds that are essential for human health, their marketing must integrate the themes of sustainable production and distribution processes (Girgenti et al. 2013). Supply chain sustainability must consider packaging management, particularly in sectors where packaging is integral to handling and transportation and where cool temperatures are not guaranteed. The use of materials derived from renewable sources could provide a good opportunity for the development of the postharvest supply chain.

Raspberry fruits stored at 0–0.5°C and 90–95% relative humidity (RH) can be maintained in a normal atmosphere (NA) for 5–7 days (Salunkhe and Desai 1984), although high CO₂ treatments and controlled atmospheres (15–20% CO₂ and 5–10% O₂) have also been studied (Callesen and Møller Holm 1989; Agar and Streif 1996; Kader 2001) for improving the shelf life of berries. Modified atmosphere packaging (MAP) can supplement proper temperature
management and translate into reduced qualitative and quantitative losses of soft fruits. The modified atmosphere extends the shelf life of berries, and the sealed container protects them from exposure to disease and other environmental contaminants. MAP techniques involve the use of plastic films that limit gas diffusion, leading to CO₂ enrichment and O₂ reduction (Waghmare and Annapure 2013). When raspberries are stored in gaseous mixtures containing 10% O₂ and 15% CO₂, decay is significantly reduced, and the berries have more attractive color compared with berries stored under NA conditions (Haffner et al. 2002). The final gaseous composition depends on a series of factors such as the weight of the product packed, the storage temperature, the commodity respiration rate, the cultivar and the ripening stage. In addition, the exchange of gases between the atmosphere in the container and the exterior is affected by concentration differences both inside and outside the package, the exposed surface and the permeability of the selected film. Several films with various permeability values for water vapor, CO₂ and O₂ for packaging fruits and vegetables under modified atmosphere conditions are commercially available (Linke and Geyer 2013), but the gas permeability values of most plastic films are too low to allow gas exchange and permit slow respiration (Guillaume et al. 2010). When temperatures change during shipping, handling or retail display, a MAP storage system could cause O₂ depletion and CO₂ accumulation due to an increase in respiration that exceeds the increase in the permeability of the film (Exama et al. 1993; Jeong et al. 2013). Thus, the permeability of the packaging film or perforation must change at the same rate as the respiration over the temperature range of interest (Talasila et al. 1995). The fluctuating temperatures encountered in the postharvest supply chain can negatively influence MAP storage because of the development of high humidity inside the package, which promotes the development of decay and blocks O₂ diffusion into fruit tissues and through the film (Cameron et al. 1995; Brecht et al. 2003). Further, CO₂ levels greater than 20% can cause discoloration, softening and an off-flavor in raspberries (Agar and Streif 1996).

Packaging in the soft fruit sector is changing, and the reduction of packaging weights and the use of sustainable materials are essential to respond to the desires of retailers and customers. Alternative packaging materials that are “eco-friendly,” biodegradable, and made from natural resources and can be used in place of petroleum-based polymers such as polyethylene terephthalate and high- and low-density polyethylene are being developed to package fresh and cut produce (Peelman et al. 2013). Several studies have shown interest in the use of these alternative materials for postharvest storage (Marsh and Bugusu 2007; Ioo et al. 2011; Peelman et al. 2013). For example, the shelf life of strawberries cv. Camarosa was improved by including an oxygen absorber in bio-based packages (Aday and Caner 2013). A biodegradable laminate was found to be suitable as a MAP material in the inert temperature range for fresh products, such as shredded lettuce and cabbage, head lettuce, cut broccoli, whole broccoli, tomatoes, sweet corn and blueberries (Makino and Hirata 1997). Seglina et al. (2009) examined the possibility of extending the shelf life of the raspberry cultivar Polana by packaging the fruits in different materials. The authors observed that the samples stored in MAP with a polyactic acid (PLA) film maintained the best headspace gas composition. Research on starch-based films has shown that such films could be suitable alternatives to conventional plastics for different food products (Peelman et al. 2013), but data on the use of these materials to store highly perishable raspberry fruits under passive MAP conditions are limited (Peano et al. 2013).

The objectives of this study were as follows: (1) to evaluate the performance in terms of gas transfer of the noncommercial biodegradable and compostable films under different temperature conditions; (2) to evaluate the capacity of the new films to manage a passive MAP to store a new everbearing variety of red raspberry, the cv. Grandeur, for up to 12 days at a cool storage temperature (1 ± 1°C) and at the most common temperature at European retail points (20 ± 1°C); and (3) to evaluate the impact of the resulting gas conditions on the quality and nutraceutical compounds of raspberry fruits at various storage times.

### MATERIALS AND METHODS

#### Plant Material

Red raspberry (R. idaeus L.) cv. Grandeur fruits were obtained from a commercial orchard of the Agrifrutta Soc. Coop. SRL (Piedmont, Italy). This cultivar is a new everbearing variety that is characterized by a large fruit size, high fruit firmness, a light red color, conical shape, even color and good flavor (Ackerman and Adams 2009). The fruits were hand-picked in the middle of September at the red-ripe stage of maturity. The fruits were graded for the uniformity of color and size, and damaged berries were removed. The fruits were individually packed in PLA trays and transported to the packing house (Peveragno, Cuneo, Italy) in less than an hour. The different storage treatments were started approximately 3 h after harvest. The raspberries were packed in rigid PLA trays, each containing 0.125 kg of fruit. Each tray (size 9.5 × 14 × 5 cm; consumer unit) was hermetically sealed with a flowpack machine using one commercial polypropylene macroperforated film (6-mm holes) that is actually used in the retailer distribution (Trepack, Siena, Italy) (F1) and three noncommercial biodegradable, nonperforated and compostable films.
Permeation Tests on the Biodegradable and Compostable Films

The Multiperm Oxygen and Carbon Dioxide Analyzer (Extra Solution s.r.l., Pisa, Italy) was used to measure the oxygen transmission rate (ASTM 2008) and the carbon dioxide transmission rate (ASTM 2005) values (cm³/m²/day/bar) of the three noncommercial biodegradable and compostable films. Permeability tests were conducted at 38, 30, 23, 20, 15 and 10°C and at 90% RH instead of 1°C, the temperature at which raspberry fruits were stored for up to 5 days because it was not possible to reach temperatures as low as 1°C with the apparatus used to measure the permeability of the films. The system consisted of two chambers, with the test film (S = 50 cm²) hermetically separating the two chambers. Gases at atmospheric pressure flowed continuously through the upper chamber. Nitrogen was used as the sweep gas in the lower chamber. The flow rate of the permeation gas was 73 mL/min. At steady state, the permeated gases in the sweep gas stream were analyzed to obtain the gas transmission rates. The pressure from the instrument was given in bar units. To obtain the data value in kPa, the primary SI unit, it is necessary to use the following conversion factor: 1 bar = 100 kPa, according to NIST Special Publication 811 (National Institute of Standards and Technology (NIST) 2008).

Gas permeability (mmol·cm/cm²/h/kPa) was calculated according to Eq. (1) based on Fick’s first law of diffusion for thin and infinite films (Crank and Park 1968):

$$J = \frac{Pe \times S}{e} \times \Delta P$$

(1)

To determine the gas barrier properties of the films under real working conditions, the equation from an Arrhenius plot of the data was used (Beaudry et al. 1992; Exama et al. 1993).

Packaging Procedure and Postharvest Storage Conditions

A set of three trays of 0.375 kg for each time point was left unpacked and used as the control. For the flowpack equipment, a Taurus 700 (Delphin, Italy) electronic horizontal wrapping machine including a take-up reel with translational movement of the clamping jaws was used. All of the packages were sealed under ordinary atmospheric conditions (0.2 kPa CO₂ and 21.2 kPa O₂).

The fruits were stored at 1 ± 1°C at 90–95% RH in a cold room for 5 days. After cool storage, the fruits were removed and held in the laboratory for 7 additional days at 20 ± 1°C to simulate retailer conditions.

Sampling Procedures

All analyses, with the exception of the headspace gas composition, were performed for each sample at five time points: at harvest (0); after 3 and 5 days at the constant temperature of 1 ± 1°C; at 24 h from the change of the storage temperature at 6 days (20 ± 1°C); and at the end of the storage period (12 days: 5 days at low temperature + 7 days at high temperature). Three randomly selected trays (0.375 kg of raspberry fruits) were used for each package.

Headspace Gas Composition

The headspace gas composition inside each package changed during storage due to the combined effect of the respiration of the cv. Grandeur, the films acting as a barrier to gases, and the temperature. Therefore, to measure the relative changes of the carbon dioxide and oxygen concentrations, we used a CO₂ and O₂ analyzer (CheckPoint II, PBI Dansensor, Milan, Italy). The changes in gas composition values were measured daily over the trial period and are expressed as v/v kPa. To avoid modifications in the headspace gas composition due to gas sampling, the same air volume (free volume 330 mL) was maintained in the packages during the trial period (due to a modification to the made by the supplier) because the analyzer introduced
the same quantity of air that it removed for the analyses. To
prevent gas leakage during the measurement, an adhesive
single septum system (Septum white 15-mm diameter, PBI
Dansensor) was placed on the surface of the package. The
results are expressed as an average of three replicates.

**Fruit Quality Assessment**

**Weight Loss.** The weight (water) loss of each raspberry
tray was measured using an electronic balance (SE622,
WVR, Radnor, PA) with an accuracy of 0.01 g. The weight
of each tray was recorded at harvest and at the end of each
storage period. The weight losses are reported as a percent-
age of the initial fruit weight of each package. The results
are expressed as an average of three replicates.

**Total Soluble Solids (TSS) and Titratable Acidity
(TA).** TSS analysis was conducted using squeezed raspber-
ries at 20C. The TSS concentration was determined through
the homogenization of five individual fruits from each lot
with an Atago Pal-1 pocket refractometer (Atago Co. Ltd.,
Tokyo, Japan) and is expressed in units of “Brix at 20C
(Aday and Caner 2011). The TA was measured using an
automatic titrator (Titritino 702, Metrohm, Herisau,
Switzerland) and was determined potentiometrically using
0.1 N NaOH to an end point of pH 8.1 in 5 mL of juice
diluted in 50 mL of distilled water.

**Color.** Color was measured on the first 15 sound,
nonmoldy fruits from each basket (three baskets were ran-
domly chosen for each package). The mean of the 30 fruit
measurements was used for data analysis. Color was mea-
sured on the side of a slightly flattened whole fruit using a
tristimulus color analyzer (Chroma Meter, model CR-400,
Minolta, Langenhagen, Germany) equipped with a measur-
ing head with an 8-mm-diameter measuring area. The
analyzer was calibrated to a standard white reflective plate
(Aday and Caner 2011). The mean of the 30 fruit
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Minolta, Langenhagen, Germany) equipped with a measur-
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tristimulus color analyzer (Chroma Meter, model CR-400,
Minolta, Langenhagen, Germany) equipped with a measur-
ing head with an 8-mm-diameter measuring area. The

analyzer was calibrated to a standard white reflective plate
(Aday and Caner 2011). The mean of the 30 fruit
measurements was used for data analysis. Color was mea-
sured on the side of a slightly flattened whole fruit using a

tristimulus color analyzer (Chroma Meter, model CR-400,
Minolta, Langenhagen, Germany) equipped with a measur-

analysis of variance (ANOVA) was applied, and significant

Hue angle was calculated as follows:

\[ h^o = \arctangent \left( \frac{b^o}{a^o} \right) \]  

where \( 0^o = \) red-purple, \( 90^o = \) yellow, \( 180^o = \) bluish-green
and \( 270^o = \) blue (McGuire 1992).

**Total Anthocyanin, Phenolic Content and Antioxi-
dant Activity.** To determine the total anthocyanin content,
the total phenolic content and the total antioxidant capacity,
an extract of berries was obtained using 10 g of fruit added
to 25 mL of extraction buffer (500 mL of methanol, 23.8 mL
of de-ionized water and 1.4 mL of 37% hydrochloric acid).
After 1 h in the dark at room temperature, the samples were
thoroughly homogenized for a few minutes with an ULTRA TURRAX (IKA, Stau-
fen, Germany) and centrifuged for 15 min at 3,019 g.

The supernatant obtained by centrifugation was collected
and transferred into glass test tubes and stored at −20C
until analysis.

The total anthocyanin content was quantified according
Anthocyanins were estimated by the difference in absorb-
ance at 510 and 700 nm in a buffer at pH 1.0 and pH 4.5,
where \( A_{515} = (A_{700} - A_{515}) \) pH 1.0 \( - (A_{700} - A_{515}) \) pH 4.5. The
results are expressed as milligrams of cyanidin-3-glucoside
(C3G) equivalents per 100 g of fresh weight (FW). The total
phenolic content was measured using Folin–Ciocalteu
reagent with gallic acid as a standard at 765 nm following
the method of Slinkard and Singleton (1977). The results
are expressed as milligrams of gallic acid equivalents (GAE)
per 100 g of FW. Antioxidant activity was determined using
the ferric reducing antioxidant power (FRAP) assay follow-
ning the methods of Pellegrini et al. (2003), with some
modifications.

The antioxidant capacity of the dilute berry extract was
determined by its ability to reduce ferric iron to ferrous iron
in a solution of 2,4,6-tripyridyl-s-triazine (TPTZ) prepared
in sodium acetate at pH 3.6. The reduction of iron in the
TPTZ-ferric chloride solution (FRAP reagent) results in the
formation of a blue-colored product (ferrous tripyridyl-
triazine complex), the absorbance of which was read spec-
trophotometrically at 595 nm 4 min after the addition of
appropriately diluted berry extracts or antioxidant stan-
dards to the FRAP reagent. The results are expressed as
mmol Fe²⁺ per 1 kg of fresh berries. All of these analyses
were performed using the UV-vis spectrophotometer 1600
PC VWR International.

**Statistical Analysis**

For the qualitative analysis and the nutraceutical com-
pounds, a bifactorial model (time of storage × film) analysis
of variance (ANOVA) was applied, and significant
differences were calculated using Tukey’s test. When the interactions were significant, the mean values were compared by a least significant difference multiple range test, with \( P < 0.05 \) considered significant. SPSS Statistics 20 statistical package software (SPSS Statistics 20, 2013, IBM, Milan, Italy) for Windows was used.

## RESULTS AND DISCUSSION

### Gas Barrier Properties of the Biodegradable and Compostable Films

The measured oxygen transmission rate (O2TR) and the carbon dioxide transmission rate (CO2TR) for the tested films are listed in Table 2. The changes in the barrier properties of the biodegradable and compostable films for both gases are expressed as a function of temperature, as reported by Beaudry et al. (1992). The Arrhenius plot of the data measured indicated that the natural log of the permeability coefficient for both gases depended linearly on the reciprocal temperature (K):

\[
\ln P_e = \ln A + \left(\frac{E_a}{RT}\right)
\]

where \( P_e \) is the O2 or CO2 permeability (mmol·cm/cm²·h/kPa), \( A \) is the Arrhenius constant (mmol·cm/cm²·h/kPa), \( E_a \) is the activation energy of O2 or CO2 permeation (kJ/mol), \( R \) is the universal gas constant (0.00831448 kJ/mol/K) and \( T \) is the temperature (K).

In Figs. 1 and 2, the oxygen (O2) and carbon dioxide (CO2) permeability values for all of the noncommercial films used for packages (F2, F3 and F4) correlated well with the Arrhenius equation. All of the innovative films showed a

### TABLE 2. VALUES OF THE OXYGEN TRANSMISSION RATE (O2TR) AND CARBON DIOXIDE TRANSMISSION RATE (CO2TR) OF NONCOMMERCIAL BIODEGRADABLE AND COMPOSTABLE FILMS

<table>
<thead>
<tr>
<th>Film</th>
<th>Temperature (°C)</th>
<th>O2TR (ASTMF2622-08) (cm³/m²/day/bar)</th>
<th>CO2TR (ASTMF2476-05) (cm³/m²/day/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2</td>
<td>38</td>
<td>1,312</td>
<td>4,164</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1,018</td>
<td>3,265</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>798</td>
<td>2,581</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>729</td>
<td>2,544</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>622</td>
<td>2,226</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>518</td>
<td>1,913</td>
</tr>
<tr>
<td>F3</td>
<td>38</td>
<td>2,192</td>
<td>7,874</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1,637</td>
<td>6,221</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>1,316</td>
<td>5,125</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1,197</td>
<td>4,748</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1,031</td>
<td>4,086</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>897</td>
<td>3,545</td>
</tr>
<tr>
<td>F4</td>
<td>38</td>
<td>1,559</td>
<td>5,355</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1,185</td>
<td>4,255</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>956</td>
<td>3,576</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>865</td>
<td>3,272</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>732</td>
<td>2,875</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>615</td>
<td>2,492</td>
</tr>
</tbody>
</table>

**FIG. 1.** ARRHENIUS PLOT OF CARBON DIOXIDE PERMEABILITY FOR THE NONCOMMERCIAL BIODEGRADABLE AND COMPOSTABLE FILMS
high determination coefficients ($R^2 = 0.99$), and the slope of the fitted line allowed the estimation of the $E_a/R$.

For both $O_2$ or $CO_2$ and for all of the biodegradable and compostable films, the permeability values increased with an increase in temperature, but the range within which the $O_2$ and $CO_2$ values changed was different for the two storage temperatures (Table 3).

As for other materials, the selectivity ($PeCO_2/PeO_2$) of the biodegradable and compostable films suggested that the $CO_2$ flow was greater than the $O_2$ flow, but the ratio varied as a function of temperature (Cameron et al. 1995).

For all of the biodegradable and compostable films at 1°C, the $PeCO_2$ and $PeO_2$ values showed small differences. Therefore, the selectivity values ($PeCO_2/PeO_2$) were similar and ranged between 3.9 (F2) and 4.3 (F4).

Conversely, for both gases, the values of gas permeability for the films at 20°C were much more variable. The $PeCO_2$ values were one order of magnitude higher than those for $PeO_2$.

At 20°C, the selectivity values ($PeCO_2/PeO_2$) of each biodegradable and compostable film were lower, suggesting increased $O_2$ mobility at high temperatures. The values ranged between 3.5 (F2) and 4.1 (F3).

These differences could suggest higher solubility and greater hydrophilicity of $CO_2$ than $O_2$ in the matrix of the noncommercial films used and inside each package, which could explain the highest difference in the headspace $CO_2$ to $O_2$ ratio with the change of temperature. Based on the values of most permeable plastic films (Cameron et al. 1995), the new tested films showed intermediate selectivity, which is important for controlling the respiratory exchange of fresh fruits, particularly at high temperature (Guilbert et al. 1996). The F3 film was the only one able to maintain a similar value of selectivity ($PeCO_2/PeO_2$) at both temperatures (4.2 and 4.1 at low and high temperatures, respectively), which could suggest better control of the atmosphere in the packed raspberries throughout the storage time.

**Headspace Gas Composition**

The $O_2$ and $CO_2$ levels detected in the sample package headspace during storage are reported in Figs. 3 and 4, respectively. The atmosphere inside the packages with the F1 film did not change at any storage time because of the macro hole (6-mm diameter).

The initial atmosphere gas composition changed in the packages with all of the innovative films (0.2 kPa $CO_2$ and 21.2 kPa $O_2$); the exchange area (550 cm$^2$) through the film packages was constant, so the evolution of the internal atmosphere inside the trays was passively created by the respiration rate of the cv. Grandeur and the permeability of the films to $O_2$ and $CO_2$ (Beaudry et al. 1992), both of which were affected by temperature (Kader et al. 1989). Differences had already been observed between the gas levels

**TABLE 3. O$_2$ AND CO$_2$ PERMEABILITIES OF NONCOMMERCIAL BIODEGRADABLE AND COMPOSTABLE FILMS**

<table>
<thead>
<tr>
<th>Film</th>
<th>Temperature (°C)</th>
<th>$PeCO_2$ (mmol cm$^2$/cm$^2$/h/kPa)</th>
<th>$PeO_2$ (mmol cm$^2$/cm$^2$/h/kPa)</th>
<th>$PeCO_2/PeO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2</td>
<td>20</td>
<td>1.10E$^{-12}$</td>
<td>3.20E$^{-13}$</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>6.64E$^{-13}$</td>
<td>1.70E$^{-13}$</td>
<td>3.9</td>
</tr>
<tr>
<td>F3</td>
<td>20</td>
<td>1.28E$^{-12}$</td>
<td>3.11E$^{-13}$</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7.39E$^{-13}$</td>
<td>1.75E$^{-13}$</td>
<td>4.2</td>
</tr>
<tr>
<td>F4</td>
<td>20</td>
<td>1.42E$^{-12}$</td>
<td>3.75E$^{-13}$</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>8.71E$^{-13}$</td>
<td>2.03E$^{-13}$</td>
<td>4.3</td>
</tr>
</tbody>
</table>
established in the packages wrapped with the three different biodegradable and compostable films a few hours after packaging.

As expected, a decrease in the headspace $O_2$ and an increase in the headspace $CO_2$ during the entire storage time were observed.

A characterization of the F2, F3 and F4 films indicates that the ratio between the $O_2$:TR and the $CO_2$:TR is approximately 1:4 (Table 2). Thus, assuming that the respiratory quotient $RQ = 1$ and that the $O_2$ changes by 5% on the first day, the $CO_2$ should increase by less than 8%. This did not occur, most likely due to the different velocities of the respiration of the fruits and because the mass transfer rate of the gas must account for the concentration gradient between the inside and the outside of the package, which differs for $O_2$ and $CO_2$.

The $O_2$ decreased by up to 1.3, 7.3 and 16.9 kPa, whereas $CO_2$ increased by up to 18.6, 13.2 and 7.8 kPa with F4, F2 and F3 films, respectively, during fruit storage at 1 ± 1°C for up to 5 days. The lowest $O_2$ observed for the F4 film was due to the highest $PeO_2$ (Table 3), which affected the respiration rate of the cv. Grandeur. As a result, there was an increase in the concentration of $CO_2$, although the $PeCO_2$ for this film was greater than that of the other biodegradable and compostable films. The equilibrium of partial pressures achieved with the F3 film could be considered the same as that recommended for raspberry fruits at low temperature (Callesen and Møller Holm 1989; Agar and Streif 1996; Kader 2001).

At 6 days, with an increase in storage temperature (20 ± 1°C), the changes in the atmospheric composition for all packages were greater than those at the previous temperature, most likely due to the relative increase in the respiration rate of fruits and the changes in film permeability. In particular, $CO_2$ permeability responded more than $O_2$ permeability (Table 3), and the rate of growth of $CO_2$ was higher than that of $O_2$. In fact, the $O_2$ values observed were 1.2, 3.1 and 10.9 kPa for the F4, F2 and F3 films, whereas $CO_2$ increased to 37.1, 17.0 and 14.8 kPa. At this point, the $O_2$ and $CO_2$ gas composition achieved for the F4 film became potentially harmful to fruit quality; according to Joles et al. (1994), the induction of anaerobic respiration in a high $CO_2$ atmosphere can cause multiple undesirable changes in the fruits, including the development of off-flavors (Argenta et al. 2002). In fact, the raspberry fruits packed with the F4 film could not be held to the end of the storage period, instead lasting only up to 6 days. However, as early as the fourth day, the gas values were critical, and the fruits were not marketable by visual analysis. At the end of the storage period (12 days), the $O_2$ values were 1.4 and 2067
5.7 kPa, and the CO₂ values were 51.0 and 31.6 kPa for the F2 and F3 films, respectively. Although the fruits packed with the F2 film were kept until the end of the storage period, the gas values had reached the peak. In fact, the CO₂ value was already high from the eighth day.

The F3 film was the only one able to establish and maintain an equilibrated headspace gas composition, with O₂ values of 5.7 kPa and CO₂ values of 31.6 kPa as a result of the higher CO₂ permeability in these packages compared with those with the F2 film (Table 3).

**Fruit Quality Assessment**

**Weight Loss.** Generally, the weight loss (water loss) of the cv. Grandeur due to transpiration and respiration of the fruits increased with time, and its rate was dependent on the film used (Table 4). In fact, statistically significant differences were observed among the films used and different time points.

All of the wrapped fruits (F1, F2, F3 and F4 films) showed minimal weight loss, with values below 1% for 5 days in cold storage (1 ± 1C). As reported in the literature, these values cannot be considered critical aspects of raspberry marketability (Callesen and Møller Holm 1989; Haffner et al. 2002).

With the change and increase in temperature (20 ± 1C) already evident after 6 days, the weight loss was significant for all of the packed fruits and unpacked fruits (control), showing a significant difference in weight of 2.96% compared with the other films. The lower weight loss in fruits packed with the biodegradable and compostable films compared with unpacked fruits (control) stemmed from the low rates of water loss in the MAP fruits, which occurred because the atmosphere of the packed fruits was limited; however, for the macroperforated film (F1), the reduction of weight loss was due to protection from mechanical damage. At 6 days of storage, neither the fruits stored with the F1 film nor the unwrapped fruits (control) were marketable, unlike the fruits packed with the other films.

The F2 and F3 films were the only films suitable for storing fruits for up to 12 days because they limited weight loss at high temperature (20 ± 1C) due to a good barrier to humidity. In fact, water condensation did not develop inside the packages, and no fungi were observed on the fruits (data not shown). It is well documented in the literature that bioplastics made from starch have a natural high

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**TABLE 4. WEIGHT LOSS, TOTAL SOLUBLE SOLIDS (TSS), TITRATABLE ACIDITY (TA) AND COLOR OF CV. GRANDEUR RASPBERRY FRUITS**

<table>
<thead>
<tr>
<th>Storage times (days)</th>
<th>Film</th>
<th>% weight loss</th>
<th>TSS (°Brix)</th>
<th>TA (meq/L)</th>
<th>L</th>
<th>Chroma (°)</th>
<th>Hue (°h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Harvest</td>
<td>–</td>
<td>9.2 ± 0.2</td>
<td>15.9 ± 0.2</td>
<td>31.6 ± 2.7</td>
<td>44 ± 4.4</td>
<td>29.8 ± 1.9</td>
</tr>
<tr>
<td>3</td>
<td>F1</td>
<td>0.44 ± 0.1</td>
<td>9.6 ± 0.1</td>
<td>13.1 ± 0.2</td>
<td>27.1 ± 1.3</td>
<td>39.5 ± 5.9</td>
<td>25.9 ± 2.8</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>0.30 ± 0.1</td>
<td>9.2 ± 0.1</td>
<td>13.5 ± 0.4</td>
<td>28.7 ± 2.0</td>
<td>40.6 ± 2.4</td>
<td>28.7 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>0.51 ± 0.1</td>
<td>9.2 ± 0.0</td>
<td>14.9 ± 0.3</td>
<td>29.3 ± 2.3</td>
<td>37.6 ± 4.9</td>
<td>26.6 ± 2.6</td>
</tr>
<tr>
<td></td>
<td>F4</td>
<td>0.38 ± 0.1</td>
<td>9.3 ± 0.1</td>
<td>12.9 ± 0.1</td>
<td>29.8 ± 2.5</td>
<td>38.9 ± 5.8</td>
<td>27.5 ± 2.9</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>1.18 ± 0.3</td>
<td>9.9 ± 0.1</td>
<td>13.7 ± 0.2</td>
<td>26.9 ± 2.6</td>
<td>32.8 ± 6.1</td>
<td>24.1 ± 2.4</td>
</tr>
<tr>
<td>5</td>
<td>F1</td>
<td>0.66 ± 0.66</td>
<td>9.4 ± 0.1</td>
<td>11.4 ± 0.6</td>
<td>26.5 ± 2.0</td>
<td>31.7 ± 4.7</td>
<td>24.4 ± 1.7</td>
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<tr>
<td></td>
<td>F2</td>
<td>0.45 ± 0.08</td>
<td>9.2 ± 0.2</td>
<td>12.6 ± 0.3</td>
<td>28.7 ± 3.2</td>
<td>36.2 ± 5.2</td>
<td>25.9 ± 3.0</td>
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<tr>
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<td>F3</td>
<td>0.75 ± 0.08</td>
<td>9.2 ± 0.2</td>
<td>13.3 ± 0.2</td>
<td>29.4 ± 3.7</td>
<td>38.6 ± 6.1</td>
<td>26.1 ± 2.3</td>
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<td>F4</td>
<td>0.62 ± 0.10</td>
<td>9.3 ± 0.1</td>
<td>13.9 ± 0.1</td>
<td>30.6 ± 3.3</td>
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<tr>
<td></td>
<td>Control</td>
<td>1.76 ± 0.35</td>
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<td>11.4 ± 0.9</td>
<td>26.3 ± 2.4</td>
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<tr>
<td>6</td>
<td>F1</td>
<td>1.02 ± 0.15</td>
<td>9.6 ± 0.1</td>
<td>12.6 ± 0.1</td>
<td>25.8 ± 2.1</td>
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<tr>
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<td>F2</td>
<td>0.81 ± 0.18</td>
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<td>15.4 ± 0.2</td>
<td>29.7 ± 2.5</td>
<td>38.7 ± 7.2</td>
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<tr>
<td></td>
<td>F3</td>
<td>1.15 ± 0.14</td>
<td>9.3 ± 0.2</td>
<td>15.1 ± 0.3</td>
<td>28.9 ± 2.1</td>
<td>33.6 ± 4.7</td>
<td>25.2 ± 2.0</td>
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<tr>
<td></td>
<td>F4</td>
<td>1.19 ± 0.21</td>
<td>9.4 ± 0.1</td>
<td>14.8 ± 0.5</td>
<td>29.6 ± 3.7</td>
<td>39.4 ± 6.6</td>
<td>27.1 ± 2.9</td>
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<tr>
<td></td>
<td>Control</td>
<td>2.96 ± 0.83</td>
<td>9.9 ± 0.1</td>
<td>13.4 ± 0.3</td>
<td>26.0 ± 2.2</td>
<td>29.3 ± 4.1</td>
<td>22.7 ± 1.2</td>
</tr>
<tr>
<td>12</td>
<td>F1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>2.2 ± 0.23</td>
<td>9.1 ± 0.1</td>
<td>15.3 ± 0.2</td>
<td>26.6 ± 2.4</td>
<td>34.1 ± 1.7</td>
<td>28.7 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>2.9 ± 0.30</td>
<td>9.2 ± 0.1</td>
<td>13.9 ± 0.1</td>
<td>29.0 ± 2.3</td>
<td>36.4 ± 2.1</td>
<td>26.5 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>F4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
</tbody>
</table>

LSD (5%)

<table>
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<tr>
<th>Storage time</th>
<th>Film</th>
<th>Storage time × Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0.14</td>
</tr>
<tr>
<td>0.001</td>
<td>0.000</td>
<td>0.122</td>
</tr>
<tr>
<td>0.155</td>
<td>0.000</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Least significant difference (LSD) values for P < 0.05.

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permeability to water vapor (Muller et al. 1991); at the end of the storage period, weight loss values of 2.2 and 2.9% were observed for the F2 and F3 films, respectively. The data showed that weight loss was not a limiting factor for the quality of the cv. Grandeur fruits during storage, even when the berries were subjected to metabolic stress due to the change of temperature.

**TSS and TA.** The TSS and TA contents contribute to fruit flavor, and high values are required for good berry flavor (Kader 1991). After 3 days of storage at 1 ± 1°C, the macroperforated film (F1) and unwrapped fruits (control) already showed the highest TSS values (9.6 and 9.9°Brix, respectively), and higher values than those of the biodegradable and compostable films were maintained throughout the storage time as a result of the highest water loss. The storage times, the film used and their interaction were the factors that significantly affected the TSS values. The F2 and F3 films maintained TSS values close to those of the fresh fruits (9.2°Brix) throughout the storage time and particularly at 6 days of storage, whereas the F4 film showed intermediate TSS values with the increase of temperature. This was most likely due to the good barrier properties with respect to water vapor for the films used (Peelman et al. 2013), even at high temperatures.

The TA of red raspberries cv. Grandeur decreased with storage time compared with the TA of fresh fruits (15.9 meq/L), thus corroborating the findings of Robbins et al. (1989) and Haffner et al. (2002). The lowest value was achieved after 12 days of storage with the F3 treatment (13.9 meq/L), but the values were generally maintained within a range that is not critical for consumer acceptability. The interaction between storage time and the film was statistically significant. The fruits maintained at low temperature (1 ± 1°C) (F1 and control) showed the lowest acidity (11.4 meq/L) after 5 days of storage because of the highest weight loss. An increase in the TA values was observed for all of the packages as the temperature increased. In particular, the highest value was observed for the fruits stored in MAP. At the end of the storage period, the F2 film showed the highest TA value (15.3 meq/L) because it had the highest CO2 headspace concentration, thus corroborating the results of Malhotra and Prasad (1999) and of Remon et al. (2003) for packed cherries.

**Color.** The chromatic characteristics of stored cv. Grandeur are shown in Table 4. The external color derived from anthocyanins is related to consumers’ perception of quality and is an important parameter for fruit ripeness and freshness (Krüger et al. 2011). According to the literature, fruit color changes after storage (Varseveld and Richardson 1980; Sjulin and Robbins 1983).

All of the color parameters (L*, C* and h*) were significantly affected by the film used (Table 4). At both storage temperatures (1 ± 1 and 20 ± 1°C), the biodegradable and compostable films (F2, F3 and F4) showed a positive effect on the retention of external color of the cv. Grandeur compared with the macroperforated film (F1) and unwrapped fruits (control) due to the modification of the atmosphere inside each package, with a relative accumulation of CO2. A decrease in the L value reflected the darkening of fruits by anthocyanin accumulation and indicated that the ripening process had occurred in the fruits. At the end of refrigerated storage (5 days), berries packed with the macroperforated film (F1) and unwrapped fruits (control) lost more of their luminosity (i.e., showed greater decreases in L*) than berries packed with the other films (F2, F3 and F4), with L* values of 26.5 and 26.3, respectively. The F4 film showed the highest L* value (30.6), as a consequence of the high CO2 in the headspace gas composition (Fig. 4). At 6 days of storage, L* values decreased, and the same trend was found for each film; however, at the end of the storage period (12 days), differences in the L* values were observed between the F2 and F3 films due to the different gas compositions inside the packages.

During storage, the color of the fruits became less vivid than at the time of harvest (44.0; lower chroma), and this trend was more evident for fruits packed with the macroperforated film (F1) and unwrapped fruits (control) than the others. The C value was significantly affected by the storage time, the film used and their interaction.

A reduction in the fruit hue angle (h°; less vivid fruits) from harvest (29.8°) was observed during storage for all of the packages, and this parameter was significantly affected by the storage time, the film used and their interaction. This decrease reflected the change in fruit colour from light green to deep purple due to the accumulation of anthocyanin (Fig. 6). The h° values were directly related to the humidity during storage (Goncalves et al. 2007); in fact, the highest h° value for each quality control was achieved by the biodegradable and compostable films (F2, F3 and F4), corresponding to high water vapor barrier properties at both storage temperatures. The h° values of the cv. Grandeur stored at 20 ± 1°C decreased faster than did those stored at 1 ± 1°C; in particular, the lowest values were observed after 6 days for the macroperforated film (F1) and unwrapped fruits (control), with values of 23.1° and 22.7°, respectively.

**Total Anthocyanin and Phenolic Contents and Antioxidant Activity.** Although anthocyanin, phenolic content and antioxidant activity of raspberry fruits have been previously reported, this is the first report on changes in cv. Grandeur after storage using different biodegradable and compostable films for packages.
Anthocyanins are the main compounds that contribute to the bright, red color of fruits; their synthesis continues after fruits are harvested, and factors that favor the stability of the pigments include the absence of oxygen, low pH and low processing/storage temperatures (Kalt et al. 1999). The cv. Grandeur was confirmed as a valuable source of potentially healthy compounds. In fact, the total content of anthocyanins in fresh raspberry fruits of cv. Grandeur (37.60 mg/100 g FW; Fig. 5) was in the range of values reported in the literature for red raspberries (Deighton et al. 2000; Weber et al. 2008; Sariburun et al. 2010). All of the packages showed an increase in total anthocyanins compared with the values at harvest because of the decreases in TA and increases in weight loss during storage, as reported by Mazza and Minati (1993). The interconversion of organic acids and carbohydrates may provide carbon skeletons for the synthesis of phenolics, including both anthocyanin and non-anthocyanin phenolics. The anthocyanin content was significantly different between packages. Raspberries stored with the macroperforated film (F1) and unwrapped fruits (control) showed darker colors (Table 4), with the pigment levels increasing after 5 days, whereas storage in packages with a modified atmosphere (F2, F3 and F4) protected the integrity of the fruits and kept the pigment content relatively unchanged, thereby preventing color change during storage at 1 ± 1°C. According to Kalt et al. (1999), smaller changes in anthocyanin content were reported after storage at low temperature. In fact, after 5 days of storage, the total anthocyanin content values were 49.38, 47.18 and 44.33 mg C3G/100 g FW for the F2, F3 and F4 films, respectively. An increase was observed for each package as the temperature changed (6 days) due to an increase in sugar synthesis (Table 4), as described in other soft fruit species (Mori and Sakurai 1994; Perkins-Veazie et al. 2000) and in agreement with Seglina et al. (2009). The F2 and F3 films showed a similar increase (12–13.8%), whereas the F4 film showed an increase of 20.5%. At the end of the storage period (12 days), the total anthocyanin content of the cv. Grandeur ranged from 79.47 (F2) to 64.74 mg C3G/100 g FW (F3; Fig. 6).

The behaviour of the polyphenol content in the cv. Grandeur was similar to that observed for the anthocyanin content. A strong positive correlation ($r = 0.81$) was found between the total anthocyanin and the phenolic content,
showing that fruits with a higher anthocyanin content had a higher phenolic content. The evolution of the total polyphenol content of the cv. Grandeur (Fig. 6) was in agreement with that reported by Wang and Lin (2000), and all stored raspberries showed values higher than those of fresh fruits (210.15 mg GAE/100 g FW).

In our study, the change in the total polyphenol content occurred more slowly at the lower temperature (1 ± 1°C), and the macroperforated film (F1) and unwrapped fruits (control) generally maintained higher values compared with the biodegradable and compostable films. After 5 days of storage, the total polyphenol contents were 318.78, 299.16 and 286.26 mg GAE/100 g FW for the F2, F3 and F4 films, respectively. As reported by Kalt et al. (1999), raspberries stored at temperatures greater than 1°C showed an increase in the total phenolic content, and the magnitude of the increase was related to the storage temperature. The highest value was observed at the end of the storage period (12 days) for the F2 and F3 films (366.02 and 345.92 mg GAE/100 g FW, respectively).

Due to its high anthocyanin and polyphenol content, cv. Grandeur has good antioxidant potential. Wang and Lin (2000) observed an increase in the antioxidant activity of red raspberries from the pink to the red ripe stage, corresponding to increased levels of anthocyanin and total phenolics. Similarly, storage had an important influence on the evolution of antioxidant capacity, and all of the packages showed values greater than those of fresh fruits (0.81 mmol Fe²⁺; Fig. 7) throughout the supply chain. The increase in antioxidant capacity corresponded to the evolution of the total phenolic and anthocyanin content, and at the end of the storage period (12 days), the highest value was found for the F2 film (2.20 mmol Fe²⁺).

**CONCLUSION**

This study indicated that the new films used to wrap the packages are good substitutes for traditional plastic film (polypropylene macroperforated film) and could be used throughout the supply chain of the cv. Grandeur. The new tested films minimized changes in weight loss and color of the raspberries, showing the best performance at a lower temperature (1 ± 1°C) and changed the initial atmospheric composition inside the packages due to the good permeability properties of films to the gas and the respiration of cv. Grandeur. As expected, all of the qualitative traits of the fruits were affected by the temperature increase, but the F2 and F3 films were able to maintain the qualitative traits of the cv. Grandeur for up to 12 days. However, the F2 film showed critical gas values during storage, particularly after the temperature increase. Generally, the thinner biodegradable and compostable film (F3) was more likely to maintain the most important qualitative and nutraceutical traits closest to those at harvest because it showed more equilibrated film selectivity throughout the storage time, preserving the metabolic stress of the fruit that was inevitable with a change of temperature. The potential application of these noncommercial films for packages combined with the introduction of the new cv. Grandeur could increase the accessibility on the market affected by potential temperature fluctuations during commercial postharvest, and the extension of the marketability up to 12 days could justify the likely high costs of using these materials.

**ACKNOWLEDGMENTS**

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