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New edible coatings composed of galactomannans and collagen blends to improve the postharvest quality of fruits – Influence on fruits gas transfer rate

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ABSTRACT

The objective of this work was to produce new edible coatings, based on a mixture of galactomannans from novel sources (seeds of *Adenanthera pavonina* and *Caesalpinia pulcherrima*), collagen and glycerol, and to determine their influence in gas transfer rates when they are applied on mangoes and apples. The first part of the work consisted in obtaining coating solutions with the convenient values of wettability for each fruit; such coating solutions were then characterized in terms of their permeability (to CO_2, O_2 and water vapour), mechanical properties, colour and opacity. Gas transfer rates from mangoes coated with a solution of *A. pavonina* galactomannan (0.5%), collagen (1.5%) and glycerol (1.5%) were compared with those of mangoes without coating: 28% less O_2 consumption and 11% less CO_2 production were observed in coated mangoes. The same procedure was performed in apples (in this case using *C. pulcherrima* galactomannan (0.5%), collagen (1.5%) and no glycerol); the CO_2 production and the O_2 consumption was approximately 50% lower in apples with coating than in apples without coating. The results suggest that these coatings can reduce gas transfer rates in these fruits, and can be therefore important tools to extend their shelf life.

1. Introduction

One of the most important problems in fruit trading is their short shelf life. Fruits are living organisms which continue to respire after harvesting. Shelf-life can be extended by reducing gases transfer rates and by controlling factors such as the gas composition (O_2, CO_2 and ethylene), of the gas surrounding the fruit, water vapour permeability, temperature, relative humidity and light. An important strategy to control some of these factors is the use of modified atmospheres (Lin and Zhao, 2007). When the fruit is harvested, there is a change of the gaseous balance between the consumption of oxygen and the production of carbon dioxide. In this new condition the cells are not renewed and the gas transfer rates increase, causing a metabolic loss and taking the fruit to a gradual maturation and eventual senescence. The gas transfer rates depend of both of internal and external factors. The internal factors include the species, the cultivar, and the growth state, while the external factors include the atmospheric composition O_2, CO_2 and ethylene ratios, the temperature and other stress factors (Kluge et al., 2002).

Edible films and coatings act as semipermeable barriers which may be able to keep the quality of the food. Being biodegradable they, offer alternative packaging systems which cause reduced environmental damages. The modified atmosphere created by the coating generates a physical capture of CO_2 inside the fruit and a partial sealing of the pores, reducing the gaseous exchange and reducing the gas transfer rates.

Edible films and coatings can consist of three types of biological materials: polysaccharides, proteins and lipids (Lin and Zhao, 2007). In general, due to their hydrophilic nature, polysaccharide films generally exhibit poor water vapour barrier ability. However, certain polysaccharides, applied in the form of high moisture viscous coatings, can retard moisture loss from coated foods by functioning as sacrificing agents rather than moisture barriers (Kester and Fennema, 1986). Galactomannans, being reserve carbohydrates, are found in various albuminous or endospermic seeds. The physicochemical and conformational properties of the galactomannans are mainly related with the ratio mannose/galactose (M/G) and the distribution of galactose residues throughout the main chain (Cerqueira et al., 2009). The galactomannan species used in the present work were two plants of Leguminosae family, *Adenanthera pavonina* and *Caesalpinia pulcherrima*. *A. pavonina* is native from tropical Asia and is used in reforestation, as ornamental plant

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and constitutes an important source of wood. The baking of the seeds and of the wood allows its use in the treatment of pulmonary infections, and also in the treatment of chronic ophthalmia (Fonseca and Perez, 2003). *C. pulcherrima* is an ornamental plant found throughout India, but it can be found in other countries as well, especially in Brazil. Some of the constituents extracted from *C. pulcherrima* were found to possess anti-tumour (Che et al., 1986; Patil et al., 1997) and antimicrobial properties (Ragasa et al., 2003). Galactomannans from *A. pavonina* and *C. pulcherrima* present a different mannose/galactose ratio. By using these two galactomannan species, the authors wanted to evaluate the effect of different monosaccharide composition in the coatings behaviour.

The polar nature of proteins confers to protein films the property of being excellent barriers to oxygen (apolar), possibly due to their impermeability to apolar substances and the high value of cohesive energy that they contain, however they are poor water vapour barriers (Kester and Fennema, 1986). Collagen is an abundant protein constituent of connective tissue in vertebrate (about 50% of total human protein) and invertebrate animals (Johnston-Banks, 1990).

Blending has acquired importance in improving the performance of the polymeric materials. It has become an economical and versatile way to obtain materials with a wide range of desirable properties. Biodegradable protein and polysaccharide films with satisfactory mechanical properties and good appearance are potential and ecological alternatives to synthetic packaging in pharmaceutical and food applications.

Based in this type of knowledge, a strategy deserving to be evaluated is the development of films produced from blends of galactomannans and collagen, with the purpose of improving coating properties through the possible synergism between them.

Apple is pomaceous fruit, of the species *Malus domestica*, from the rose family *Rosaceae*. It is one of the most widely cultivated fruits. Forty five million tons of apples were grown worldwide in 2002, with a value of about 10 billion USD. China produced almost half of this total. Argentina is the second leading producer, with more than 15% of the World production. The United States is the third leading producer, accounting for 7.5% of World production. France, Italy, South Africa and Chile are among the leading apple exporters (Dobrzanski et al., 2006).

Mango (*Mangifera indica*) is a tropical fruit that belongs to the genus *Mangifera* which consists of about 35 species, in the flowering plant family *Anacardiaceae*. Mango is one of the most appreciated fruits of tropical origin, being currently cultivated in practically all the countries of the tropical and equatorial zone of the World. In 1998, it was the fruit that more contributed to the Brazilian exports of fresh fruits (Souza, 2002). In 2003, Brazil was responsible for the production of 845,000 tons in an area of 67,000 hectares, occupying the second place as main exporting country in amount of mangoes (FAO, 2006).

Apple and mango are climacteric fruits. They suffer a predictable elevation in respiration rates and typically ripen and show an increase of ethylene production at or just prior to the onset of ripening and a necessity for ethylene to complete the process (Giovannoni, 2007).

Due to the economical relevance of these two fruits and the problems occurring in their preservation, they were selected as targets for the present work. Apples have a considerably longer shelf-life than those of many other climacteric species, nevertheless fruit quality deteriorates gradually after ripening (Wang et al., 2009). There are great differences in the rates of deterioration among cultivars, presenting loss of firmness, softness and mealiness as the main problems (Varela et al., 2008; Wang et al., 2009). Mango ripens quickly after harvest (between 3 and 9 days). This short period seriously restricts long distance marketing (Gomez-Lim, 1997). Sensitivity to disease as well as perishability due to ripening or softening of the fruit, limit its potential in terms of storage, packaging and transport (Mitra and Baldwin, 1997).

The objective of the present work was to produce new edible coatings, based in the mixture of novel galactomannans (extracted from seeds of *A. pavonina* and *C. pulcherrima*, two plants which are widespread in Brazil and have no commercial exploitation so far), collagen and glycerol, to characterize the coatings presenting the best coating ability (determined based on the wettability) in terms of their physical–chemical properties and to evaluate the use of these coatings on commercially important fruits (apple and mango) featuring different respiration patterns.

2. Materials and methods

2.1. Plant material

The seeds of *A. pavonina* and *C. pulcherrima* were collected in the Federal University of Ceará, Campus of Pici, Fortaleza, CE, Brazil during June 2006 and after being cleaned they were maintained in a cool, dry place until further use.

2.2. Animal material

The soluble anionic collagen was prepared by alkaline treatment of bovine intestinal submucosal tissue, at 20 °C for a period of 72 h, followed by homogenization in 0.5 mol L^{-1} acetic acid (Merck, Germany) solution and brought to a final collagen concentration of 10 g L^{-1} (Goissis et al., 1994).

2.3. Galactomannan extraction

The polysaccharide extraction was performed as described previously (Cerqueira et al., 2009). In this process, the seeds were removed from the pods, cleaned and placed in a blender, where they were mechanically broken. After this operation, the endosperm was manually separated from the germ and the hull and was suspended in ethanol (purity 99.8%, Riedel-de Haën, Germany) at 70 °C for 15 min. The ethanol was decanted and distilled water was added in a proportion of 1:5 (endosperm:water); the resulting suspension was left to rest for approximately 24 h. Then water, in a proportion of 1:10 (suspension:water) was added and mixed in a blender for 5 min. The endosperm mixed in the blender was filtered through a nylon net followed by a centrifugation step at 3800*g* (Sigma 4K, B. Braun, Germany) for 20 min at 20 °C. The precipitation of the galactomannan was achieved by adding the supernatant to ethanol (purity 99.8%, Riedel-de Haën, Germany) at a ratio of 1:2. The ethanol was decanted and the precipitated galactomannan was lyophilized (Christ, alpha 2–4, Germany) and maintained in a dry place until further use.

2.4. Coating and film preparation

The coating solutions (blends) were prepared dissolving the lyophilized galactomannans in distilled water followed by the addition of the collagen solution and the plasticizer (glycerol 87%, Panreac, Spain). Analyses were performed with different galactomannan concentrations (0.5%, 1.0% and 1.5% (w/v)) with different collagen concentrations (0.5%, 1.0% and 1.5% (w/v)), obtaining different galactomannan/collagen ratios, and varying plasticizer (glycerol) concentrations (0%, 0.5%, 1.0% and 1.5% (v/v)) (see Table 1 for details). The concentrations were chosen based on preliminary experiments. Galactomannan and collagen blends present good miscibility at the concentrations used. Solutions were homogenized during 5 min at room temperature (20 °C) and left to stabilize during 10 min. The wettability of these solutions was

Table 1
Galactomannan (from *A. pavonina* and *C. pulcherrima*), collagen, and glycerol concentrations used in coating formulation, and galactomannan/collagen ratios.

Sample	Galactomannan % (w/v)	Collagen % (w/v)	Galactomannan/ collagen ratio	Glycerol % (w/v)
S.1	0.5	1.5	1/3	0.0
S.2	1.0	1.0	1	0.0
S.3	1.5	0.5	3	0.0
S.4	0.5	1.5	1/3	0.5
S.5	1.0	1.0	1	0.5
S.6	1.5	0.5	3	0.5
S.7	0.5	1.5	1/3	1.0
S.8	1.0	1.0	1	1.0
S.9	1.5	0.5	3	1.0
S.10	0.5	1.5	1/3	1.5
S.11	1.0	1.0	1	1.5
S.12	1.5	0.5	3	1.5

determined (see Section 2.6) in order to select the blends with the best wettability values in mango and apple. The films were prepared with a constant amount (28 mL) of solution, which was cast onto a 9 cm diameter glass plate in order to maintain the film thickness. The films were dried in an oven at 35 °C during 16 h. Films were maintained at 20 °C and 50% RH, before permeability, colour and mechanical tests were performed.

2.5. Fruits conditioning

Mangoes and apples were purchased from a local supermarket (Braga, Portugal). All fruits were kept at 8–10 °C until further use. The fruits were selected for their uniformity, size, colour and absence of damage and fungal infection. Before testing, the fruits were left at room temperature (20 °C) and their surface was cleaned with distilled water. Thin portions of the outer surface (skin) of the fruits were cut with a knife and placed on a glass plate. Three fruits were used for each of the contact angle and surface tension measurements, providing a total of 20 skin portions.

2.6. Wettability

The wettability was studied by determining the values of the spreading coefficient (W_s) and the works of adhesion (W_a) and cohesion (W_c). The adhesive forces promote the liquid spreading in a solid surface and the cohesive forces promote their contraction. The wetting behaviour of the solutions will mainly depend on the balance between these forces. The surface tension of the coating solution was measured by the pendant drop method using the Laplace–Young approximation (Song and Springer, 1996).

The contact angle (θ) of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: solid–vapour (γ_{SV}), solid–liquid (γ_{SL}), and liquid–vapour (γ_{LV}). The equilibrium spreading coefficient (W_s) is defined by Eq. (1) (Rulon and Robert, 1993) and can only be negative or zero.

$$W_s = W_a - W_c = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (1)$$

where W_a and W_c are the works of adhesion and cohesion, defined by Eqs. (2) and (3), respectively.

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (2)$$

$$W_c = 2\gamma_{LV} \quad (3)$$

To obtain this parameter it is necessary to determine the contact angles of the coating on the surface of the fruits. Contact angle (θ) and liquid–vapour surface tension (γ_{LV}) were measured in a face contact angle meter (OCA 20, Dataphysics, Germany). The samples of the coatings were taken with a 500 μL syringe (Hamilton, Switzerland), with a needle of 0.75 mm of diameter. The contact angle at the fruit surfaces was measured by the sessile drop method (Newman and Kwok, 1999). In order to do this, a droplet of the tested liquid was placed on a horizontal surface and observed with a face contact angle meter. Measurements were made in less than 30 s. Twenty replicates of contact angle and surface tension measurements were performed at (20 ± 1) °C.

An estimation of the critical surface tension (γ_c) of the fruits' surface was obtained by extrapolation from the Zisman plot (Zisman, 1964), which was built using water, formamide and bromonaphthalene as reference liquids. The Zisman method, described below, is applicable only to systems with a surface tension below 100 mN m^{-1} (low-energy surfaces); therefore it is necessary to determine the surface energy of apple and mango to confirm the applicability of that method.

Several authors had developed the idea that interfacial liquid–vapour tension can be separated in polar and dispersive components (Owens and Wendt, 1969; Kaelble, 1970).

The polar and dispersive contributions to the superficial tension are added, yielding:

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad \gamma_S = \gamma_S^d + \gamma_S^p \quad (4)$$

For a pure liquid, polar (γ_L^p) and dispersive (γ_L^d) interactions are known, and if the contact angle between that liquid and a solid is obtained, the interaction can be described by:

$$W_a = W_a^d + W_a^p \Longleftrightarrow W_a = 2 \cdot \left(\sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \right) \quad (5)$$

$$\frac{1+\cos\theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \quad (6)$$

The contact angle determinations of at least three pure compounds on the surface of vegetables will allow the calculation of both the independent variable, $\left(\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} \right)$, and the dependent variable, $\left(\frac{1+\cos\theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} \right)$, from Eq. (6).

The surface tension, the dispersive and the polar component were, respectively, 72.10, 19.90 and 52.20 mN m^{-1} for water, 44.40, 44.40 and 0.00 mN m^{-1} for bromonaphthalene and 56.90, 23.50 and 33.40 mN m^{-1} for formamide (Busscher et al., 1984).

The estimation of the critical surface tension (γ_C) was performed by extrapolation from Zisman plots (Zisman, 1964). Zisman plots have long been used to characterize the wettability of low-energy surfaces. Zisman plots are obtained by plotting the cosine of the contact angle of pure liquids on a solid surface to be studied against the surface tension of the same series of liquids. The intercept of these curves with $\cos\theta = 1$ is known as the critical surface tension (γ_C). The critical surface tension is an imaginary point of the γ_{SV} value and it is frequently used to describe the wettability of a surface. It represents the value of γ_{LV} of a liquid above which the spreading of this liquid in a solid surface is complete. The critical surface tension (γ_C) is defined as:

$$\gamma_C = \lim \gamma_{LV} \quad \text{as } \theta \to 0 \quad (7)$$

2.7. Film thickness

The film thickness was measured with a hand-held digital micrometer (No. 293–561, Mitutoyo, Japan) having a sensitivity of 0.001 mm. This measurement was carried out at the end of the permeability test to avoid the effect of mechanical damage that could be caused on the film during the thickness measurement. Five thickness measurements were taken on each testing sample in different points and the mean values were used in permeability and mechanical calculations.

2.8. Oxygen and carbon dioxide permeability

Oxygen permeability (O_2P) and carbon dioxide permeability (CO_2P) were determined based on ASTM D 3985-02 (2002) method. The films were sealed between two chambers, having each one two channels. In the lower chamber O_2 (or CO_2) was supplied at a controlled (J&W Scientific, ADM 2000, USA) flow rate to maintain its pressure constant in that compartment. The other chamber was purged by a stream of nitrogen, also at controlled flow. Nitrogen acted as a carrier for the O_2 (or the CO_2).

In the case of O_2P measurement, the flow leaving this chamber was connected to an O_2 sensor (Mettler Toledo, Switzerland) which measured the O_2 concentration in that flow on-line. In the case of CO_2P measurement the flow leaving this chamber was collected in a syringe for CO_2 quantification. To determine CO_2 concentration, 1 mL of sample was injected in a gas chromatograph (Chrompack 9001, Middelburg, The Netherlands) at 50 °C with a column Porapak Q 80/100 mesh 2 m × 1/8 in. × 2 mm SS, using a thermal conductivity detector (TCD) at 110 °C. Helium at 23 mL min^{-1} was used as carrier gas. A standard mixture containing 10% CO_2, 20% O_2 and 70% N_2 was used for calibration.

The flows of the two chambers were connected to a manometer to ensure the equality of pressures (both at 1 atm.) between both compartments. As the O_2 (and the CO_2) was carried continuously by the nitrogen flow, it was considered that partial pressure of O_2 (and the CO_2) in the upper compartment is null, therefore ΔP is equal to 1 atm. Three replicates were obtained for each sample, in each case (O_2P and CO_2P).

2.9. Water vapour permeability measurement

The water vapour permeability (WVP) of the films was determined gravimetrically based on the ASTM E96-92 method (Mc Hugh et al., 1993; Guillard et al., 2003). The test film was sealed on the top of a permeation cell containing distilled water (100% RH; 2.337×10^3 Pa vapour pressure at 20 °C), placed in a desiccator which was maintained at 20 °C and 0% RH (0 Pa water vapour pressure) with silica gel. The water transferred through the film and adsorbed by the desiccant was determined from the weight loss of the permeation cell. The cups were weighed at intervals of 2 h for 10 h. Steady-state and uniform water pressure conditions were assumed by maintaining the air circulation constant outside the test cup by using a fan inside the desiccator (Mc Hugh et al., 1993). The slope of weight loss versus time was obtained by a linear regression. The measured WVP of the films was determined as follows:

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \cdot L}{\Delta P} \tag{8}$$

where WVTR is the water vapour transmission rate (g m^{-2} s^{-1}) measured through a film, L is the mean film thickness (m), and ΔP is the partial water vapour pressure difference (Pa) across the two sides of the film. The measurements were repeated three times for each film.

2.10. Colour and opacity

The colour and opacity of films were determined with a Minolta colorimeter (Cr 400; Minolta, Japan). A white standard colour plate ($Y = 93.5$, $x = 0.3114$, $y = 0.3190$) was used as a background for colour measurements of the coated films, and the L^*, a^*, b^* values of each film were evaluated by reflectance measurement.

The opacity of a material is an indication of how much light passes through it: the higher the opacity, the lower the amount of light that can pass through the material. Generally, the opacity is calculated from reflectance measurements. The opacity of the samples was determined according to the Hunter lab method, as the relationship between the opacity of each sample on a black standard (Y_b) and the opacity of each sample on the white standard (Y_w) (Eq. (9)). The measurements were repeated three times for each film.

$$\text{Opacity } (\%) = \frac{Y_b}{Y_w} \cdot 100 \tag{9}$$

2.11. Mechanical properties

TS and E were measured with an Instron Universal Testing Machine (Model 4500, Instron Corporation, USA) following the guidelines of ASTM method D 882-91 (1991). The initial grip separation was set at 30 mm and the crosshead speed was set at 5 mm min^{-1}. TS was expressed in MPa and was calculated by dividing the maximum load (N) by the initial cross-sectional area (m^2) of the specimen. E was calculated as the ratio of the final length at the point of sample rupture to the initial length of a specimen (30 mm) and expressed as a percentage. According to the ASTM standard, film strips with a length of 45 mm and a width of 20 mm were used. The measurements were repeated five times for each film.

2.12. Coating application

The fruits, after being cleaned with distilled water, were coated with the selected solution by brushing the surface until all of it was covered, being the residual coating allowed to drip off. Fruits were left during 4 h at 20 °C until the coating was dry. Two groups of coated fruits were prepared: with apples coated with 0.5% *C. pulcherrima* galactomannan, 1.5% collagen and no glycerol, an another with mangoes coated with 0.5% *A. pavonina* galactomannan, 1.5% collagen and 1.5% glycerol. Two control groups, one of each of the fruits, without coatings were also prepared. These fruits were used for the determination of O_2 and CO_2 transfer rates.

2.13. O_2 and CO_2 transfer rates

The O_2 and CO_2 production/consumption rates in apple and mango were measured by placing fruits inside a hermetic jar and closing it. The air circulation was promoted inside the jar by using a miniature fan. The atmosphere inside the jar was measured by drawing the gas samples with a 1 mL syringe through a septum fitted in the jar lid. The O_2 and CO_2 content in the jar was determined using a gas chromatograph (Chrompack 9001, Middelburg, Netherlands) at 50 °C with a column mol sieve 5A 80/100 mesh 1 m × 1/8 in. × 2 mm to separate the O_2 and a column Porapak Q 80/100 mesh 2 m × 1/8 in. × 2 mm SS to separate the CO_2 using a thermal conductivity detector (TCD) at 110 °C. Helium at 23 mL min^{-1} was used as carrier gas. A mixture containing 10% CO_2, 20% O_2 and 70% N_2 was used as standard for calibration. All determinations were performed at 20 ± 1 °C during 60 h. For O_2 and CO_2 transfer rates determination three replicates were performed for each of the control group and for each of the coated fruits groups. In each of the replicates three fruits were used.

2.14. Statistical analyses

The statistical analyses of the data were performed using Analysis of Variance (ANOVA), Tukey mean comparison test ($p < 0.05$) and regression analysis (SigmaStat, Trial Version, USA). The W_s data presented in the surface plots was adjusted to polynomial equations using Statistica software (Release 7, Edition 2004, Statsoft, Tulsa, OK, USA).

3. Results and discussion

3.1. Surface and critical surface tension

The estimated values of the polar and dispersive components of the surface tension are 1.71 and 24.77 mN m^{-1} for mango, and 0.68 and 27.13 mN m^{-1} for apple, respectively. The surface tensions of the mango and apple are the sum of the two components (26.48 and 27.81 mN m^{-1}, respectively). Both fruits have therefore low-energy surfaces. This type of surface interacts with liquids primarily through dispersion forces (Rulon and Robert, 1993).

Once both values of the surface tension are lower than 100 mN m^{-1}, the Zisman method can be applied to estimate the critical surface tension by extrapolation from the corresponding Zisman plot. The values obtained in the present work were 19.5 mN m^{-1} for mango and 25.4 mN m^{-1} for apple, and are in agreement with those published in other works with values of 17.4 mN m^{-1}, 18.8 mN m^{-1} and 23 mN m^{-1} to tomato, strawberry and orange, respectively (Casariego et al., 2008; Hagenmaier and Baker, 1993). It must be noted that critical surface tension values should be lower than the surface tension values for a given surface (Dann, 1970). The results obtained in the present work are in agreement with this requirement.

3.2. Wettability

The optimization of the composition of the coating solutions based on their ability to spread over a surface can be made considering three parameters: the wettability, the adhesion and the cohesion coefficients. The control of the adhesion and cohesion coefficients is very important because if the former promotes the spreading of the liquid, the later promotes its contraction (Ribeiro et al., 2007) and an adequate equilibrium between these two forces is necessary. The wettability was evaluated by determining the values of the spreading coefficient (W_s). Wettability is one of the most important properties when evaluating the capacity of a solution to coat a designated surface.

Fig. 1a represents the variation of the spreading coefficient of the coating solutions on mango versus their glycerol concentrations, for different ratios of galactomannan of *C. pulcherrima* – collagen in the coating solution. The experiments were repeated with mango using the galactomannan of *A. pavonina*, in replacement of the galactomannan of *C. pulcherrima*; the results are shown in Fig. 1b.

Fig. 1a and b shows that W_s values increase (approaching zero) for higher glycerol concentrations when a galactomannan/collagen ratio of 1/3 was maintained. Similar results were observed for the coatings with a galactomannan/collagen ratio of 1. Results also show that the increase of galactomannan/collagen ratio (corresponding to an increase of galactomannan concentration and a decrease of collagen concentration) leads to lower values of W_s. This behaviour is clear from Eq. (10) that represents the surface plotted in Fig. 1a, where GCR stands for "galactomannnan/collagen ratio". The equation coefficients show that the glycerol concentration has a statistically significant effect on W_s ($p > 0.05$); only when multiplied by galactomannan/collagen ratio (GCR) or when its squared value is considered. Eq. (11) represents the surface fitted in Fig. 1b. In this case, glycerol concentration only exerts statistically significant influence ($p < 0.05$) when multiplied by the galactomannan/collagen ratio.

$$W_s = -42.7390 - 15.8008\ \mathrm{GCR} + 4.4881\ \mathrm{GCR}^2 + 4.0350\ \mathrm{glycerol}^2 - 5.2180\ \mathrm{GCR}\cdot\mathrm{glycerol} \quad (p < 0.05) \quad R^2 = 0.76 \qquad (10)$$

$$W_s = -26.6101 - 31.0150\ \mathrm{GCR} + 8.1603\ \mathrm{GCR}^2 - 2.2649\ \mathrm{GCR}\cdot\mathrm{glycerol} \quad (p < 0.05) \quad R^2 = 0.77 \qquad (11)$$

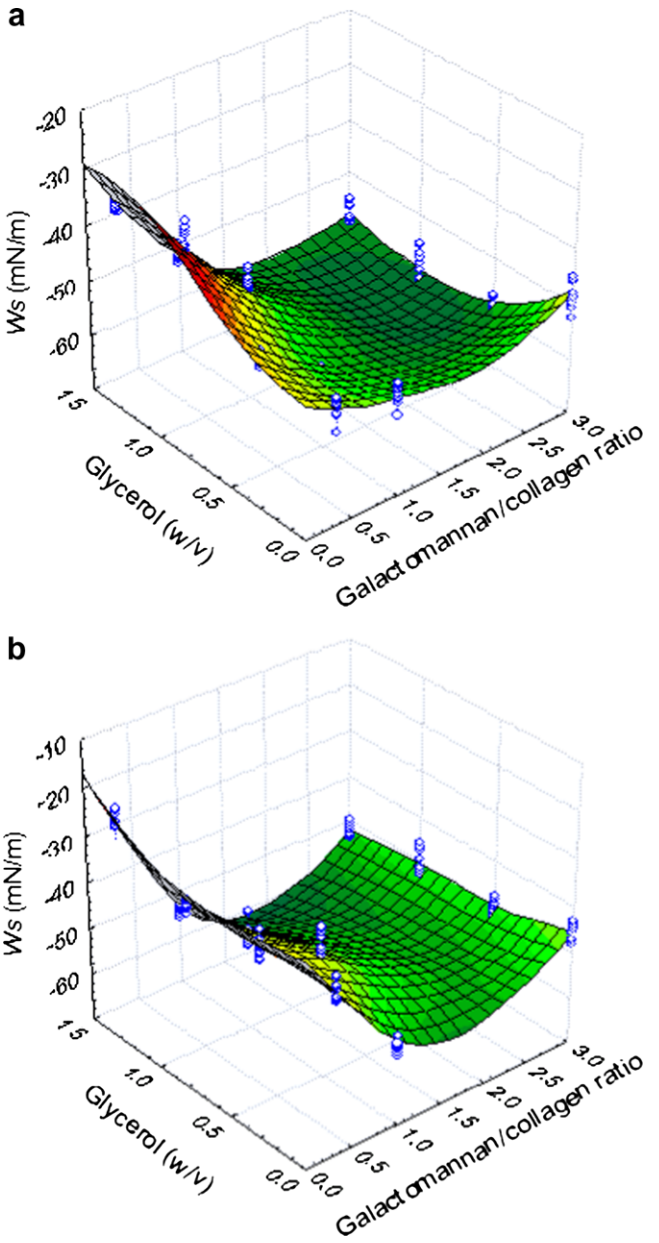

Fig. 1. Spreading coefficient (W_s) values (surface colours indicate different values of W_s) for different galactomannan of *C. pulcherrima* – collagen ratios and glycerol (a) and for the galactomannan of *A. pavonina* – collagen ratios and glycerol (b) on mango.

As shown in Eq. (1), W_s values are influenced by the values of the work of adhesion (W_a) and work of cohesion (W_c). While W_c presents a similar behaviour for all the studied coatings (results not shown), it was observed that W_a displays a similar trend to the values of W_s (results not shown). This means that the W_s values of the coatings on the studied fruits were mostly influenced by the adhesion of the coatings to the fruit surface, and not by the cohesion forces within the coating solution. These are usually influenced by the presence of surfactants, which were not used in this work (see e.g. Choi et al., 2002).

Fig. 1 shows that the coatings formed with galactomannan from *A. pavonina* present lower values of W_s when compared with coatings formed with galactomannan of *C. pulcherrima*. The W_s values ranged from −53.38 to −29.07 mN m^{-1} for *A. pavonina* coatings and between −59.63 and −36.59 mN m^{-1} for *C. pulcherrima* coatings. These differences may be explained by the different monosac-

charide composition of each galactomannan. *C. pulcherrima* galactomannan contains a higher relative amount of mannose and, when dissolved in aqueous solutions, it also presents higher values of intrinsic viscosity, when compared with solutions formulated with galactomannan of *A. pavonina* (Cerqueira et al., 2009). In some way these properties may explain the W_s values obtained for the coatings of these two galactomannans, considering that the higher viscosity possibly contributes to a decrease of the values of W_a.

Fig. 2a represents the variation of the spreading coefficient of the coating solutions on apple versus their glycerol concentrations, for different ratios of galactomannan of *C. pulcherrima* – collagen. Fig. 2b represents the variation of the spreading coefficient of the coating solutions on apple versus their glycerol concentrations, for different ratios of galactomannan of *A. pavonina* – collagen in the coating solutions. Fig. 2a and b shows that the best W_s values obtained for the coatings on apple correspond to the coating solutions without glycerol. This is possibly associated to the particularity that the apple surface presents a high dispersive component, denoting a predominance of apolar forces, while glycerol is a polar substance; therefore, its presence would decrease the spreadability of the coating. In the case of mango (see Fig. 1a and b), which has a lower dispersive component, the presence of glycerol improves the spreadability of the solution. Following this line of thought, it should be highlighted here that the values of W_s are closer to zero (thus corresponding to a better spreadability) when the coatings were applied on the mango surface. As explained above, W_c values present similar trends for all the studied coatings, but the adhesion forces (represented by W_a) present higher values for mango surfaces. This behaviour is consistent with the idea of the higher polar and lower dispersive component of the mango surface presenting a better interaction with the polar solutions used in the coatings' formulation.

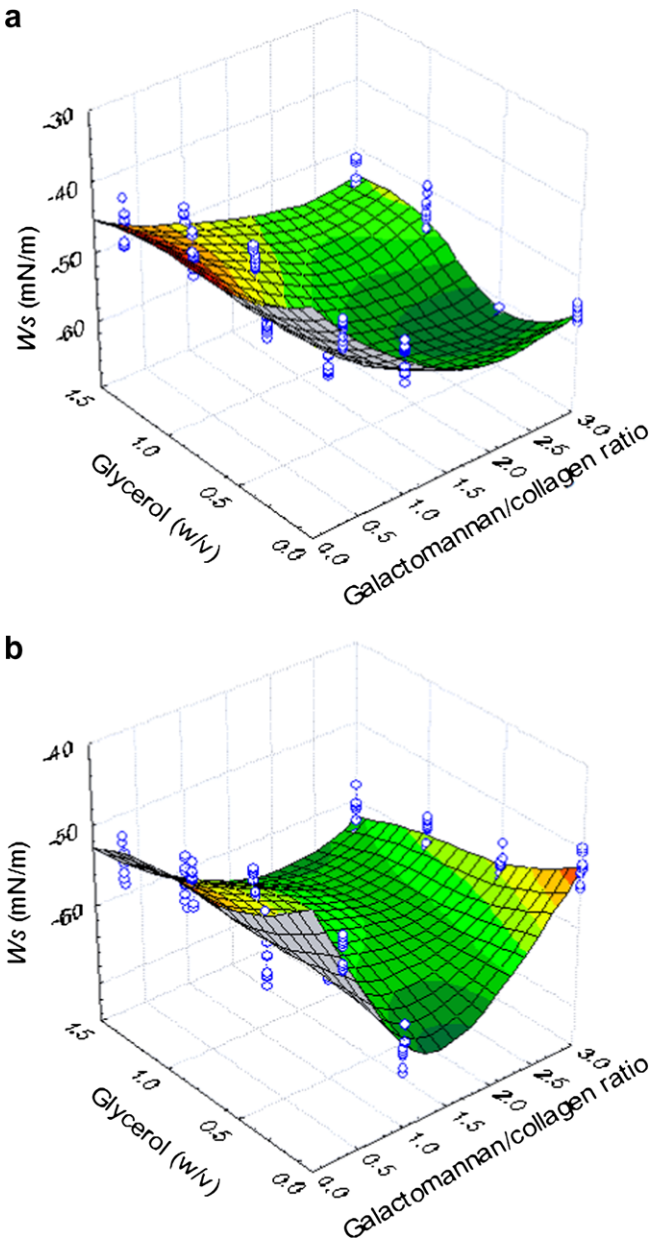

Fig. 2. Spreading coefficient (W_s) values (surface colours indicate different values of W_s) for different galactomannan of *C. pulcherrima* – collagen ratios and glycerol (a) and for different galactomannan of *A. pavonina* – collagen ratios and glycerol (b) on apple.

Eq. (12) represents the surface plotted in Fig. 2a, where GCR stands for "galactomannan/collagen ratio". This equation shows that all the factors are statistically significant ($p < 0.05$). When *A. pavonina* galactomannan is used in the coatings formulation, the fitted regression to the surface (represented in Fig. 2b) shows that glycerol concentration is significant only when multiplied by the galactomannan/collagen ratio (Eq. (13)).

$$W_s = -39.2385 - 14.4117\,\mathrm{GCR} + 2.7733\,\mathrm{GCR}^2 - 10.0921\,\mathrm{glycerol} + 5.3869\,\mathrm{glycerol}^2 + 1.7179\,\mathrm{GCR}\cdot\mathrm{glycerol} \quad (p < 0.05) \quad R^2 = 0.64 \tag{12}$$

$$W_s = -49.5081 - 15.5014\,\mathrm{GCR} + 4.6242\,\mathrm{GCR}^2 - 1.9550\,\mathrm{GCR}\cdot\mathrm{glycerol} \quad (p < 0.05) \quad R^2 = 0.53 \tag{13}$$

The best values of the spreading coefficients for mango were obtained with blends of 0.5% of galactomannan of *A. pavonina*, 1.5% of collagen and 1.5% of glycerol ($W_s = -29.07$ mN m^{-1}). The best values of the spreading coefficients for apple were obtained with blends of 0.5% of galactomannan of *C. pulcherrima*, 1.5% of collagen and no glycerol ($W_s = -42.79$ mN m^{-1}).

The best solutions in terms of wettability (represented by the spreading coefficient – W_s) were analyzed for the permeability to water vapour, oxygen and carbon dioxide and also characterized in terms of their mechanical properties.

3.3. Water vapour, oxygen and carbon dioxide permeability

Fig. 3 shows the differences of oxygen permeability (O_2P), carbon dioxide permeability (CO_2P) and water vapour permeability (WVP) between the films made with the coating solutions under consideration. The sample with 0.5% of *A. pavonina* galactomannan, 1.5% of collagen and 1.5% glycerol is less permeable to oxygen (O_2P) than the sample with 0.5% *C. pulcherrima* galactomannan, 1.5% of collagen and no glycerol with values of 1.08×10^{-15} and 4.07×10^{-15} g m Pa^{-1} s^{-1} m^{-2}, respectively. It is known that the addition of plasticizer decreases the presence of cracks and pores, improving the dispersion and decreasing the gas permeability (Garcia et al., 2000), thus the results shown here can be explained in light of these facts. Similar results were obtained for carbon dioxide permeability (CO_2P). For this particular property, the film with 0.5% of *A. pavonina* galactomannan, 1.5% of collagen and 1.5% glycerol is approximately 18 times less permeable to CO_2 than the one with 0.5% of *C. pulcherrima* galactomannan; 1.5% of collagen and no glycerol with values of 0.20×10^{-15} and 3.62×10^{-15} g m Pa^{-1} s^{-1} m^{-2}, respectively. The obtained values are in agreement with the results of other authors. Brindle and Krochta (2008) obtained values ranging between of 1.70×10^{-15} and 1.82×10^{-15} g m Pa^{-1} s^{-1} m^{-2} of O_2P for films made from blends

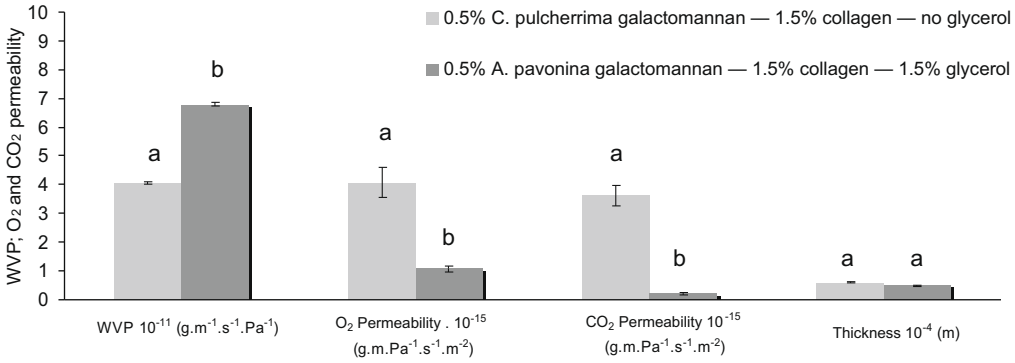

Fig. 3. Water vapour permeability (WVP), oxygen permeability (O_2P) and carbon dioxide permeability (CO_2P) properties of coatings based on galactomannan–collagen blends and the respective standard deviations (Δ 0 5% *C. pulcherrima* galactomannan, 1.5% collagen, no glycerol; ▲ 0.5% *A. pavonina* galactomannan, 1.5% collagen, 1.5% glycerol). Different letters indicate a statistically significant difference (Tukey test, $p < 0.05$; values reported are the means ± standard deviations; $n = 3$, 95% confidence interval).

of whey protein and hydroxypropylmethylcellulose. Gounga et al. (2007) present values of O_2P ca. 5.79×10^{-15} g m Pa^{-1} s^{-1} m^{-2} for films with ratios of pullanan and whey protein isolate similar to those used in this work. In 2007, Han and Krochta reported that whey protein films have O_2P values of 2.09×10^{-15} g m Pa^{-1} s^{-1} m^{-2}.

In terms of the water vapour permeability (WVP) the opposite occurs as observed for CO_2 and O_2 permeability values. The coating with 0.5% *C. pulcherrima* galactomannan, 1.5% collagen and no glycerol is approximately 60% less permeable to water vapour than the coating with 0.5% *A. pavonina* galactomannan; 1.5% collagen and 1.5% glycerol, with the values of permeability decreasing from 6.79×10^{-11} to 4.06×10^{-11} g m^{-1} s^{-1} Pa^{-1}. The plasticizer decreases the intermolecular attractions between polymeric chains, facilitating the penetration of polar water vapour molecules (Kester and Fennema, 1986). Glycerol is a hydrophilic molecule (polar) and an increase of its concentration causes an increase of water vapour mass transfer. Being apolar, CO_2 and O_2 possibly do not penetrate so easily in such a polar moiety. Gómez-Estaca et al. (2009) obtained similar values for the WVP of bovine-hide and tuna-skin gelatine films (6.11×10^{-11} and 4.58×10^{-11} g m^{-1} s^{-1} Pa^{-1}, respectively). Fig. 3 shows the values for the thickness of the films. There is no statistical difference between them ($p > 0.05$) possibly due to the fact that the same concentrations of galactomannan and collagen were used.

3.4. Colour and opacity

The colour measurement was performed by determining the values of the parameters L^*, a^* and b^*, and the results are presented in Table 2. Comparing the two coatings it is possible to observe that the coating with 0.5% *A. pavonina* galactomannan, 1.5% collagen and 1.5% glycerol has higher values of L^* (94.52) and b^* (5.84). Its colour tended to yellowish as indicated by the increase of b^*. The coating with 0.5% *C. pulcherrima* galactomannan, 1.5% collagen and no glycerol presented a somewhat lower L^* value (91.85) and a higher a^* value (5.23) as compared to the *A. pavonina* coating. It indicates that the colour of this coating tends to be somewhat darker and reddish. These values are similar to the colour values obtained for films of whey protein isolate, with values of 97.09 and 3.54 to L^* and b^*, respectively. However, the films presented in the present work have shown a positive a^*, while the values of a^* for whey protein isolate films were negative; that can be explained by the presence of the polysaccharide, in one case, and the different origin of the protein, in the other (Sothornvit et al., 2009).

In terms of opacity, the coating with 0.5% *A. pavonina* galactomannan, 1.5% collagen and 1.5% glycerol is less opaque than the other coating tested. This characteristic is typical of protein-based coatings and it is one of the advantages of using collagen in the formulation, as transparency is a very valued property in films and coatings.

3.5. Mechanical properties

Mechanical properties can give good information on the compatibility of polymer mixtures. Normally, positive interactions between the components lead to a significant improvement in mechanical properties (Brindle and Krochta, 2008). The film with 0.5% *C. pulcherrima* galactomannan – 1.5% collagen – no glycerol has a higher value of tensile strength (TS) (117.56 MPa) and a lower value of elongation at break (E) (18.74%) when compared with the *A. pavonina* film (8.34 MPa and 47.17%, respectively). These results were expected due the presence of glycerol (plasticizer) that causes a reduction in the strength of the film although increasing its elasticity. Brindle and Krochta (2008) have shown a decrease of TS and an increase of E with the increase of glycerol and protein concentrations. The values of TS and E obtained for the film containing 0.5% *A. pavonina* galactomannan – 1.5% collagen – 1.5% glycerol are in agreement with the values obtained for similar

Table 2
Colour and opacity values of the selected films.

Film	L^* (black-white)	a^* (green-red)	b^* (blue-yellow)	Opacity (%)
0.5% C. pulcherrima Galactomannan – 1.5% Collagen – no glycerol	91.85 ± 0.38[a]	5.23 ± 0.01[a]	4.85 ± 0.12[a]	13.67 ± 0.01 [a]
0.5% A. pavonina Galactomannan – 1.5% Collagen – 1.5% glycerol	94.52 ± 0.66[b]	4.61 ± 0.04[b]	5.84 ± 0.03[b]	11.34 ± 0.01 [b]

[*] Values reported are the means and standard deviations ($n = 3$, 95% confidence interval). Different superscript letters in the same column indicate a statistically significant difference (Tukey test, $p < 0.05$).

amounts of whey protein: hydroxypropylmethylcellulose: glycerol, which were of 7.8 MPa and 47% for TS and *E*, respectively (Brindle and Krochta, 2008). Also, Osés et al. (2009) presented similar results of TS (11.5 MPa) for films of whey protein isolate and mesquite gum and sorbitol; on the other hand, a lower value of *E* (6.7%) was reported, which was explained by the lower value of plasticizer used in their work.

3.6. O_2 and CO_2 transfer rates in fruits

Apples were coated using a solution of 0.5% of *C. pulcherrima* galactomannan, 1.5% of collagen and no glycerol and their O_2 and CO_2 transfer rates were determined and compared with those of apples without coating. The coated apples were more glossy than the uncoated fruits. Visually inspection of the coated apples revealed a uniformly distributed coating, with no cracks or lamps, thus confirming the good wettability of the coating solution.

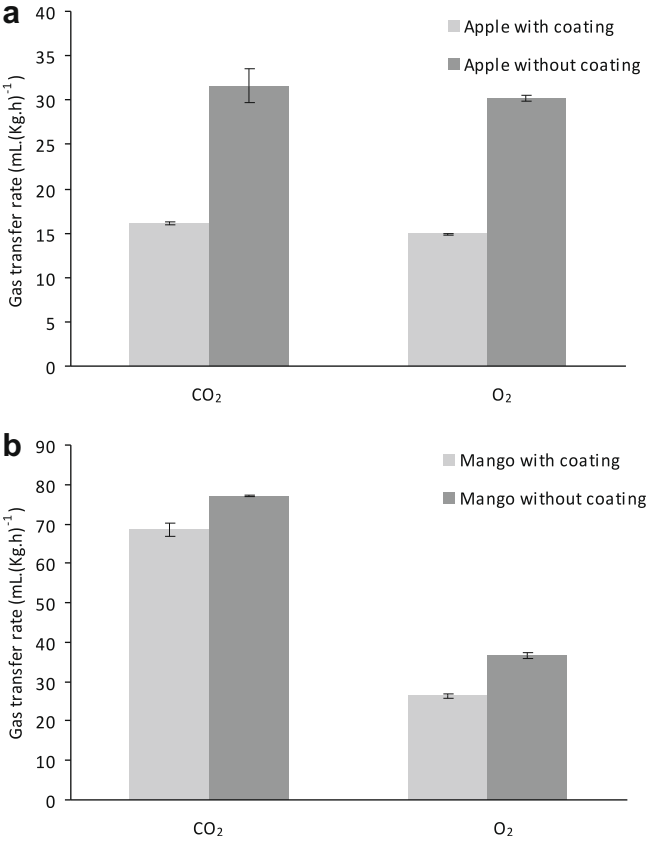

Fig. 4. O_2 and CO_2 transfer rate in coated and uncoated apples (a) and mangoes (b) (values reported are the means ± standard deviations; $n = 3$, 95% confidence interval).

The concentrations of the gases were measured during 60 h, the gas transfer rate was calculated and the results are presented in Fig. 4a. The coated apple permits a lower gas exchange. The CO_2 production and the O_2 consumption is approximately 50% lower in apples with coating than in apples without coating. The rate of CO_2 production is higher than that of O_2 consumption, both in coated an uncoated fruits. This is very important because it means that the presence of the coating does not alter the gas balance in the fruit; it just retards the gas transfer rates.

Mangoes were coated using a solution of 0.5% of *A. pavonina* galactomannan, 1.5% of collagen and 1.5% of glycerol. The mangoes were subjected to a visual inspection, similar to the one performed on apple. Also here the fruits were well coated, with a glossy appearance and no cracks or lumps were observed at the surface of the coating.

The O_2 and CO_2 transfer rates were compared with mangoes without coating. The gas concentrations were measured during 120 h, the gas transfer rate was calculated and the results are presented in Fig. 4b. The coated mango permits lower gas exchange rates. A 28% less O_2 consumption and 11% less CO_2 production is observed in coated mangoes when compared with mangoes without coating. Again, this is very important to maintain the gas balance inside the fruit.

The values obtained are in agreement with those reported in other works (Table 3). The higher values presented in this work are possibly related with the higher temperature at which the experiments were performed (20 °C), as the other works show that the increase of the temperature has a great influence in the values of the gas transfer rates.

4. Conclusions

This work shows how galactomannan–collagen blends can be used to decrease the fruits gas transfer rates, and how the wettability (W_s) can be used as a parameter for coating optimization. The fruits surfaces were found to be of low-energy and therefore the Zisman method was used to determine their wettability. Mango and apple fruits have the ability to participate in non-polar interactions, as a consequence of the higher values of the dispersive component, which was found to be higher in apples than in mangoes. The best values in terms of W_s were obtained for mango and apple with the following formulations, respectively: 0.5% of galactomannan of *A. pavonina*, 1.5% collagen and 1.5% of glycerol; and 0.5% of galactomannan of *A. pavonina*, 1.5% of collagen and no glycerol. This procedure is important in order to ensure that the application of the coating solutions on the fruits is made uniformly and easily, in view of future industrial uses. These two coatings were further characterized in terms of WVP, O_2P, CO_2P, TS, *E*, colour and opacity.

A 28% less O_2 consumption and 11% less CO_2 production were observed in coated mangoes when compared with mangoes without coating. In apples, the CO_2 production and the O_2 consumption was approximately 50% lower in the presence of the coating. It is important to note that in both cases (more in the case of apples

Table 3
Comparison of the gas transfer rates of different fruits and vegetables.

Fruit	RO_2 (mL kg^{-1} h^{-1})	RCO_2 (mL kg^{-1} h^{-1})	Conditions	Reference
Mango	26.4	68.7	20 °C, with coating	This study
Mango	36.6	77.1	20 °C, without coating	This study
Apple	14.9	16.1	20 °C, with coating	This study
Apple	30.2	31.6	20 °C, without coating	This study
Mango	14.5	16.5	5 °C, without coating	Ravindra and Goswami (2008)
Apple	19	22	20 °C, without coating	Mahajan and Goswami (2001)
Apple	–	1.0	0 °C, without coating	Kim et al. (1993)

than in the case of mangoes, but still relevant for both fruits), the gas balance inside the fruit was reasonably maintained due to reductions in both CO_2 production and O_2 consumption.

The results suggest that these coatings can reduce gas transfer rates in the studied fruits, and can therefore be important tools to extend their shelf-life.

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