Impact of Biodegradable Materials on the Quality of Plums

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Abstract: Edible starch-based materials have shown a positive impact on quality parameters. In this study, plums (Prunus domestica cv. Jojo) were divided into five groups: a control, two coating treatments (starch and starch-whey protein (80–20%), and two film systems (starch and starch-whey protein (80–20%). Biodegradable packaging, particularly the coating treatment, had no negative effect on color parameters. After 28 days of performed tests, firmness was boosted with starch and starch-whey protein (80–20%) films. With the coated materials, there was no significant difference compared to control group. The lowest transpiration velocity was of plums wrapped in starch films. In the case of respiration rate, no significant difference was observed between the packaging and control samples. After the conducted trials, the weight loss of untreated plums was at 10%, while 5% of weight loss was noticed for plums wrapped in starch materials, and around 6% was noticed for the other materials. Oxygen permeability was higher for S-WP films, the thickness of S and S-WP films were comparable and thickness of starch coating was around 60% higher than S-WP. Both films have an affinity to water and both show typical behavior of water vapor sensitive hydrophilic biopolymers. The starch film with the addition of 20% of proteins increased the resistance of gas exchanges, which represents one of its great benefits.

Keywords: edible films; coatings; packaging; plum; starch; whey protein

1. Introduction

Plums are a seasonal fruit. Postharvest storage life due to the acceleration of quality parameters loss such as firmness, color, total acidity and total soluble solids is relatively short. A cold storage is a method that inhibits fruit ripening by extenuation of the production of ethylene, respiration and transpiration rates, softening, pigment changes, boosting in total soluble solids, and the reduction in total acidity [1]. However, proper storage conditions are not enough to stop the perishable nature of plums and to preserve the fruit quality during transportation, storage, and marketing. Accordingly, additional postharvest technologies such as wrapping and coating in biodegradable matrices are necessary [1,2].

Coatings are soluble formulations applied on food surfaces as a thin layer of edible solution (based on saccharides, proteins, fats, their hybrids). After application (by casting, spraying, brushing, foaming, rolling or dipping) they are formed directly on the food surface or between different layers of components. Edible coatings might be applied onto food products as fish, meat, cheese, vegetable, and fruit to prevent at least the migration of selected gases, such as oxygen and water vapor. By the control of mass transfer, water vapor permeability, and aroma losses, edible coatings can potentially extend the lifespan.
and improve the quality of coated food stuff. In turn, films are thin layers produced separately from the food product. Beyond the barrier function, films act as information for the customers (printability) and have both a marketing function and protective function (lack of the direct contact with packaged product) [1–3].

Very promising biodegradable packages can be made from starch. Starch is a bio-based material with the potential to become a future environmentally friendly and every-day-use bio-plastic. Some selected natural polymers such as proteins or other polysaccharides blended with starch can create eco-friendly materials, and some of the drawbacks of starch could be improved by addition of other biomatrices [4].

In plants, transpiration is the substantial evaporation of water. This parameter is strongly affected by temperature and relative humidity. Respiration is an interchange of gas with an environment. During this exothermic redox reaction, energy, carbon dioxide, and water vapor are released while oxygen is absorbed. Subsequently, after harvest the weight of fruits and vegetables is constantly being reduced. These changes decrease the fruit firmness, having a negative effect on quality of the fruits and influencing parameters such as titratable acidity and microbiological factors. Consumers perceive this negatively. Fruits and vegetables that are quick to putrefy not only causing economic losses but, in the case of developing microbes, negatively affect peoples’ health (in particular, molds) [5].

The main goal of this work was the limitation of mass transfer, and therefore an increasing of the shelf-life of plums, with a film and coating made from starch and mixture of starch and whey protein (80–20%).

2. Materials and Methods
2.1. Materials

Wheat starch (S) was obtained by Hortimex (Konin, Poland). The whey protein isolate (WP, ~90% protein) BiPRO was purchased from Davisco Foods International Inc. (Le Sueur, MN, USA). Anhydrous glycerol (99.9% purity) was supplied from Sigma-Aldrich (Germany). 600 plums of the Prunus domestica variety Jojo were picked from the garden of the Institute for Agricultural Engineering Potsdam-Bornim ATB (Potsdam, Germany).

Materials Pretreatment

A total of 600 plums of the Prunus domestica variety Jojo were harvested in ripening time from 4 trees. Plums were picked from the garden of the Institute for Agricultural Engineering Potsdam-Bornim ATB (Potsdam, Germany) and they were directly transported to the laboratory. Fruits were put in a storage chamber (3.5 °C, 35% RH) and were kept there for one day. After that, the fruits were divided into five parts: fresh fruit in open plastic trays, coated in starch solution, coated in starch-whey protein solution (80%/20%), non-coated plums in plastic trays covered with starch films and non-coated plums in plastic trays covered with starch-whey protein films (80%/20%). There were six plums on each of these trays. That means that 20 trays with the same treated fruit were prepared for 10 days of measurements. Every week from the cooling room four trays of each sort were taken. Two trays were used for measurements on the same day and the next two were kept for four to five days at room temperature (to achieve the same conditions as in a grocery). The tests were then executed and the experiments were conducted for 28 days.

2.2. Preparation of Starch and Starch/Whey Protein Edible Films and Coatings

Wheat starch (S) and wheat starch-whey protein (S-WP) (in ratio 80–20%) film-forming aqueous solutions were prepared by casting method. Glycerol was used as a plasticizer at 50% w/w of the biopolymer dry weight (i.e., 50% of its total dry weight).

2.2.1. Starch and Whey Protein Gelatinization and Preparation

Wheat starch film-forming solutions were prepared by dissolving 5 g of wheat starch powder in 100 mL distilled water. Whey protein film-forming solutions were also prepared by dissolving 5 g of whey protein isolate in 100 mL distilled water. The solutions were
heated separately in beakers in a water bath under a 700 rpm stirring at 85 °C for 30 min to denature the whey protein and to obtain a complete gelatinization of starch to shift from crystalline structure of the starch granules into amorphous starch suspension. Then, film-forming solutions were cooled down to 40 °C. Glycerol was added. Solutions were cooled down to ambient room temperature (25 °C). Then, part of the solutions was used for films, and the second part as coatings.

2.2.2. Coating Process

A total of 120 plums in each of the groups (Figure 1a–c) were coated. The coated fruits were hung with a special holding fixture in order to prevent damage to the coating and at the same time to ensure unrestricted natural convection.

Figure 1. (a) Fresh, (b) coated, and (c) wrapped plums.

2.2.3. Film Casting and Making

In order to prepare the films, 30 mL of film-forming solutions (starch and starch-whey protein) were poured onto a Petri plate to obtain a constant film thickness of about 80 µm. Films were dried at 25 °C and 30% relative humidity (RH) for 48 h. Dry films were peeled off and stored for seven days in desiccators at 25 ± 1 °C and 53% ± 1% RH and using saturated magnesium nitrate prior to testing. With the second part of solutions (starch and starch-whey protein), fruits were immersed for 60 s, directly before the experiment. They were dried for several hours, until a light white coating appeared on the skin. The coating solution and fruit had the same temperature [6].

2.3. Transpiration Rate

In the beginning, each kind of plums (fresh, coated in starch solution, coated in starch/whey protein solution, wrapped in starch film, wrapped in starch/whey protein film) were taken out from cooling room (3.5 °C, 35% of RH) to the higher temperature...
room (around 22 °C, 35% of RH). In order to achieve the smallest losses in respiration and transpiration, the fruits were covered by a towel. The plums were kept there for around 4–5 h until the temperature of the fruit was equal to the temperature of the environment. After that, transpiration was conducted on fruits from two trays of each sort. The third and fourth trays with plums of each sort were kept under the towel for a couple of days, and the transpiration experiments were conducted. Prior to the measurement, the plums had been removed from the trays. Such differentiation was supposed to reflect the real conditions in greengrocers, markets, and bazars (i.e., places where plums are sold). Plums were weighed on a CPA 1003S balance (Sartorius, Göttingen, Germany), then the surface temperature was measured by a D-series microscanner (Exergen, Germany) in 5 points. To determine the transpiration rate, the weight loss over a time interval of 1.5 h was measured. The plums were placed on a wire mesh to ensure unrestricted natural convection. Both relative humidity and air temperature were measured in 2-min intervals using a capacitive humidity sensor FHA 646 R connected to an Almemo 2290-8 datalogger (Ahlborn, Holzkirchen, Germany). Total resistance (s·m⁻¹) of the plums was calculated by using special software set up for this measurement [7].

2.4. Respiration Rate

After the transpiration test measurement, the plums were weighed by CPA 1003S (Sartorius, Göttingen, Germany) and placed onto respiratory mesh at the same distance of 10 cm each other on the wire mesh (around 1 m × 1 m). The chambers were tightly closed and software for respiration (Atmung, ATB Potsdam, Germany) was switched on to monitor the gas composition in the chamber. After reaching the appropriate difference in gas levels, the chambers were opened and the temperature and weight were measured once again.

Respiratory CO₂ release of plums was determined in a closed system fitted with infrared sensors FYA600CO₂ (Ahlborn, Holzkirchen, Germany; range 0–5000 ppm) and resistance thermometers Pt100. Data were recorded with a Netdaq 2680 Series data acquisition unit (Fluke Deutschland, Kassel, Germany) at 2 min intervals. From the increase in CO₂ concentration over time within the closed Perspex cylinder (8.2 L) and the surface area of the fruit, respiration rates were calculated as mg CO₂ cm⁻²·h⁻¹.

2.5. Mass Loss

To characterize water losses in plum tissue, mass changes were calculated over time. At the beginning of the experiment, before and after every measurement, the fruit was weighed on a CPA 1003S balance (analytical balance, measuring range 210 g with readability 0.001 g) (Sartorius, Germany). The following equation was used:

\[
\text{weight loss} \, (\%) = \left( W_i - W_{sp} \right) / W_i \times 100\%
\]

where \( W_i \) is the initial weight (g) and \( W_{sp} \) is the weight at sampling period (g) [8].

2.6. Oxygen Permeability

Oxygen permeability was measured only for films using the manometric method according the ISO 15105-1 standard using the Brügger equipment, Type GDP-C (resolution 0.1 cm³/(m²·d·bar) (Brügger Feinmechanik GmbH, Germany). The test chambers of the permeation cell were first degassed in a vacuum, then the upper side was swept by an humidified oxygen flow at a rate of about 80 mL·min⁻¹ at atmospheric pressure. The increase in pressure in the downside chamber during the test period was assessed and displayed by an external computer. Data were recorded and permeability was calculated by GDP-C software (with temperature compensation). The sample temperature (25 °C) was adjusted using an external thermostat (HAAKE F3, Karlsruhe, Germany). The desired RH was regulated in an external saturation system (53% and 75% RH), so humidified oxygen gas circulated in the permeation cell [9].
2.7. Moisture Sorption Isotherms

The sorption isotherm of films was determined at 25 °C. Samples of films were cut into stripes (2 cm × 2 cm) and weighed to the nearest 0.0001 g into pre-weighed vials. Films (ten sets of samples) were equally stored in 10 sets of samples in desiccators, each containing a different saturated salt solution which fixed the relative humidity (RH) at 25 °C. A wide range of RH was selected: calcium chloride (~3%), lithium chloride (11%), potassium acetate (22%), magnesium chloride (33%), potassium carbonate (43%), magnesium nitrate (53%), sodium nitrate (65%), sodium chloride (75%), ammonium sulphate (81%) and ammonium dihydrogenphosphate (93% RH). Film samples were weighed to detect the weight when equilibrium moisture content was attained. The water content was checked for up to nine months in each desiccator. The final (equilibrium) water content was checked by drying the films at 105 °C for 24 h. The amount of water absorbed is expressed as a gram of water per gram of dry matter. Measurements were made in triplicate for each film recipe.

Sorption isotherms of water vapor were fitted with the Guggenheim-Anderson-deBoer GAB model (Equation (2)), for water activities up to 0.85 [10]:

\[
m = \frac{m_0 \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C \cdot K \cdot a_w)}
\]

where \( m \) is the water content at equilibrium, \( m_0 \) is the water of water related to the monolayer, \( a_w \) is the water activity of the sample, and \( C \) and \( K \) are constants relating to the sorption enthalpy of the first and of subsequent layers, respectively. The GAB model was fitted to experimental values using TableCurve (Systat Software, Inc., San Jose, CA, USA).

2.8. Coating Thickness

Using the measurements of water content in the films, data from sorption isotherms and the fresh mass of the coating thickness were calculated. These were assessed according to the following equations:

\[
V = \frac{\Delta m}{\rho}
\]

\[
e = \frac{V}{A}
\]

\[
A = 0.809 \times FM + 19.405
\]

where \( V \) is the volume of film-forming solution (cm³), \( \Delta m \) the mass of film forming solution (g), \( \rho \) the density of film-forming solution (g cm⁻³), \( e \) the mean thickness of coating layer onto a fruit (cm), \( FM \) the fruit mass (g), and \( A \) the fruit surface area (cm²). The equations were established from preliminary experiments. 36 plums were scanned using a camera-supported 3D scan system ScanBook along with ScanWare Enterprise 3.8 software (Scanbull, Hameln, Germany). The measured surface area was set into relation to fruit mass, found by a regression analysis. This formula (Equation (5)) is valid only in the range between 30 and 80 g of fruit mass.

The relevant mass of film forming solution \( \Delta m \) was determined from the weight variation of plums after the coating process (dipping) [7].

2.9. Film Thickness

Film thickness was measured with a PosiTector 6000 (DeFelsko, Ogdensburg, NY, USA) digital micrometer to the nearest 1 µm in 0–100 µm range and to the nearest 5 µm in the 100–1000 µm. Prior to film thickness measurements, the electronic gauge was calibrated at 74 and 139 µm using standards to be close to the thicknesses of samples. The thickness of each film was measured in five places (one in the center part of the film and four around its perimeter), and an average value was taken for the calculations. At least 10 replications of each formulation have been made [9].
2.10. Colour Parameters of Films and Coated Plums

The color of the films was determined using a colorimeter Model CR-300 (Minolta, Japan) using the CIE LAB color parameters: \( L^* \), from black (0) to white (100); \( a^* \), from green (−) to red (+); and \( b^* \), from blue (−) to yellow (+). The film color was expressed as the total color difference (\( \Delta E \)) and color chroma \( C \) according to the following equations [11]:

\[
\Delta E = \sqrt{(L - L^*)^2 + (a - a^*)^2 + (b - b^*)^2} \quad (6)
\]

\[
C = \sqrt{a^2 + b^2} \quad (7)
\]

where \( L^* \), \( a^* \), \( b^* \), and \( C \) are the color parameters of a white standard support used as the film background (\( L^* = 96.74, a^* = 0.09, b^* = 2.20 \)).

The same color parameters of coated and uncoated plum skin were determined individually in the six fruits of each replicate (measured in three places of each fruit surface), using the Minolta colorimeter CM-2600d model (Minolta Camera Co., Osaka, Japan). Three determinations were performed for the fruit samples.

2.11. Firmness

The firmness of the fruit was measured using a TA.XT plus texturometer (Stable Microsystems, UK) equipped with a special 4 mm tip for this study. The plum skin was removed as thin as it was possible (with a new sharp razor) and the flesh was located on the texturometer table. Measurements were made in 15 repetitions [12].

2.12. Statistical Analysis

Statistical analysis of data was performed with SPSS 13.0 software (Stat-Packets Statistical analysis Software, SPSS Inc., Chicago, IL, USA). After an analysis of variance (ANOVA) in order to determine the significant difference, the mean comparison test used was LSD (least significant difference) at the significance level of 95% (\( p \)-value < 0.05).

3. Results and Discussion

3.1. Physiological Parameters: Transpiration, Respiration, and Mass Loss

Transpiration rate results of the Jojo plum over 28 days of experiments are presented in Table 1. The presented results at 3.5 °C are the values of fruit where transpiration was measured after a few hours from taking samples out of the cooling chamber. Results at 22 °C present the transpiration values imitating grocery store conditions. It can be seen that there is a significant difference between both storage conditions. Higher values of unit \( s \cdot cm^{-1} \) are linked with longer fruit storage rather than lower values of mass loss per unit (i.e., the transpiration rate itself). Over the total storage period of 28 days, a decrease in transpiration rate was observed in all variants (control and treatments). The reason for this is related to the increasing degree of ripeness of the fruit. The outer tissue layers become more permeable with increasing time [13]. The stored variants with a coating consistently showed lower transpiration rate compared to the control. Anyway, the differences were not significant in all cases, so that we can only speak of a tendency here. This was not in line with expectations, since it was expected that the coatings create an additional resistance in the water vapor pathway [7].

A comparison of the plums measured a short time after storage at 3.5 °C with the fruits after the grocery sales simulation (22 °C) showed slightly lower values, which suggest a further increasing degree of ripeness with more permeable tissue layers. Significant differences between the two coating variants (100S C; 80/20 C) were practically undetectable. The fruits stored in the trays (covered with starch-based films) showed overall lower transpiration rate compared to the fruits directly coated. However, the differences were only significant in a few cases. Here too, the trend was confirmed that with increasing maturity, less resistance could be observed.
Table 1. Transpiration rate of plums [s·cm⁻¹], fresh uncoated (control), coated in starch solution (100S C), coated in starch/whey protein solution (80/20 C), in trays covered with starch film (100S F) and in trays covered with starch/whey protein film (80/20 F) (mean values ± SD).

| Temperature | 3.5 °C | 22 °C |
|-------------|--------|-------|
|             | Days   |       |       | Days   |       |       |
|             | 1      | 8     | 15    | 22     | 28     | 1      | 8     | 15    | 22   | 28 |
| control     | 50.4   | ± 6.23 a | ± 7.35 a | ± 2.03 a | ± 1.90 a | ± 3.88 a | ± 3.64 a | ± 2.54 a | ± 0.78 a | ± 7.03 a | ± 4.64 a |
| 100S C      | 65.1   | ± 6.84 a | ± 3.14 b | ± 5.91 bc | ± 2.84 bc | ± 5.70 bc | ± 3.98 bc | ± 3.80 ab | ± 3.62 b | ± 6.56 b | ± 5.44 ab |
| 80/20 C     | 65.9   | ± 3.53 a | ± 1.48 bc | ± 5.82 b | ± 6.44 ab | ± 6.86 ab | ± 9.33 a | ± 2.70 a | ± 6.91 ab | ± 0.85 a | ± 3.14 a |
| 100S F      | 59.9   | ± 5.60 ab | ± 2.95 ab | ± 3.95 b | ± 8.18 b | ± 3.35 b | ± 12.95 ab | ± 13.21 a | ± 2.87 a | ± 7.47 ab | ± 3.67 ab |
| 80/20 F     | 48.2   | ± 4.54 a | ± 9.05 a | ± 0.86 a | ± 10.68 a | ± 2.36 a | ± 7.41 ab | ± 9.05 a | ± 0.86 a | ± 10.68 a | ± 2.36 a |

Values in the same column denoted by the same letter were not significantly different (p < 0.05).

Respiration rates for plums moved from cooling chamber the same day and for plum kept in conditions similar to grocery store are revealed in the Table 2.

Table 2. Respiration rate of plums [mg CO₂ cm⁻² h⁻¹] of fresh uncoated (control), coated in starch solution (100S C), coated in starch/whey protein solution (80/20 C) in trays covered with starch film (100S F), and in trays covered with starch/whey protein film (80/20 F) (mean values ± SD).

| Temperature | 3.5 °C | 22 °C |
|-------------|--------|-------|
|             | Days   |       |       | Days   |       |       |
|             | 1      | 8     | 15    | 22     | 28     | 1      | 8     | 15    | 22   | 28 |
| control     | 0.0196 ± 0.00177 d | 0.0171 ± 0.00117 c | 0.0149 ± 0.00154 b | 0.01473 ± 0.00013 a | 0.0123 ± 0.00134 a | 0.01945 ± 0.00253 c | 0.01833 ± 0.00166 b | 0.01764 ± 0.00166 b | 0.01611 ± 0.00179 ab | 0.01539 ± 0.00115 a |
| 100S C      | 0.01987 ± 0.00173 d | 0.01612 ± 0.00119 c | 0.01393 ± 0.00195 a | 0.01366 ± 0.00108 b | 0.01078 ± 0.00310 a | 0.02401 ± 0.00112 d | 0.02103 ± 0.00159 c | 0.02001 ± 0.00110 c | 0.01815 ± 0.00110 c | 0.01529 ± 0.00110 c |
| 80/20 C     | 0.01887 ± 0.00149 d | 0.0159 ± 0.00150 c | 0.01448 ± 0.00195 a | 0.01243 ± 0.00119 a | 0.0119 ± 0.00143 a | 0.02286 ± 0.00110 b | 0.01995 ± 0.00102 d | 0.01887 ± 0.00102 d | 0.01814 ± 0.00102 d | 0.01768 ± 0.00102 d |
| 100S F      | 0.01981 ± 0.00365 d | 0.01796 ± 0.00218 c | 0.01616 ± 0.00112 a | 0.0146 ± 0.00112 a | 0.01396 ± 0.00106 a | 0.02249 ± 0.00106 a | 0.02265 ± 0.00106 a | 0.01849 ± 0.00106 a | 0.01846 ± 0.00106 a | 0.01622 ± 0.00106 a |
| 80/20 F     | 0.02 ± 0.00159 d | 0.01937 ± 0.00183 cd | 0.01718 ± 0.00195 b | 0.0169 ± 0.00078 a | 0.01308 ± 0.00072 c | 0.02176 ± 0.00072 c | 0.02125 ± 0.00072 c | 0.02013 ± 0.00072 c | 0.01972 ± 0.00072 c | 0.01721 ± 0.00072 c |

Values in the same column denoted by the same letter were not significantly different (p < 0.05).

The respiration rates of the coated plums after storage at 3.5 °C showed a tendency towards lower values compared to the control variant. Significant differences between the two coating variants (100S C, 80/20 C) could not be found. This statement also applies to the fruits stored in the covered trays in a modified atmosphere. The slightly higher values compared to the control variant could be due to the fact that at the time of the measurements, there was still a slightly increased CO₂ gas concentration in the intercellular spaces of the fruit. The respiration rates measured after the sales simulation, all of which were significantly higher than the values after storage, could have two causes. On the one hand, this could indicate the increasing degree of maturity (climacteric) in the higher temperatures over a few days. On the other hand, the onset of microbial activities cannot be completely excluded. Anyway, the respiration rate of plums kept in the cooling chamber does not reveal the significant impact of biodegradable packages (coatings and films) on gas changing reductions. This means that coated and wrapped plums in starch and starch-whey protein (80/20%) matrices probably cannot be kept for longer than fresh fruit. Anyway, the lowest respiration rate in the first seven days was noticed for starch-protein coated plum in 3.5 °C. The most stable respiration rate was for plums stored in boxes with starch-whey protein (80%/20%) films. The results received for fruit preserved in greengrocer
conditions showed the lowest respiration rate of all samples (especially of uncoated plum and starch coated plums). When the temperature of the environment was boosted, higher amounts of ethylene are formed since the metabolic processes accelerate, the demand of energy is higher, and the respiration rate increases. This quickens the ripening of fruit and, thereupon, a superior number of produced gases. Anyway, plums warehoused on plastic trays and wrapped by starch and starch-whey protein (80%/20%) films had the highest respiration rate. When fruits are garner on a plastic tray with permeable film covers, they make carbon dioxide and absorb oxygen. Ethylene which is emitted over this process reacts with water condensation from outside (biodegradable films are penetrable for water vapor permeability). The concentration of atmospheric gases is controlled, albeit accumulated under foil. Consequently, carbon dioxide is emitted, the formation of oxygen is lower, and transpiration rate is higher. Therefore, there is no space between the fruit surface and the coating material. Thus, the exchange of gases is lower since starch and starch whey protein (80%/20%) coatings have a supremely high barrier against oxygen. Carbon dioxide is emitted at lower levels than in the case of plum without any additional coating. Despite this, in greengrocer conditions the gases are accumulated under the film. This conclusion has a confirmation in literature. Choi et al. [14] packaged Prunus salicina L. variety Formosain plums in biofilms containing essential oils in hydroxypropyl methylcellulose. After two weeks of storage at room temperature, the respiration was 15.41 mL CO$_2$ kg$^{-1}$·h$^{-1}$ and 7.06 mL CO$_2$ kg$^{-1}$·h$^{-1}$ for wrapped and fresh samples. It is respiration rate in CO$_2$ volume units based on the mass of the product. In this paper, the mass of CO$_2$ in relation to a unit of area is presented. The respiration rates have different units of measurement. However the tendencies should be the same for both versions (just not the absolute values).

During the transpiration and respiration processes there is an exchange of water and gases. The fruits lose part of their mass. These weight loss changes are depicted in Table 3 for plums kept in 3.5 °C and 35% RH and for plums held at 22 °C and 35% RH. Comparing the presented data, we can see that mass loss depends on factors such as temperature. However, it is worthy to say that the mass loss is primarily dependent on the water vapor partial pressure difference WPD between the surface and the surrounding air. Water permeability is calculated from the relative humidity and the temperature. Higher temperatures caused boosting of energy by emission process. Metabolic processes are quicker, hereof the mass loss is upper. Dependingly from the preservation temperature, fresh fruits lost the highest quantum of bulk. Valero et al. [2] labored with four varieties of European plums Prunus salicina L. Authors reported that after 35 days of preservation at 2 °C, the mass loss of the Blackamber variety sample was 10.8%, 5.8% when coated in alginate solution, and thus at 20 °C 16.2% and 10.2%, respectively. Anyway, the layer of coating significantly reduced mass loss for all plum cultivars. Poverenov et al. [15], Chiumarelli and Hubinger [16], Chien, Sheu, and Yang [17], Brasil et al. [18], Das et al. [19], Gol, Patel, and Rao [20], Hong et al. [21], Guerra et al. [22], and others covered red bell peppers, mangoes, papayas, tomatoes, apples, strawberries, guavas, and grapes, respectively, in different coating materials. The results revealed that the coated vegetables and fruits had lower weight loss than these without coating. The lowest losses of plum weight are measured for starch and starch-weight protein (80–20%) films. This is confirmed in the transpiration and respiration results. For biodegradable materials, transpiration and respiration are the lowest, so the weight loss is at its smallest as well. After 25 days of storage, the fruits’ mass loss was 1.8 and 1.6 times slighter for fruits wrapped in films and 1.6 and 1.5 times smaller for coated plum than for fresh plum in room and cooling conditions, respectively. Valero et al. [23], Mistriotis et al. [24], Rux et al. [25], Vázquez-Celestino et al. [26] packaged carrots, cherry, tomatoes, and peach, mushrooms, strawberries, and mangoes, respectively, in plastic boxes and wrapped by different biodegradable polymers. Calculated values (Table 3) also reveal that the wrapped fruits and vegetables have a several percent lower weight loss than unpackaged fruits.
Table 3. Mass loss of plums [%] of fresh uncoated (control), coated in starch solution (100S C), coated in starch/whey protein solution (80/20 C) in trays covered with starch film (100S F), and in trays covered with starch/whey protein film (80/20 F) (mean values ± SD).

| Temperature | 3.5 °C | 22 °C |
|-------------|--------|-------|
| Days        | 5      | 8     | 12    | 15    | 20    | 25    | 5      | 8     | 12    | 15    | 20    |
| control     | 2.47   | 3.44  | 4.61  | 5.22  | 6.70  | 7.02  | 4.32   | 5.55  | 6.28  | 7.77  | 9.78  | 11.11 |
| ±0.11 b     | ±0.04 b| ±0.06 b| ±0.22 c| ±0.06 b| ±0.09 b| ±0.76 c| ±0.32 e| ±0.69 c| ±0.11 c| ±0.81 c| ±0.01 c| ±0.09 b|
| 100S C      | 0.97   | 0.91  | 3.02  | 3.81  | 5.11  | 5.98  | 3.55   | 4.60  | 5.01  | 6.59  | 7.23  |     |
| ±0.11 a     | ±0.64 a| ±0.11 a| ±0.41 b| ±0.40 ab| ±0.12 a| ±0.11 ab| ±0.11 ab| ±0.11 ab| ±0.04 b| ±0.22 b| ±0.05 a|
| 80/20 C     | 1.06   | 1.95  | 3.43  | 4.01  | 5.23  | 6.00  | 1.24   | 1.46  | 1.67  | 2.42  | 3.46  | 4.60  |
| ±0.10 a     | ±0.71 a| ±0.17 ab| ±0.17 ab| ±0.17 ab| ±0.16 a| ±0.16 a| ±0.16 a| ±0.16 a| ±0.16 a| ±0.16 a| ±0.16 a| ±0.16 a|
| 100S F      | 0.9    | 1.76  | 2.76  | 3.26  | 5.60  | 1.10  | 2.51   | 3.22  | 3.57  | 5.07  | 6.32  |     |
| ±0.10 a     | ±0.02 a| ±0.12 a| ±0.82 ab| ±0.82 ab| ±0.10 a| ±0.82 ab| ±0.10 a| ±0.10 a| ±0.10 a| ±0.10 a| ±0.10 a| ±0.10 a|
| 80/20 F     | 0.96   | 1.64  | 2.76  | 3.29  | 4.32  | 5.32  | 1.17   | 2.42  | 3.46  | 4.00  | 5.80  | 6.45  |
| ±0.10 a     | ±0.76 a| ±0.32 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a| ±0.69 a|

Values in the same column denoted by the same letter were not significantly different (p < 0.05).

It is also noteworthy the RH of conducted tests. All of the tests were performed in 35% of RH.

As you can see in Table 4, the starch and starch–whey protein films show a typical behavior of water vapor sensitive hydrophilic biomatrices since: (a) a network of stiff strands and pores formed by amyllose present in the network could possibly entrap more water; (b) some amount of water in polymer acts as plasticizer; and (c) glycerol (plasticizer) has a hydrophilic character. In 33% of RH the films are not significantly different. However, both have an affinity to water, which could influence water absorption of the films and coatings [27,28].

Table 4. Moisture sorption isotherm of starch (S), starch–whey protein (80/20) films [g water g⁻¹ dry mass].

| RH (%) | 100S | 80/20 |
|--------|------|-------|
| 3      | 0.1757 ± 0.0036 a| 0.1593 ± 0.0093 a|
| 11     | 0.1844 ± 0.0082 a| 0.1755 ± 0.0044 a|
| 22     | 0.3077 ± 0.0157 b| 0.3066 ± 0.0053 b|
| 33     | 0.3212 ± 0.0071 b| 0.3525 ± 0.0118 b|
| 43     | 0.4311 ± 0.0169 c| 0.3582 ± 0.0755 b|
| 53     | 0.4458 ± 0.0609 c| 0.3883 ± 0.0418 b|
| 65     | 0.5335 ± 0.1015 c| 0.5373 ± 0.0303 c|
| 75     | 0.7476 ± 0.0832 d| 0.5675 ± 0.1004 c|
| 81     | 0.8052 ± 0.0502 d| 0.7581 ± 0.0847 d|
| 93     | 2.0418 ± 0.1289 e| 1.8109 ± 0.0316 e|

Letters in the same column are not significantly at 0.05 p level.

In principle, it can be assumed that the plums will have a longer keeping quality due to the lower water loss of the coatings and the tray variants. The fact that the fruits with a coating show lower respiration intensity tends to indicate a longer shelf life. Differences between the starch-based coatings or films were not found. It is believed that the proportion of whey protein was too small. The respiration rate of plums kept in the cooling chamber do not show the significant impact of biodegradable polymers on gas changing reductions. Or it shows but the effect is hidden by carbon dioxide which could be derived from the coating. However, the highest respiration rate in the first week was slightly noticed for starch–whey protein films in 3.5 °C, for starch–whey protein coatings in 22 °C and for starch films in 3.5 °C, starch–whey protein coatings in 22 °C the last week. The respiration rates are higher in 22 °C. When the temperature of the environment booster, higher amounts of ethylene are produced since the metabolic processes growth, the demand of energy is
higher and the respiration rate increases. Another hypothesis is that ethylene is trapped in the film wrapped fruit packages and could have a contribution to respiration rate changes. This could accelerate the ripening of fruit and, thereby, a higher number of produced gases. Anyway, plums kept on plastic trays and wrapped by starch and starch-whey protein (80%/20%) films had the highest respiration rate. When fruits are stored in a plastic box with permeable film covers, they produce carbon dioxide and absorb oxygen [29].

In terms of mass losses, clear and significant differences were observed between the control variant and both the variants with coating and the variants stored in the covered trays. The predominant part of these losses includes moisture losses. The loss of mass as a consequence of respiration (CO$_2$ release) should be negligibly small considering the short periods of time and the comparatively moderate respiration rates of plums.

The higher water losses in all measurements after the sales simulation (under indoor climate conditions) are due to the greater difference in partial pressure of water vapor between the fruit surface and the air unaffected by the produce. There were practically no differences in the water losses of the two coating variants. The same statement can be made for a comparison of the plums that were stored in the trays covered with different starch-based films. The water losses from the coated fruits tended to be somewhat higher than the fruits stored in the trays under a modified atmosphere. The reason for this can be seen in the fact that the variants covered with coating were stored with unrestricted free convection, whereas the tray variants were stored with limited free convection with correspondingly higher boundary layer resistances.

Storage temperature plays a significant role, especially in case of fruits coated by starch solution (Table 1). However, between fresh, coated, and wrapped fruit in the same temperature of storage, apparent differences were observed. The highest rate of transpiration (3.5 °C) was noticed for coated plums, where by after one week of storage the fruit coated by starch solution with whey protein addition significantly decreased of 17% and 24% after 28 days. Thus, starch coatings after one week of storage decreased by 5% and 11% after four weeks. Anyway, compared to fruit in films and untreated fruit starch and starch/whey protein coatings have the lowest transpiration rate. The transpiration rate of fruit wrapped in starch films was comparable to both coatings (the same homogenous group).

Interestingly, 20% addition of proteins to starch films significantly decreased the rate of gas exchanges. It is noteworthy that the oxygen permeability of starch and starch/whey protein films (80/20) is linked with it. For starch films, permeability of oxygen is equal 81 × 10$^{-14}$ (cm$^3$$\cdot$mm$^{-1}$$\cdot$s$^{-1}$$\cdot$Pa$^{-1}$) and 117 × 10$^{-14}$ (cm$^3$$\cdot$mm$^{-1}$$\cdot$s$^{-1}$$\cdot$Pa$^{-1}$) for starch films with whey proteins addition (80/20). So, water movement from fruit to environment has been increased by higher permeability. Permeability is a measure of how easily the water vapor or a gas can pass through a dense material according the Fick’s and Henry’s laws. Water vapor transfers quickly through material with high permeability and very slowly through material with low permeability. Thus, the thickness of starch and starch-whey protein (80%/20%) films is comparable: 80.8 and 79.7 μm for starch and starch/whey protein films respectively and 7.1 and 4.2 μm for starch and starch/whey protein coatings respectively [7]. Quite similar results were obtained for fresh fruit as for plums packaged in starch films, but during the last week of observation, the transpiration rate significantly decreased by almost 9%. In turn, under greengrocer store conditions, the lowest rate was observed for films with proteins addition. Thus, starch-protein films had the lowest ratio of transpiration in 3.5 °C. Independent of their storage temperature, these materials have a supreme transpiration resistance for fruits and vegetables (even with a very high water content).

The gradient of water vapor pressure between the plum and the environment conditions determined the transpiration process. The cuticle and epidermal cell layer usually reduced transpiration. Thereby, different plum varieties have a different surface, volume, cuticle structure, and epidermis. Comparing physiological parameters such as transpiration between different varieties should not reveal the obtained values (only fruit behavior). Biodegradable coatings and films act as a layer covering the stomata and other water vapor
pathways such as microcracks, leading to a decrease in transpiration rate. The thickness of both kinds of films was comparable and cannot explain the difference observed. However, it was displayed that starch films with 20% addition of proteins significantly decreased the ratio of gas exchanges. Indeed, the oxygen permeability of starch and starch/whey protein films (80/20) reduce the oxygen uptake for the plums. In parallel, the high water vapor permeability favoured the water movement (loss) from fruit to environment. Thus, coatings and films can be used for different fruits and vegetables varieties [2].

3.2. Firmness

One of the crucial factors affecting fruits and vegetables shelf life is flesh firmness, which is directly related to postharvest product ripeness [2]. The firmness of plums stored in 3.5 and 22 °C was presented in the Table 5. In the first two weeks of storage, the highest firmness is noticed for fruits wrapped by starch material and for plums coated by starch-based solution at both temperatures. After the next two weeks, firmness is the highest for fruits wrapped in starch-whey protein (80%/20%) films. During the whole storage process, the lowest firmness is observed for fresh uncoated plums. The loss of firmness depends on the loss of water and the degree of ripeness of the fruit (i.e., the resistance to respiration and the respiration rate). Fresh fruits in storage temperatures of 3.5 and 22 °C lose their firmness fastest.

Table 5. Firmness of fresh, coated in starch solution, coated in starch/whey protein solution (80/20), wrapped in starch film, and wrapped in starch/whey protein (80/20) film plums in 3.5 and 22 °C [N].

| Temperature | 3.5 °C | 22 °C |
|-------------|--------|--------|
|             | Days   |        |        |
| control     | 1      | 1.78   | 1.29   |
|             | ± 0.25 | ± 0.38 | ± 0.18 |
| 100S C      | 1.82   | 1.05   | 2.64   |
|             | ± 1.05 | ± 0.15 | ± 0.29 |
| 80/20 C     | 2.80   | 1.31   | 2.23   |
|             | ± 0.41 | ± 0.83 | ± 0.70 |
| 100S F      | 2.87   | 2.10   | 1.79   |
|             | ± 0.56 | ± 1.25 | ± 0.63 |
| 80/20 F     | 2.49   | 1.85   | 1.87   |
|             | ± 0.45 | ± 1.05 | ± 1.09 |

Letters in the same column are not significantly at 0.05 p level.

Firmness depends also on factors as fruit maturity, harvesting time, and variety of fruit, so values in literature for different kinds of plums at different maturity stages are not comparable with those ones presented in this study. However, the general trend is the same [30].

Results presented by Hussain et al. [31] reveal that the coating process significantly prolongs the firmness of agriculture products. Prunus domestica L. cv. Santa Rosa covered by carboxymethyl cellulose coatings after 12 days of storage had a firmness even 3 times higher than fresh fruit. Liu et al. [32] worked with Prunus salicina L. cv. Sanhuali plums. Some of the fruits were kept in plastic baskets for 20 days wrapped by chitosan films, and some were coated by chitosan solution. After 3 weeks of storage at 5 °C and 90% of RH, the firmness of fresh fruit decreased by more than 5 times, and the firmness of coated and wrapped Japanese plums was 2 and 2.5 times lower for treated plums. Choi et al. [14] also revealed that the Prunus salicina L. plum cv. Formosa covered by hydroxypropyl methylcellulose with essential oils have higher firmness in storage and in room conditions. After 14 days of storage at 23 °C, the firmness of fresh plums was at approximately 5.33 and 9.58 Nm⁻¹ for HPMC coating with essential oil addition. Results obtained after 14 days of storage at 5 °C showed a higher value of firmness than in room conditions. At 5 °C, the respiration is lower so mass and water losses are lower as well. Firmness for control plums in 5 °C was 11.68 and 15.45 Nm⁻¹ for HPMC coating.
3.3. Surface Colour

The surface color alterations of plums was observed for fresh, coated, and wrapped plums. Table 6 present the obtained results for fruit storage at 3.5 °C. At a higher temperature (22 °C), no significant differences were noticed. However, significant differences were recorded between fresh and coated and wrapped plums. During the storage time, the fruit color changed from violet to navy violet. Coating materials and films delayed this process. After 28 days storage time, the L parameter decreased by 18% for fresh plums, and for plums coated in starch and starch-whey protein (80%/20%) and plums wrapped in starch and starch-whey protein (80%/20%) only half of this value, 9%. In the a and b parameters no significant changes were noticed. Anyway, the coated and wrapped fruits showed slower rates of change in peel color than the control plums. Choi et al. [14], Liu et al. [31], Valero et al. [2] obtained similar results for coated and wrapped European and Japanese varieties of plums. Also, Sun et al. [33], who coated the strawberries in chitosan and cellulose coatings reported similar conclusion. The L* value of coated fruit decreased by less than 2, which means the coating act as indicator, helping to preserve the lightness of strawberries. Such trend was observed also for a* and b* values. López-Serrano and Ros Barceló [34] and Sacks and Shaw [35] reported that color change in strawberries is linked with the formation of the brown polymer-polyphenoloxidase in a (+) catechin oxidation process. Also, Gull et al. [36] reported the L* value of treated apricot fruits indicates that chitosan coatings delayed chlorophyll breakdown and synthesis of carotenoids.

Table 6. The surface color changes of fresh (control), starch coated (100S C), starch/whey protein coated (80/20 C), wrapped in starch films (100S F) and wrapped in starch/whey protein films (80/20 F).

| Time   | Parameter | Control | 100S C | 80/20 C | 100S F | 80/20 F |
|--------|-----------|---------|--------|---------|--------|---------|
| 1st day| L         | 38.82 ± 1.23 c | 40.01 ± 1.51 d | 40.43 ± 1.60 d | 95.47 ± 0.34 h | 94.75 ± 0.50 h |
|        | a         | 13.06 ± 3.02 b | 13.41 ± 2.01 b | 11.92 ± 1.02 a | 0.24 ± 0.06 b | 0.55 ± 0.11 b |
|        | b         | 6.99 ± 0.76 c | 5.87 ± 0.98 c | 6.29 ± 1.89 c | 3.18 ± 0.28 b | 4.27 ± 0.75 b |
|        | ΔE        | -        | 1.67 ± 0.52 c d | 2.09 ± 0.14 d | 1.46 ± 0.43 c | 2.78 ± 0.73 d |
| 8th day| L         | 37.02 ± 1.03 b | 38.11 ± 1.36 c | 39.42 ± 1.32 c d | 95.12 ± 0.14 h | 94.05 ± 0.41 h |
|        | a         | 12.74 ± 2.75 a b | 13.01 ± 1.71 b | 11.24 ± 1.74 a | 0.23 ± 0.05 a | 0.49 ± 0.90 b |
|        | b         | 6.66 ± 0.73 c | 5.67 ± 1.49 c | 6.00 ± 1.17 c | 2.98 ± 0.17 a b | 4.03 ± 0.82 b |
|        | ΔE        | -        | 1.50 ± 0.03 c | 2.91 ± 0.21 d | 0.40 ± 0.22 a | 0.74 ± 0.18 b |
| 15th day| L        | 36.01 ± 1.17 b | 39.00 ± 1.39 c d | 38.06 ± 1.06 c | 94.97 ± 0.19 h | 93.33 ± 0.43 f g |
|        | a         | 12.39 ± 3.20 a b | 12.97 ± 1.58 a b | 10.75 ± 1.36 a | 0.22 ± 0.13 a | 0.43 ± 0.10 b |
|        | b         | 6.39 ± 0.51 c | 5.39 ± 0.54 c | 5.87 ± 1.52 c | 2.49 ± 0.15 a | 3.69 ± 0.74 b |
|        | ΔE        | -        | 3.12 ± 0.15 e | 2.01 ± 0.14 d | 0.84 ± 0.13 b | 1.54 ± 0.24 c |
| 28th day| L        | 34.36 ± 1.11 a | 36.74 ± 1.12 a b | 36.98 ± 1.41 b | 94.12 ± 0.45 h | 92.82 ± 0.37 f |
|        | a         | 12.11 ± 2.45 a b | 12.72 ± 3.00 a b | 10.14 ± 1.51 a | 0.21 ± 0.25 a | 0.41 ± 0.23 b |
|        | b         | 6.01 ± 0.41 c | 5.20 ± 0.78 c | 5.69 ± 1.76 c | 2.13 ± 0.78 a | 3.44 ± 0.56 b |
|        | ΔE        | -        | 2.59 ± 0.23 d | 3.29 ± 0.54 e | 1.71 ± 1.22 c | 2.10 ± 0.95 c d |

Letters in the same column are not significantly at 0.05 p level.

4. Conclusions

European Prunus domestica cv. Jojo plums were covered and wrapped in coatings and films made from starch and starch-whey protein (80%/20%) suspensions. Fresh and packaged samples were stored for 28 days at 3.5 °C. Physiological tests were made weekly at room temperatures. Compared to the control sample, delayed changes in color parameters were observed for plums that were covered and wrapped in films. The transpiration rate of wrapped and coated plums is similar to untreated fruits. Biodegradable coatings and films act as an additional layer covering the outer tissue layers and leading to slightly decrease in transpiration rate. The thickness of both kinds of films was comparable and cannot explain the difference observed. However, it was demonstrated that starch films with 20% addition of proteins increased the resistance of gas exchanges. Indeed, the oxygen permeability
of starch and starch/whey protein films (80/20) reduce the oxygen access for the plums. In parallel, the high-water vapor permeability favored the water movement (loss) from fruit to environment. The lowest respiration is noticed for fruit coated in films. During the storage time the fruit colour changed from violet to navy violet. Coating materials and films delayed this process compared to fresh fruit. The mass loss of untreated fruits is even 1.8 times higher than that of wrapped plums and 1.6 times higher than that of coated samples. Fresh fruits lost highest amount of mass. Metabolic processes being faster, hereof the weight loss is accelerated. Starch film with the addition of 20% of proteins increased the resistance of gas exchanges, which is a great benefit of them.

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