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Packaging and storage condition affect the physicochemical properties of red raspberries (*Rubus idaeus* L., cv. Erika)

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14 Packaging and storage condition affect the physicochemical properties of red raspberries (*Rubus*
15 *idaeus* L., cv. Erika)

16

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24 Abstract

25 Packaging material and the storage temperature on red raspberries (*Rubus idaeus* L.) were studied
26 in this paper. Raspberries were stored following their harvesting in different conditions: in the
27 fridge at 1 °C and in the freezer at -20 °C, using different packaging materials: two Nanoactive
28 films, Nanoactive A (NA) and Nanoactive B (NB), a biaxially oriented polyethylene terephthalate
29 (PET) film and some other fruits were stored without any film (WF). Biometrics, color, titratable
30 acidity, soluble solid content and moisture, were determined during storage. A loss of weight
31 (24.87%) was found during storage at room temperature from 5.02 g to 4.02 g in two days. During
32 the freezer storage was found a significant average higher Solid Soluble Content (9.44 °Brix) in
33 PET, a significant higher Titratable acidity (2.08%) in WF, and no significant differences between
34 different packaging for Moisture content. The O₂ and CO₂ concentrations were measured daily in
35 the refrigerated fruits and the O₂ concentration on the 7th day was 5.0% (NA), 19.8% (NB) and
36 17.1 (PET). CO₂ percentage increased significantly during storage in the NA package from 9.6 (1st
37 day) to 20.3 (14th day), whereas an inverse trend was found in the NB package from 4.4 (1st day) to
38 1.0 (4th day).

39

40 Keywords:

41 Syndiotactic polystyrene

42 Polyethylene terephthalate

43 Post-harvest

44 Raspberry

45 Rubus

46 Shelf life

47 Small fruits

48 Nanoporous crystalline phases

49

50 1. Introduction

51 Red raspberry (*Rubus ideaus* L.) is a shrub which is widely cultivated in all temperate regions of the
52 world. Fruit is soft and it is consumed as fresh, frozen, purée, juice and dried. Red raspberry fruit
53 has a very short shelf life due both to the high respiration rate and to the absence of peel or rind and
54 as a consequence raspberry rapidly loses water and weight.

55 For this reason fresh consumption of refrigerated fruits should be within 2–3 days after manual
56 picking. The visual aspect of quality includes freshness, color and absence of decay or physiological
57 disorders, plays a key role in primary selection by the consumer. From this point of view the use of
58 a packaging is often desirable. Over the last two decades, nanotechnologies have revolutionized the
59 material industry, leading to high performance improvements (Cushen, Kerry, Morris, Cruz-
60 Romero, & Cummins, 2012), in particular the food packaging industry, the role of nanotechnologies
61 has been very important in improving overall packaging performance (mechanical, barrier) leading
62 to functional, intelligent, and active packaging (Yam, Takhistov, & Miltz, 2005). Among the active
63 functions, one of the most important is antimicrobial (Appendinia & Hotchkissb, 2002; Durango,
64 Soares, & Andrade, 2006). Other important active functions are oxygen scavenger, that is the
65 capture of the oxygen that penetrates the outer environment, as well as ethylene scavenger, that is
66 the capture of the ethylene produced by the degradation of the fruit. The company NanoActive Film
67 s.r.l. has patented active packaging (Albunia et al., 2012), multilayer films based on the common
68 polypropylene (PP) and including a core layer of nanoporous syndiotactic polystyrene (s-PS).
69 Syndiotactic polystyrene (s-PS) is a robust (D'Aniello, Rizzo, & Guerra, 2005), cheap and
70 commercially available thermoplastic material essential within the polymeric framework
71 (Schellenberg, 2009, pp. 17–29). Host-guest co-crystalline phases are obtained by solvent procedure

72 and, after suitable solvent-extraction procedures, nanoporous crystalline phases named: δ (De Rosa,
73 Guerra, Petraccone, & Pirozzi, 1997), ϵ (Petraccone, Ruiz de Ballesteros, Tarallo, Rizzo, & Guerra,
74 2008), disordered (Rizzo, Iannello, Albunia, Acocella & Guerra, 2014) or triclinic (Acocella, Rizzo,
75 Daniel, Tarallo, & Guerra, 2015) can be easily achieved.

76 The ability of polymeric nanoporous phases to absorb low-molecular-mass molecules in their
77 crystalline cavities leading to stable host/guest co-crystalline phases is well-described in the
78 literature (Albunia, Rizzo, & Guerra, 2013; Guerra, Daniel, Rizzo, & Tarallo, 2012; Musto, Rizzo,
79 & Guerra, 2005; Pilla et al., 2009). Co-crystalline phases, can be formed with gaseous molecules at
80 room temperature, such as carbon dioxide (Annunziata, Albunia, Venditto, Mensitieri, & Guerra,
81 2006), ethylene (Albunia, Minucci, & Guerra, 2008) as well as with liquid guest molecules as
82 carvacrol, a relevant natural antimicrobial molecule (Albunia, Rizzo, Iannello, Rufolo, & Guerra,
83 2014).

84 Recent studies based on active packaging films containing s-PS nanoporous-crystalline layer have
85 shown that these innovative materials are able to prolong the shelf-life of non-climacteric fruits,
86 such as oranges (Sicari, Dorato, Giuffrè, Rizzo, & Albunia, 2017).

87 A study on oxygen and carbon dioxide concentrations in the environment of packaged non-
88 climacteric fruits as well as in s-PS nanoporous-crystalline layers has been also recently combined
89 in order to understand the transport phenomena in active s-PS packaging films that control O₂ and
90 CO₂ concentrations in the fruit environment, which are determinant in fruit and vegetable
91 preservation (Rizzo et al., 2018).

92 The aim of this study was to highlight the best packaging material for the red raspberries, between
93 the polyethylene terephthalate (PET) film and two Nanoactive films (NA) and (NB). The
94 physicochemical evolution of raspberry during storage was also compared between refrigerated
95 and frozen fruits, with and without film. This is the first paper where raspberry (cv. Erika) and PET,
96 NA and NB films are related.

97

98 2. Materials and methods

99 2.1. Vegetable material

100 The red raspberries (cv. Erika) were cultivated in a greenhouse in the Reggio Calabria Province
101 (Southern Italy) which is characterized by a typical Mediterranean climate, warm to hot, dry
102 summers and mild to cool, wet winters. Fruits were randomly, manually and carefully picked

103 at 7 a.m. on May 27, 2015 at the white stage of color, i.e. when they showed a faint pink color.

104 2.2. Films

105 Three-layer films (PP/sPS/PP) with overall thickness of nearly 50 μm made in lab-scale and
106 composed by isotactic polypropylene (PP) and syndiotactic polystyrene (sPS) in the ratio 80:20
107 (PP/sPS/PP) were prepared.

108 Films were co-extruded by blown process: after extrusion, the core layer of syndiotactic polystyrene
109 is amorphous (NB film) only after a patented treatment (Albunia et al., 2012) the s-PS film core
110 layer is transformed in the disordered nanoporous crystalline phase (NA film) (Rizzo, Iannello,
111 Albunia, Acocella & Guerra, 2014).

112 The s-PS used in this study to prepare Nanoactive film was manufactured by Dow Chemical
113 Company under the trademark Questa 101.

114 The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads
115 was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC)
116 in trichlorobenzene at 135 $^{\circ}\text{C}$ was found to be $M_w=3.2\times 10^5$ with the dispersity index, $M_w/M_n=3.9$.

117 PET film $\approx 12 \mu\text{m}$ thick: Biaxially oriented polyethylene terephthalate film presents the following
118 characteristics: low permeability to water and O_2 , high resistance to acid and basic compounds, high
119 permeability to alcohols and oils, high aptitude for food packaging use.

120 2.3. Packaging

121 After picking, the fruits were placed in disposable PET containers (90 g each) and immediately
122 brought to the laboratory by a refrigerated vehicle. Packaging utilized three different flexible films
123 NA, NB and PET with a thickness of ≈ 50 , 50 and 12 μm respectively. The sealing was performed in
124 the lab using a Multivac Vacuum apparatus (Tecno Pack). After sealing, a silicone rubber disc
125 (15mm diameter; 2mm thickness) was applied on the film of each package. At this point,
126 raspberries were put in the fridge at 1 $^{\circ}\text{C}$. Some other samples were put in the fridge in PET pans
127 and at the same temperature (1 $^{\circ}\text{C}$) but without film (WF) and they were used as a control, other
128 non-film protected fruits were left at room temperature (RT). Daily three PET containers for each
129 packaging method were taken and analyses were conducted in duplicate on each packaging. The O_2
130 and CO_2 concentrations were also taken daily before starting the analysis. A complete set of fruits
131 packaged with NA, NB, PET and WF were put in the freezer at $-20 \text{ }^{\circ}\text{C}$ after harvesting, these
132 samples were analysed monthly for 11 months.

133 2.4. Titratable acidity (TA)

134 The value of total titratable acidity is expressed in percentage terms (AOAC 942.15, 2005). A 10 g
135 aliquot of mashed raspberries was mixed with 100 mL of deionized water. Then, the sample was
136 titrated with a 0.1 N NaOH solution until a pH 8.1. The results were expressed as % of anhydrous
137 citric acid.

138 2.5. Soluble solid content (SSC)

139 The °Brix is the percentage of total soluble solids calculated in a system previously calibrated with
140 a sucrose solution at known concentration. The determination was performed at 20 °C in the
141 refractive index value which rises to the value of Brix degrees by means of the tabular data, via
142 refractometer ATAGO model DR -A1.

143 2.6. Moisture content

144 Twenty grams of the fruit were weighed into a ceramic container and placed in the oven at 102 °C,
145 until constant weight. The moisture was determined by the following formula: $[(Fw - Dw)/Fw] \times 100$,
146 where Dw: dry weight; Fw: fresh weight.

147 2.7. Color

148 This analysis was performed using a colorimeter (Konica Minolta, model CM-A177) measuring L*,
149 a* and b*. When a color is expressed in CIELAB, L* defines lightness, a* denotes the red/green
150 value and b* the yellow/blue value. Color determination was conducted on the external side of each
151 fruit.

152 2.8. Oxygen and carbon dioxide detection

153 A PBI Dansensor (Ringsted, Denmark) model Check Point was used to quantify O₂ and CO₂
154 percentages in the atmosphere of the package.

155 2.9. Statistical analysis

156 Results are the mean \pm SD of six replicates (2 analyses x each of three PET containers, for each
157 packaging method). Excel software (Office 2010) was used to calculate the means and the standard
158 deviation.

159 Statistical analyses were performed using SPSS software for Windows (SPSS Inc., Elgin, IL,
160 U.S.A.) 22.0 Version and Tukey test to determine any significant difference among all treatments at
161 $P < 0.05$.

162 3. Results and discussion

163 In the following interpretation of the results, the fruits stored at room temperature without film were
164 not taken into consideration, since they have shown a strong fungal activity the day after the harvest
165 and from the quality point of view, there is no interest in discussing the findings in these fruits.

166 3.1. Biometrics

167 Biometrics have a direct effect on the consumer's choice, fruits which are too small or too large are
168 usually rejected. All biometrics of raspberries varied during storage. Fruits stored at room
169 temperature showed a significant decrease in length from 2.64 to 2.41 cm, the fruit diameter
170 decreased from 1.97 to 1.81 cm whilst weight varied from 5.02 g at the fruit picking to 4.02 g after
171 two days (Table 1). In Table 2 the results of red raspberries stored in the fridge are listed. NA
172 allowed the longest storage (14 days) followed by PET, whereas NB showed the worst performance
173 in terms of duration. At day 7, a significant difference was found and the fruits packaged with the
174 three films showed the highest values when compared with fruits stored without film in which 2.27
175 cm (length), 1.79 cm (diameter) and 3.86 g (weight) were the lowest values. This means that film
176 protection has reduced the loss of water. These results confirm the moisture content data (Table 6)
177 in which the packaged fruits showed a higher weight if compared with fruits WF. The same trend
178 was found from day 8 to day 10, also when only NA and PET can be compared with WF in this
179 period. On the 12th day of storage, only PET and NA can be compared and NA showed the best
180 performances.

181 3.2. Color

182 It has been demonstrated that berries harvested at early stages of color development (white stage)
183 can become red during storage similarly to commercially ripe fruit (Kalt, Prange, & Lidster, 1993).
184 This indicates that these fruits harvested at certain stages of maturity can synthesize pigment during
185 storage under favorable conditions that are temperature dependent (Wang, Chen, & Wang, 2009). It
186 is common for raspberry fruit to become darker and bluer after storage (Robbins & Moore, 1990).
187 However, raspberries with a lighter red color and less blue color, such as fruit from controlled
188 atmosphere storage (Haffner, Rosenfeld, Skrede, & Wang, 2002), are considered to be more
189 attractive to consumers.

190 3.2.1. Lightness (L*)

191 Lightness ranges between 0 (black) and 100 (white). In the present study, for the fruits stored in the
192 fridge, the highest L* value (40.47) was observed when the fruits were packaged with PET on the
193 10th day, and the lowest (26.38) was observed in the fruits WFF on the 8th day of storage (Table 4).

194 For fruits stored in the freezer, the highest L^* value (46.86) was found in the NA film on the 9th
195 month of storage and the lowest (30.89) in the PET film on the 3rd month of storage. In the
196 refrigerated fruits, the L^* values showed an initial decrease and a subsequent increase; this trend
197 was mainly pronounced for the WF and PET packaged fruits whereas it was less evident for NA
198 and NB packaged fruits. There was highly significant difference in L^* ($P < 0.01$) during both
199 refrigeration and freezing storage methods, when the fruits were packed in the NA, while, this
200 parameter was not significantly different when the fruits were packed with the NB film.
201 Considering the fruits packaged with PET film and the fruits stored WF, L^* was significantly
202 different during storage in the fridge ($P < 0.01$ and $P < 0.05$) but it was not significantly different
203 during the storage in the freezer (Tables 4 and 5). If L^* is considered daily and films are compared
204 amongst themselves during storage in the fridge, no significant difference was found until day 4,
205 where L^* was significantly influenced by the type of packaging from day 5 (Table 4). In the frozen
206 fruits, significant differences were only found between films in the 4th and the 9th months (Table
207 5). The lightness decreased from day 0 -at harvest- (Table 3), when the fruits were stored in the
208 fridge (Table 4). When red raspberries were frozen, L^* increased slightly except in the fruits
209 packaged with PET. The color trend based on the storage period in the fridge and the freezer
210 showed that the lowest peak of L^* was observed on the 5th and the 8th day of storage in the fridge
211 for both NA and PET; on the 3rd day for NB and the 8th day for fruits WF. The highest peak was
212 observed during the 4th and the 6th day for PET and NA respectively (Table 4). Then a decrease
213 was again observed. When the fruits were frozen, a slight decrease of L^* was observed until the 4th
214 month for NA, NB and WF, then it increased until the 9th month for NA and the 7th month for NB
215 and WF (Table 5). The results of the two-way ANOVA analysis are reported in Table 9. L^* was not
216 influenced by the packaging variable when the fruits were stored in the fridge. Packaging, storage
217 duration and their combination did not influence L^* in frozen fruits. Storage duration and its
218 interaction with packaging produced a significant ($P < 0.05$) and a high significant effect ($P < 0.01$)
219 respectively in the refrigerated fruits.

220 Peano, Girgenti, Palma, Fontanella, and Giuggioli (2013) in fruits picked at the end of July at red
221 ripe stage of maturity and used as a control (Himbo Top cv, grown in North Italy), found 27.09 as
222 L^* value and a decrease to 25.38 during the four days of experimentation, i.e. a L^* value always
223 lower when compared to the data obtained in our work. Maro, Pio, Guedes, Abreu, and Moura
224 (2014) used the same instrument that we used for measurements and in four red raspberry cultivars
225 studied in Brasil consistently found L^* values lower than in our work.

226 3.2.2. Red/green coordinate (a^*)

227 This parameter indicates the green-red coordinate. The highest a^* value (31.36) was found in the
228 refrigerated fruits packaged with NB on the 7th day of storage and the lowest (9.89) was found in
229 the fruits packaged with PET on the 6th day of storage. In the frozen fruits, the highest value
230 (34.14) was observed in the fruits without film in the 9th month of storage and the lowest (17.36)
231 was found in the PET film in the 7th month of storage. In comparison to the a^* value at harvest
232 16.93, there was an increase in red color, except for some storage days in the fridge, in the fruits
233 without film (days 2, 4, 9 and 10), NA film (days 4 and 6) and PET film (days 4, 6, 9 and 10),
234 (Table 4). There was a highly significant difference between days for the fruits stored in the fridge,
235 $P < 0.01$ for NA, NB and PET; a significant difference ($P < 0.05$) was found in the fruits stored WF
236 (Table 4). In the frozen fruits, a^* showed a significant difference between months ($P < 0.05$) for the
237 fruits packed in the NA, and a high significant difference ($P < 0.01$) for the fruits packaged in the
238 NB, PET and WF (Table 5).

239 There was highly significant influence in the a^* parameter regarding the packaging method when
240 the fruits were stored in the fridge ($P < 0.01$) and significantly influenced ($P < 0.05$) when the fruits
241 were stored in the freezer (Table 9). Storage duration and its interaction with packaging, has a
242 highly significant influence on the a^* value.

243

244 3.2.3. Yellow/blue coordinate (b^*)

245 The b^* parameter indicates the blue-yellow coordinate. There was a highly significant difference (P
246 < 0.01) during storage in the fridge in all the tested packaging (Table 4); the same significance was
247 found in the frozen fruits packaged WF and with NB, whereas significant ($P < 0.05$) and no
248 significant differences were found in the frozen fruits packaged with NA and PET respectively
249 (Table 5). The highest b^* value was found in the refrigerated fruits packaged in the NB film 12.69
250 on the 5th day of storage, the lowest value (2.52) was observed in the fruits stored WF in the fridge
251 on the 9th day of storage (Table 4). Significant differences were found between packaging methods
252 for fruits stored in the fridge with the exception of day 8, whereas significant differences were
253 found for frozen fruits in the 5th month (only for NB) and in the 10th months.

254 The b^* values increased from day 0. a^* and b^* demonstrated the same trend in increasing their
255 value with fluctuations from the 4th to the 7th day of storage. The lowest b^* value was observed on
256 the 9th day in fruit without film; on the 4h day for NA, on the 1st day for NB and on the 6th day for

257 PET. The a^* and b^* values of fruits stored in the freezer followed a decrease trend until the 7th
258 month when the values increased until the 9th month.

259 3.3. Soluble solid content

260 For some Author, the flavor is derived from the interactive taste and aroma of many chemical
261 constituents. SSC and TA contribute to fruit flavor. High sugars and high acids are required for
262 good berry flavour (Kader, 1991).

263 The SSC showed no significant differences during refrigerated storage (Table 6). If the three films
264 are compared, raspberries in NA always showed the lowest value until the 10th day. In the frozen
265 storage, fruits packaged with NB and PET showed no significant differences over 11 months
266 whereas SSC was significantly different in WF fruits ($P < 0.05$) with a highly significant difference
267 ($P < 0.01$) in NA packaged fruits. A decrease in values was observed in frozen fruits from 10.87 at
268 harvest to the lowest 6.47 which was observed in the fruits packaged in NA in the 11th month of
269 storage. There was a significant ($P < 0.05$) and a highly significant ($P < 0.01$) influence in SSC in
270 packaging when fruits were respectively frozen or refrigerated (Table 9). The storage duration
271 effect was not significant in both refrigeration and freezing. The combined variables produced no
272 significant differences for refrigerated fruits and highly significant differences ($P < 0.01$) in the
273 frozen fruits (Table 9). All these values are in accordance with the non-climateric characteristic of
274 red raspberry, in which SSC has a slight variation after picking. Ali, Svensson, Alsanian, and
275 Olsson (2011), in red raspberries cv Polka, produced in Sweden in September–October, and stored
276 for 9 days at 2 °C WF, found a lower SSC with respect to our results, varying from 7.46% (at
277 harvest) to 6.50% (9th day). Maro et al. (2014) studied raspberries picked at the physiological
278 maturity stage, of 4 raspberry cultivars each one grown in two Brazilian mountain locations (918–
279 1628 m above sea-level) and found a SSC ranging from 6.60% to 10.40%, noting that in this case, 7
280 out of the 8 samples showed (at harvest) a lower SSC with respect to our results, even if our red
281 raspberries were picked at an earlier stage of ripening.

282 3.4. Titratable acidity

283 In fruit juices, citric acid, malic acid and tartaric acid are quantitatively predominant, depending on
284 the fruit. The TA increased following harvest (1.44) in both refrigerated and frozen raspberries.
285 Significant differences were found in fruits WF and highly significant differences were found when
286 NA, NB and PET were used (Table 6). No significant difference was found during freezing for the
287 four types of packaging compared (Table 7). The highest value was observed in the PET packaged
288 fruits stored in the fridge (2.72%) on the 9th day of storage, and the lowest was observed in the

289 fruits stored WF in the freezer (1.59%) in the 7th month of storage. There was a highly significantly
290 difference in TA ($P < 0.01$) during storage in the fridge, in the NA, NB, PET and WF (Table 6), but
291 it was not influenced by storage in the freezer (Table 7). Two-way ANOVA analysis showed that
292 TA was not influenced by either the storage period or the packaging method either in refrigerated or
293 in frozen fruits, but there was a highly significant influence by the interaction of packaging per day
294 ($P < 0.01$) and packaging per month ($P < 0.05$), (Table 9). Mölder, Moor, Tõnutare, and Põldma
295 (2011), after storage of the fruit at 1 °C from Glen Ample cv, found a TA varying from 2.36% in
296 the unwrapped fruits to 2.27% in fruits wrapped with polypropylene and to 2.2% in fruits wrapped
297 with oriented polypropylene. These findings are higher than those we found on the 4th day in our
298 experiment in fruits refrigerated and packaged WF, with NA and with NB, whereas they are similar
299 to our results for fruits packaged with PET.

300 3.5. Moisture

301 The highest moisture contents were observed in the PET packaged fruits stored in the freezer
302 (90.58% in the 9th month of storage) and in the NA packaged raspberries (90.35% in the 10th
303 month of storage), (Table 7); the lowest moisture content was observed in the fruits stored in the
304 fridge WF (83.88% on the 10th and last day of storage), (Table 6).

305 The storage period in the fridge did not influence the moisture content when the fruits were
306 packaged in NA ($P > 0.05$), whereas significant differences were found in PET packaged fruits ($P <$
307 0.05) and high significant differences in NB packaged fruits ($P < 0.01$), (Table 6). In the fruits
308 packaged WF a high significant decrease in moisture content was found during storage; from
309 87.40% to 83.88% (Table 6), which was due to the aerobic respiration of fruits, a biological
310 process which produces CO₂, energy and aqueous vapor which is dispersed in the atmosphere, in
311 this case the absence of the protective film increased the loss of water.

312 In the frozen fruits, no significant differences were found in the NA and NB packaged raspberries
313 during 11 months of storage. Over many months no significant difference was found in the moisture
314 content between NA and NB stored fruits (Table 7). Frozen fruits in PET packaging showed
315 significant differences ($P < 0.05$) and highly significant differences ($P < 0.01$) were found in WF
316 frozen fruits (Table 7). Two-way ANOVA analysis demonstrated that packaging and the interaction
317 packaging per day, produced a highly significant influence in the moisture content ($P < 0.01$),
318 whereas no significant influence was found by analyzing the storage duration effect (Table 9); the
319 exact contrary was found in frozen raspberries (Table 9).

320 3.6. O₂ and CO₂

321 The initial O₂ and CO₂ content was measured immediately after the sealing of the films. The O₂
322 was 20.90% and the CO₂ was 0.03% of the detected atmosphere (Table 3). After one day of
323 storage, the respiration of fruits caused a rapid variation of these values and O₂ decreased to 9.1%
324 (NA), 17.3% (NB) 16.3% (PET), whereas CO₂ increased to 9.6% (NA), 4.4% (NB) and 5.9%
325 (PET). As expected, the more or less pronounced barrier effect of each film strongly reduced the
326 gas exchange with the external atmosphere from day 1 and different effects were shown in each
327 type of packaging in relation to the wrapping film (Table 8). When raspberries are stored in a
328 modified or controlled atmosphere they are relatively tolerant to high CO₂. The recommended
329 controlled atmosphere storage conditions for raspberry fruit are 15–20% CO₂ and 5–10% O₂
330 (Kader, 2001, pp. 29–70). By comparing the two prototype films that were studied, NA showed the
331 best O₂ and CO₂ concentrations: 5.81% for O₂ and 15.58% for CO₂, which explains the longer
332 shelf life of the fruits when they were wrapped in this film. The gas concentrations observed in the
333 NB wrapping (17.31% for O₂ and 4.56% for CO₂) and in PET wrapping (16.72% for O₂ and
334 5.91% for CO₂) were outside of the recommended range (Table 9). CO₂ increased significantly
335 during storage in the NA package, whereas an inverse trend was found in the NB package, this
336 could be due to the differences in diffusivities of O₂ and CO₂ in amorphous and nanoporous-
337 crystalline phases of s-PS that could be relevant in gas concentrations in fruit packaging (Rizzo,
338 Cozzolino, et al., 2018). Within PET packaging no significant differences were found for either O₂
339 and CO₂ contents, this was probably due to the barrier effect of PET. The lowest value observed or
340 the O₂ (1.0%) was in the NA, on the 11th day of storage and the highest value was observed in the
341 NB, on the 7th day of storage. Alternatively, the lowest CO₂ value was observed in the NB 1.0% on
342 the 7th day of storage and the highest value was observed in the NA, but on the 13th day of storage.
343 The O₂ concentration was not influenced by the storage period in the fridge, the same was true for
344 CO₂ measured in NA and PET packaging (Table 8).

345 The two-way ANOVA analysis showed that the films used in this experiment had a highly
346 significant influence on both the O₂ and the CO₂ concentrations ($P < 0.01$), no significant effect
347 was caused by the days of storage ($P > 0.05$) and a significant effect was found in the film
348 interaction per day, $P < 0.05$ (Table 9).

349 Wang (2003) in the head space of polystyrene sap-on lid containers where raspberries cv Heritage
350 were stored for 10 days at 10 °C, found a constant O₂ concentration (19.36–20.32%) and a
351 tendency for CO₂ to increase from 0.55% to 1.89%.

352 4. Conclusions

353 Red raspberries without refrigeration show a very short shelf-life, maximum one day. The fruits
354 preserved with Nanoactive A have shown the highest shelf-life (14 days) and maintained valuable
355 physical-chemical characteristics. When the fruits were stored in the fridge, the packaging method
356 (with or without wrapping film) had an impact on fruit biometrics, a^* , b^* , moisture, O₂ and CO₂.
357 When the red raspberries were frozen, the packaging method influenced a^* and soluble solid
358 content. Meanwhile, the storage period in the fridge did not influence the soluble solid content, the
359 titratable acidity, the moisture content, or the O₂ and CO₂ concentrations. When the red raspberries
360 were frozen, a^* , b^* and moisture content, were highly influenced by the storage period. Nanoactive
361 films have shown good performances, in particular the fruits stored in the fridge and preserved with
362 Nanoactive A have shown the highest shelf-life (14 days) and maintained valuable physical-
363 chemical characteristics during storage for: length (2.42 cm), diameter (2.22 cm), weight (4.30 g),
364 lightness (30.05), red/green coordinate (27.87) and yellow/blue coordinate (11.98), titratable acidity
365 (2.35% as citric acid). Studies inside packages show that for three-layer active film, exhibiting a
366 nanoporous-crystalline s-PS core layer (NA), O₂ and CO₂ concentrations markedly decrease and
367 increase, respectively, with packaging time. In the same conditions, for reference films (not
368 activated three layer films (NB) or PET films), smaller variations with packaging time of O₂ and
369 CO₂ concentrations are observed. This behaviour is due to a higher barrier to O₂ and CO₂
370 diffusion, offered by the activated nanoporous-crystalline phase of s-PS layer (NA). Moreover it is
371 worth to underline that increase of CO₂ concentration inside fruit package can have also a
372 remarkable positive effect in slowing down the development of molds, due to well-known
373 anti-microbial properties of carbon dioxide.

374

375 Conflicts of interest

376 The authors have no conflicts of interest to declare.

377

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381

382 Appendix A. Supplementary data

383 Supplementary data to this article can be found online at

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448

449 Table 1

450 Effect of storage period on raspberries (cv. Erika). at harvest (0 day) and left at room temperature
 451 without film, on length, diameter and weight.

Day	Length (cm)	Diameter (cm)	Weight (g)
0	2.64 ± 0.25 ^b	1.97 ± 0.29 ^a	5.02 ± 1.07 ^b
1	2.60 ± 0.21 ^b	1.88 ± 0.11 ^a	4.69 ± 0.62 ^{ab}
2	2.41 ± 0.24 ^a	1.91 ± 0.29 ^a	4.02 ± 0.79 ^a

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453 The results are the mean of three replicates ± Standard Deviation.

454 The letters represent the significant difference vertically at P < 0.05.

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460 Table 2

461 Effect of storage period on the length, diameter and weight parameters in red raspberries (cv. Erika), stored at 1 °C in the fridge.

Day	Length (cm)				Diameter (cm)				Weight (g)			
	WF	NA	NB	PET	WF	NA	NB	PET	WF	NA	NB	PET
1	2.54 ± 0.32 ^{dA}	2.49 ± 0.27 ^{rdA}	2.59 ± 0.24 ^{dA}	2.53 ± 0.28 ^{rdA}	1.92 ± 0.22 ^{dAB}	1.87 ± 0.15 ^{rdAB}	1.81 ± 0.16 ^{dCA}	1.96 ± 0.13 ^{rdB}	4.62 ± 0.86 ^{dA}	4.45 ± 0.85 ^{rdA}	4.85 ± 0.79 ^{dA}	4.98 ± 0.92 ^{dA}
2	2.32 ± 0.34 ^{brA}	2.48 ± 0.23 ^{rdAB}	2.52 ± 0.24 ^{rb}	2.54 ± 0.28 ^{rdB}	1.78 ± 0.15 ^{brA}	1.85 ± 0.21 ^{brdA}	1.80 ± 0.13 ^{rdA}	2.01 ± 0.32 ^{rdB}	4.05 ± 0.95 ^{rdCA}	4.39 ± 0.72 ^{rdAB}	4.56 ± 0.77 ^{rdAB}	4.77 ± 0.92 ^{rdB}
3	2.42 ± 0.25 ^{rdA}	2.55 ± 0.24 ^{rdA}	2.43 ± 0.28 ^{rdCA}	2.45 ± 0.27 ^{rdCA}	1.77 ± 0.16 ^{brA}	1.82 ± 0.15 ^{brdA}	1.75 ± 0.12 ^{rdA}	1.80 ± 0.15 ^{brA}	4.23 ± 0.98 ^{brdA}	4.68 ± 0.84 ^{rdA}	4.33 ± 0.85 ^{rdCA}	4.28 ± 0.80 ^{rdA}
4	2.36 ± 0.14 ^{rdAB}	2.42 ± 0.19 ^{brdAB}	2.33 ± 0.21 ^{rdCA}	2.48 ± 0.18 ^{rdB}	1.78 ± 0.18 ^{brA}	1.82 ± 0.15 ^{brdA}	1.88 ± 0.14 ^{brdAB}	1.95 ± 0.14 ^{rdB}	4.55 ± 0.62 ^{rdAB}	4.86 ± 0.50 ^{rdB}	4.17 ± 0.63 ^{rdCA}	4.57 ± 0.60 ^{brAB}
5	2.37 ± 0.21 ^{rdAB}	2.46 ± 0.21 ^{rdB}	2.25 ± 0.17 ^{rdA}	2.35 ± 0.28 ^{brdAB}	1.85 ± 0.13 ^{rdA}	1.98 ± 0.16 ^{rdB}	1.91 ± 0.20 ^{rdAB}	1.93 ± 0.14 ^{rdAB}	4.24 ± 0.71 ^{brdAB}	4.60 ± 0.63 ^{rdB}	4.10 ± 0.65 ^{rdA}	4.40 ± 0.79 ^{rdAB}
6	1.99 ± 0.18 ^{rdA}	2.29 ± 0.17 ^{rdB}	2.27 ± 0.23 ^{rdB}	2.06 ± 0.25 ^{rdA}	1.61 ± 0.18 ^{rdA}	1.91 ± 0.13 ^{rdCA}	1.81 ± 0.10 ^{rdCA}	1.66 ± 0.11 ^{rdA}	3.81 ± 0.66 ^{rdCA}	4.64 ± 0.80 ^{rdB}	4.52 ± 0.72 ^{rdCA}	4.03 ± 0.59 ^{rdA}
7	2.27 ± 0.35 ^{brCA}	2.48 ± 0.20 ^{rdB}	2.47 ± 0.28 ^{rdB}	2.55 ± 0.21 ^{rdB}	1.79 ± 0.10 ^{brCA}	2.07 ± 0.10 ^{rdCA}	1.94 ± 0.16 ^{rdB}	2.10 ± 0.16 ^{rdCA}	3.86 ± 0.51 ^{rdCA}	4.60 ± 0.58 ^{rdB}	4.70 ± 0.82 ^{brAB}	5.07 ± 0.73 ^{rdCA}
8	2.15 ± 0.24 ^{rdA}	2.45 ± 0.16 ^{rdB}		2.48 ± 0.18 ^{rdCA}	1.72 ± 0.13 ^{rdA}	1.75 ± 0.18 ^{rdCA}		1.74 ± 0.10 ^{rdCA}	3.86 ± 0.63 ^{rdCA}	5.08 ± 0.55 ^{rdCA}		4.54 ± 0.63 ^{rdAB}
9	2.26 ± 0.17 ^{brCA}	2.39 ± 0.23 ^{brCA}		2.29 ± 0.22 ^{brCA}	1.61 ± 0.10 ^{rdA}	1.69 ± 0.14 ^{rdB}		1.68 ± 0.10 ^{rdAB}	3.96 ± 0.59 ^{rdCA}	4.82 ± 0.79 ^{rdB}		4.70 ± 0.59 ^{rdB}
10	2.28 ± 0.22 ^{brCA}	2.44 ± 0.25 ^{brdAB}		2.47 ± 0.19 ^{rdCA}	1.93 ± 0.16 ^{rdA}	2.16 ± 0.19 ^{rdAB}		2.21 ± 0.17 ^{rdB}	3.58 ± 0.65 ^{rdA}	4.41 ± 0.48 ^{rdB}		4.39 ± 0.69 ^{rdB}
11		2.43 ± 0.19 ^{brd}		2.27 ± 0.18 ^{rdB}		1.68 ± 0.12 ^{rdA}		1.74 ± 0.16 ^{rdAB}		4.35 ± 0.63 ^{rdA}		4.80 ± 0.66 ^{rdCA}
12		2.08 ± 0.30 ^{rdA}		1.94 ± 0.30 ^{rdA}		1.78 ± 0.21 ^{rdCA}		1.69 ± 0.22 ^{rdB}		4.63 ± 0.90 ^{rdB}		4.30 ± 0.80 ^{rdB}
13		2.57 ± 0.27 rd				2.33 ± 0.20 rd				4.34 ± 0.73 ^{rdAB}		
14		2.42 ± 0.20 ^{brd}				2.22 ± 0.13 ^{rdB}				4.30 ± 0.79 ^{rdB}		
Mean	2.30 ± 0.15 ^{rdA}	2.42 ± 0.12 ^{rdB}	2.41 ± 0.13 ^{rdB}	2.37 ± 0.20 ^{rdAB}	1.78 ± 0.11 ^{rdA}	1.92 ± 0.20 ^{rdB}	1.84 ± 0.07 ^{rdB}	1.87 ± 0.18 ^{rdCA}	4.08 ± 0.33 ^{rdA}	4.64 ± 0.21 ^{rdAB}	4.46 ± 0.28 ^{rdAB}	4.57 ± 0.31 ^{rdAB}
Sig.	**	**	**	**	**	**	**	**	**	n.s.	*	**

462

463 The results are the mean of six replicates ± Standard Deviation. ** (P < 0.01); * (P < 0.05); n.s. (not significant). The lowercase letters represent the

464 significant difference vertically at P < 0.05. The capital letters represent the significant difference horizontally at P < 0.05 between the three films

465 and the fruits without film for each day of analysis

466

467

468 Table 3

469 Physical parameters in red raspberries (cv. Erika), the day of the harvest and O₂ and CO₂
470 composition in the headspace of the packaging.

Day	L*	a*	b*	SSC (°Brix)	TA (% citric acid)	Moisture (%)	O ₂ (%)	CO ₂ (%)
0	38.38 ± 3.576	16.93 ± 0.63	6.86 ± 1.34	10.87 ± 0.84	1.44 ± 0.13	86.77 ± 0.51	20.90 ± 0.00	0.03 ± 0.00

471

472 The results are the mean of six replicates ± Standard Deviation.

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475 Table 4

476 Effect of storage period in the fridge at 1 °C on the color parameter in red raspberries (cv. Erika).

Day	L*				a*				b*			
	WF	NA	NB	PET	WF	NA	NB	PET	WF	NA	NB	PET
1	36.09 ± 3.51 ^{cdA}	38.91 ± 3.41 ^{dA}	36.44 ± 3.44 ^{cdA}	34.50 ± 2.98 ^{abA}	19.56 ± 0.09 ^{cd}	20.87 ± 2.97 ^{abcd}	19.30 ± 1.91 ^{cdA}	20.66 ± 4.22 ^{cdA}	6.25 ± 0.52 ^{abcd}	7.52 ± 1.45 ^{abcd}	6.43 ± 0.57 ^{cd}	8.19 ± 2.48 ^{bcd}
2	36.50 ± 3.82 ^{cdA}	38.46 ± 4.22 ^{abcdA}	34.55 ± 4.65 ^{cdA}	36.33 ± 5.27 ^{cdA}	11.69 ± 1.28 ^{cdA}	22.48 ± 4.28 ^{abcd}	23.35 ± 5.82 ^{cdB}	18.72 ± 3.15 ^{cdAB}	4.07 ± 1.09 ^{cdAB}	9.48 ± 1.33 ^{cdB}	8.25 ± 1.90 ^{cd}	6.78 ± 1.07 ^{abcd}
3	36.60 ± 5.43 ^{cdA}	31.22 ± 3.42 ^{cdA}	32.10 ± 0.66 ^{cdA}	30.28 ± 2.82 ^{cdA}	18.39 ± 7.21 ^{cdA}	26.61 ± 1.89 ^{cdA}	27.45 ± 2.90 ^{cdA}	21.87 ± 2.30 ^{cdA}	8.17 ± 3.08 ^{cdA}	11.21 ± 1.44 ^{cd}	9.62 ± 1.06 ^{cdA}	8.75 ± 0.96 ^{cdA}
4	36.40 ± 2.32 ^{cdA}	37.04 ± 1.42 ^{cdA}	37.51 ± 2.43 ^{cdA}	35.89 ± 4.43 ^{cdA}	11.81 ± 2.12 ^{cdA}	14.17 ± 1.11 ^{cdA}	20.50 ± 1.80 ^{cdB}	14.82 ± 2.55 ^{cdA}	3.46 ± 0.53 ^{cdA}	4.57 ± 0.34 ^{cd}	8.61 ± 0.83 ^{cd}	4.86 ± 1.10 ^{cdA}
5	36.13 ± 5.39 ^{cdB}	28.30 ± 0.87 ^{cdA}	37.15 ± 1.77 ^{cdB}	26.86 ± 1.49 ^{cdA}	14.13 ± 3.27 ^{cdA}	23.74 ± 3.60 ^{cdB}	30.82 ± 0.66 ^{cdC}	22.35 ± 1.09 ^{cdB}	4.90 ± 1.97 ^{cdA}	10.25 ± 2.21 ^{cdBC}	12.69 ± 0.81 ^{cd}	8.36 ± 1.21 ^{cdAB}
6	27.78 ± 1.20 ^{cdA}	37.00 ± 2.61 ^{cdB}	32.55 ± 2.40 ^{cdAB}	38.71 ± 1.93 ^{cdC}	17.25 ± 2.24 ^{cdC}	14.94 ± 3.75 ^{cdAB}	22.23 ± 3.31 ^{cdC}	9.89 ± 1.34 ^{cd}	5.18 ± 1.09 ^{cdAB}	5.41 ± 1.71 ^{cdAB}	8.17 ± 1.31 ^{cdC}	3.65 ± 0.80 ^{cdA}
7	29.87 ± 2.31 ^{cdAB}	31.55 ± 1.65 ^{cdAB}	34.53 ± 1.46 ^{cdB}	28.54 ± 3.63 ^{cdA}	15.20 ± 4.56 ^{cdA}	26.15 ± 0.81 ^{cdB}	31.36 ± 2.11 ^{cdB}	28.61 ± 1.99 ^{cdB}	5.30 ± 1.39 ^{cdA}	10.91 ± 0.52 ^{cdB}	12.41 ± 2.35 ^{cdB}	11.26 ± 1.66 ^{cdB}
8	26.38 ± 0.84 ^{cd}	28.79 ± 1.26 ^{cd}		27.90 ± 4.48 ^{cdA}	25.49 ± 2.67 ^{cdA}	23.47 ± 5.89 ^{cdA}		19.15 ± 4.21 ^{cd}	9.41 ± 1.70 ^{cdA}	8.65 ± 2.38 ^{cdAB}		6.56 ± 2.49 ^{cdAB}
9	39.37 ± 1.12 ^{cdA}	34.36 ± 3.38 ^{cdAB}		35.06 ± 4.02 ^{cdAB}	10.83 ± 2.31 ^{cdA}	25.15 ± 5.39 ^{cdB}		15.33 ± 3.88 ^{cdAB}	2.52 ± 0.83 ^{cdA}	8.03 ± 2.15 ^{cdAB}		4.98 ± 1.54 ^{cdAB}
10	34.60 ± 3.99 ^{cdAB}	36.44 ± 0.42 ^{cdA}		40.47 ± 1.65 ^{cdA}	14.78 ± 1.76 ^{cdB}	22.58 ± 4.73 ^{cdB}		13.11 ± 3.07 ^{cdA}	5.10 ± 1.39 ^{cdA}	8.05 ± 1.01 ^{cdAB}		3.87 ± 0.39 ^{cdA}
11		35.28 ± 2.37 ^{cdB}		30.40 ± 1.65 ^{cdB}		25.10 ± 0.13 ^{cd}		22.88 ± 5.96 ^{cd}		10.31 ± 0.48 ^{cdB}		8.56 ± 3.41 ^{cdB}
12		34.73 ± 3.34 ^{cdB}		29.90 ± 2.75 ^{cdB}		21.40 ± 2.53 ^{cdB}		27.73 ± 5.05 ^{cd}		8.04 ± 1.54 ^{cdB}		10.30 ± 1.81 ^{cd}
13		34.20 ± 4.40 ^{cdB}				18.37 ± 1.43 ^{cdB}				6.65 ± 1.23 ^{cd}		
14		30.05 ± 0.39 ^{cdB}				27.87 ± 4.02 ^{cd}				11.98 ± 3.45 ^{cd}		
Mean	33.97 ± 4.35 ^A	33.67 ± 3.26 ^A	34.97 ± 2.15 ^A	32.90 ± 4.49 ^A	15.91 ± 4.45 ^{AB}	22.35 ± 4.14 ^{DE}	25.00 ± 4.89 ^E	19.59 ± 5.64 ^{CD}	5.43 ± 2.07 ^{AB}	8.65 ± 2.19 ^{CD}	9.45 ± 2.31 ^D	7.18 ± 2.47 ^{BC}
Sig.	*	**	n.s.	**	*	**	**	**	**	**	**	**

477

478 The results are the mean of six replicates ± Standard Deviation. The lowercase letters represent the significant difference vertically at P < 0.05. The
 479 capital letters represent the significant difference horizontally at P < 0.05 between the three films and the fruits without film for each day of
 480 analysis.

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487 Table 5

488 Effect of storage period in the freezer at -20 °C on the color parameter in red raspberries (cv. Erika).

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Mon- th	L*	a*				b*						
		WF	NA	NB	PET	WF	NA	NB	PET			
1	37.59 ± 1.30 ^{hA}	39.02 ± 1.88 ^{hB}	39.87 ± 1.35 ^{hA}	35.21 ± 3.87 ^{hBA}	29.63 ± 1.05 ^{hDA}	30.55 ± 0.81 ^{hBA}	26.84 ± 5.65 ^{hA}	27.27 ± 3.20 ^{hBA}	10.55 ± 0.66 ^{hBA}	10.41 ± 0.63 ^{hA}	9.55 ± 2.51 ^{hA}	10.41 ± 1.97 ^{hBA}
2	37.99 ± 3.01 ^{hA}	38.22 ± 1.01 ^{hBA}	40.48 ± 1.56 ^{hA}	37.14 ± 1.03 ^{hBA}	29.49 ± 1.21 ^{hDA}	31.54 ± 0.75 ^{hBA}	30.07 ± 1.91 ^{hA}	30.26 ± 1.99 ^{hA}	9.84 ± 0.98 ^{hBA}	10.72 ± 0.55 ^{hA}	9.82 ± 1.47 ^{hA}	11.37 ± 0.26 ^{hA}
3	37.29 ± 2.45 ^{hB}	35.58 ± 1.36 ^{hBA}	37.85 ± 2.81 ^{hB}	30.89 ± 1.97 ^{hA}	27.58 ± 4.62 ^{hBA}	27.45 ± 1.94 ^{hBA}	27.10 ± 2.66 ^{hA}	25.88 ± 1.12 ^{hBA}	9.80 ± 1.78 ^{hBA}	9.39 ± 0.11 ^{hA}	8.05 ± 1.50 ^{hBA}	9.45 ± 0.45 ^{hBA}
4	35.41 ± 0.95 ^{hA,B}	33.53 ± 2.14 ^{hA}	37.03 ± 0.66 ^{hA,B}	39.73 ± 2.96 ^{hB}	28.22 ± 1.91 ^{hBA}	28.53 ± 0.27 ^{hBA}	31.02 ± 1.32 ^{hA}	30.54 ± 4.69 ^{hA}	9.77 ± 1.27 ^{hBA}	10.07 ± 0.39 ^{hA}	9.04 ± 1.05 ^{hA}	10.87 ± 2.49 ^{hBA}
5	36.33 ± 1.90 ^{hA}	38.18 ± 2.43 ^{hBA}	38.60 ± 3.16 ^{hA}	35.15 ± 0.82 ^{hBA}	27.84 ± 1.24 ^{hBA}	32.25 ± 0.95 ^{hB}	27.32 ± 1.01 ^{hA}	24.80 ± 1.89 ^{hBA}	8.73 ± 0.23 ^{hBA}	10.92 ± 0.53 ^{hB}	7.78 ± 1.00 ^{hBA}	7.80 ± 1.27 ^{hBA}
6	40.14 ± 3.04 ^{hA}	40.08 ± 1.30 ^{hBA}	40.45 ± 1.24 ^{hA}	36.50 ± 3.64 ^{hBA}	24.01 ± 3.53 ^{hBA}	28.72 ± 1.73 ^{hBA}	24.94 ± 1.07 ^{hA}	20.73 ± 1.67 ^{hBA}	7.08 ± 1.66 ^{hBA}	8.29 ± 0.42 ^{hBA}	7.39 ± 1.38 ^{hBA}	7.37 ± 1.54 ^{hBA}
7	41.50 ± 1.47 ^{hA}	43.40 ± 3.76 ^{hA}	44.25 ± 4.42 ^{hA}	37.89 ± 3.64 ^{hBA}	22.32 ± 1.93 ^{hBA}	25.60 ± 3.55 ^{hBA}	18.83 ± 4.38 ^{hBA}	17.36 ± 0.16 ^{hA}	5.99 ± 1.20 ^{hA}	7.25 ± 0.59 ^{hA}	5.31 ± 0.91 ^{hA}	6.40 ± 1.66 ^{hA}
8	38.27 ± 4.26 ^{hA}	41.79 ± 2.66 ^{hBA}	37.92 ± 2.62 ^{hA}	37.40 ± 4.29 ^{hBA}	24.27 ± 2.61 ^{hBA}	25.68 ± 4.60 ^{hBA}	29.71 ± 1.74 ^{hB}	20.72 ± 4.33 ^{hBA}	6.93 ± 1.37 ^{hBA}	7.47 ± 1.34 ^{hBA}	9.21 ± 1.20 ^{hA}	6.57 ± 2.61 ^{hBA}
9	35.71 ± 3.68 ^{hA}	46.86 ± 2.79 ^{hB}	39.18 ± 4.64 ^{hBA}	36.63 ± 3.20 ^{hBA}	34.14 ± 0.75 ^{hB}	25.02 ± 4.50 ^{hA}	27.30 ± 4.33 ^{hBA}	32.04 ± 2.63 ^{hBA}	12.41 ± 0.61 ^{hA}	9.94 ± 1.26 ^{hBA}	9.90 ± 1.13 ^{hA}	11.26 ± 1.51 ^{hA}
10	39.71 ± 2.47 ^{hA}	33.94 ± 2.81 ^{hBA}	38.17 ± 5.64 ^{hA}	38.23 ± 2.93 ^{hBA}	25.62 ± 3.28 ^{hBA}	32.11 ± 1.58 ^{hB}	20.36 ± 2.74 ^{hA}	22.27 ± 6.03 ^{hBA}	8.21 ± 1.40 ^{hBA}	11.24 ± 1.74 ^{hB}	5.79 ± 0.95 ^{hBA}	7.60 ± 2.84 ^{hBA}
11	36.15 ± 3.35 ^{hA}	34.12 ± 0.44 ^{hBA}	36.79 ± 3.91 ^{hA}	38.53 ± 4.70 ^{hBA}	31.34 ± 1.90 ^{hBA}	31.95 ± 2.80 ^{hA}	30.93 ± 2.46 ^{hA}	26.63 ± 4.56 ^{hBA}	10.21 ± 0.35 ^{hBA}	10.43 ± 2.47 ^{hA}	10.77 ± 0.68 ^{hA}	8.90 ± 3.14 ^{hBA}
Mean	37.83 ± 1.96 ^{hA,B}	38.70 ± 4.19 ^{hB}	39.14 ± 2.11 ^h	36.66 ± 2.35 ^h	27.68 ± 3.47 ^{hC}	29.04 ± 2.81 ^{hC}	26.76 ± 4.04 ^{hB}	25.41 ± 4.69 ^h	9.05 ± 1.88 ^{hA,B}	9.65 ± 1.39 ^h	8.42 ± 1.74 ^h	8.91 ± 1.87 ^{hB}
Sig.	n.s.	**	n.s.	n.s.	**	*	**	**	**	*	**	n.s.

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491 The results are the mean of six replicates ± Standard Deviation. The lowercase letters represent the significant difference vertically at P < 0.05. The
 492 capital letters represent the significant difference horizontally at P < 0.05 between the three films and the fruits without film for each month of
 493 analysis

494

495 Table 6

496 Effect of storage period in the fridge at 1 °C on the soluble solid contents (SSC), titratable acidity (TA) and the moisture parameters in red
 497 raspberries (cv. Erika).

Day	Soluble Solid Content (°Brix)				Titratable Acidity (% citric acid)				Moisture (%)			
	WF	NA	NB	PET	WF	NA	NB	PET	WF	NA	NB	PET
1	10.50 ± 0.00 ^{abA}	10.05 ± 1.85 ^{ba}	9.30 ± 0.60 ^{ab}	9.25 ± 0.15 ^{ab}	2.15 ± 0.10 ^{abD}	1.80 ± 0.03 ^{ab}	1.82 ± 0.04 ^{abB}	1.93 ± 0.04 ^{abC}	87.40 ± 0.56 ^{abA}	87.92 ± 0.27 ^{ba}	87.38 ± 0.24 ^{ab}	87.71 ± 0.05 ^{bcab}
2	9.83 ± 1.15 ^{aA}	9.20 ± 0.06 ^{abA}	9.57 ± 0.09 ^{ab}	9.00 ± 0.73 ^{aA}	1.86 ± 0.22 ^{abAB}	1.71 ± 0.10 ^{ab}	2.04 ± 0.09 ^{abAB}	2.04 ± 0.15 ^{abB}	86.16 ± 0.60 ^{cdA}	87.49 ± 0.07 ^{abab}	86.93 ± 0.84 ^{cdabAB}	87.43 ± 0.48 ^{abcdB}
3	9.63 ± 0.46 ^{aA}	8.13 ± 1.44 ^{ba}	9.43 ± 0.33 ^{aA}	8.77 ± 1.42 ^{aA}	2.52 ± 0.22 ^{ab}	1.92 ± 0.16 ^{abcdA}	2.04 ± 0.15 ^{ba}	2.12 ± 0.19 ^{abAB}	85.73 ± 0.41 ^{bcB}	87.44 ± 0.42 ^{abC}	84.71 ± 0.34 ^{abA}	87.19 ± 0.44 ^{abC}
4	9.57 ± 0.66 ^{aA}	9.23 ± 0.34 ^{abA}	10.13 ± 1.00 ^{aA}	9.37 ± 0.61 ^{aA}	2.05 ± 0.09 ^{abB}	1.85 ± 0.11 ^{abA}	2.05 ± 0.04 ^{abB}	2.36 ± 0.05 ^{bcC}	86.23 ± 0.29 ^{cdA}	87.12 ± 0.64 ^{abA}	86.39 ± 0.29 ^{bcD}	86.95 ± 0.18 ^{aA}
5	10.53 ± 0.82 ^{abA}	9.77 ± 0.33 ^{abA}	9.03 ± 0.83 ^{aA}	9.30 ± 1.28 ^{aA}	2.16 ± 0.22 ^{abA}	1.99 ± 0.06 ^{bcD}	2.13 ± 0.07 ^{bcA}	2.51 ± 0.12 ^{cdB}	85.37 ± 0.28 ^{abA}	87.39 ± 0.64 ^{abB}	85.31 ± 0.59 ^{abA}	88.09 ± 0.22 ^{cdB}
6	10.27 ± 0.74 ^{abB}	7.93 ± 0.74 ^{aA}	9.50 ± 0.16 ^{ab}	9.67 ± 0.12 ^{ab}	1.99 ± 0.09 ^{abAB}	1.86 ± 0.07 ^{abA}	2.30 ± 0.07 ^{cd}	2.13 ± 0.05 ^{abB}	84.93 ± 0.30 ^{abA}	87.89 ± 0.53 ^{abB}	87.21 ± 0.59 ^{cdB}	87.46 ± 0.45 ^{abB}
7	11.50 ± 1.10 ^{abA}	8.43 ± 0.95 ^{abA}	8.23 ± 2.42 ^{abA}	8.90 ± 0.50 ^{ab}	2.32 ± 0.09 ^{bcA}	2.09 ± 0.13 ^{cdA}	2.09 ± 0.11 ^{ba}	2.36 ± 0.14 ^{bcA}	84.72 ± 0.67 ^{abA}	87.85 ± 0.57 ^{abC}	86.04 ± 0.21 ^{bcB}	87.14 ± 0.60 ^{abC}
8	12.07 ± 1.45 ^{ab}	8.83 ± 0.61 ^{abA}		8.70 ± 0.24 ^{ab}	1.99 ± 0.19 ^{abA}	2.43 ± 0.03 ^{ab}		2.15 ± 0.04 ^{abA}	85.17 ± 0.44 ^{abA}	87.38 ± 0.59 ^{abB}		88.25 ± 0.24 ^{ab}
9	11.50 ± 0.43 ^{abB}	9.33 ± 0.96 ^{abA}		9.80 ± 0.54 ^{ab}	1.99 ± 0.07 ^{abA}	2.32 ± 0.07 ^{ab}		2.72 ± 0.19 ^{cd}	84.49 ± 1.31 ^{abA}	86.77 ± 0.54 ^{ab}		87.98 ± 0.09 ^{ab}
10	10.90 ± 0.37 ^{abB}	8.83 ± 0.39 ^{abA}		8.77 ± 0.41 ^{abA}	2.04 ± 0.12 ^{abA}	2.29 ± 0.02 ^{cdB}		1.96 ± 0.03 ^{abA}	83.88 ± 1.26 ^{abA}	87.25 ± 0.75 ^{abB}		87.69 ± 0.30 ^{abcdB}
11		9.07 ± 0.96 ^{ab}		8.13 ± 2.00 ^a		2.14 ± 0.14 ^{cd}		2.06 ± 0.02 ^a		88.10 ± 0.26 ^b		87.60 ± 0.07 ^{abcd}
12		8.53 ± 0.50 ^{ab}		8.37 ± 0.09 ^a		2.22 ± 0.16 ^{cd}		2.53 ± 0.14 ^{cd}		87.67 ± 0.20 ^{ab}		87.67 ± 0.19 ^{abcd}
13		9.70 ± 0.36 ^{ab}				1.99 ± 0.06 ^{bcD}				87.14 ± 0.28 ^{ab}		
14		9.53 ± 0.66 ^{ab}				2.35 ± 0.10 ^{bc}				87.09 ± 0.30 ^{ab}		
Mean	10.63 ± 0.85 ^C	9.04 ± 0.63 ^A	9.31 ± 0.58 ^{abB}	9.00 ± 0.50 ^A	2.11 ± 0.19 ^{abB}	2.07 ± 0.23 ^A	2.07 ± 0.14 ^A	2.24 ± 0.25 ^B	85.41 ± 1.01 ^A	87.54 ± 0.41 ^C	86.28 ± 1.00 ^B	87.60 ± 0.39 ^C
Sig.	n.s.	n.s.	n.s.	n.s.	*	**	**	**	**	n.s.	**	*

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500 Table 7

501 Effect of storage period in the freezer at $-20\text{ }^{\circ}\text{C}$ on the soluble solid contents (SSC), titratable acidity (TA) and the moisture parameters in red
 502 raspberries (cv. Erika).

Month	Soluble Solid Content (%Brix)				Titratable Acidity (% citric acid)				Moisture (%)			
	WF	NA	NB	PET	WF	NA	NB	PET	WF	NA	NB	PET
1	8.40 ± 0.50 ^{abA}	8.93 ± 0.87 ^{bcDA}	7.90 ± 0.50 ^{aA}	8.87 ± 0.58 ^{abA}	2.21 ± 0.17 ^{bcA}	2.00 ± 0.07 ^{abA}	2.01 ± 0.20 ^{abA}	1.97 ± 0.11 ^{abA}	85.62 ± 0.58 ^{abA}	85.96 ± 0.18 ^{abD}	86.12 ± 0.32 ^{abD}	86.62 ± 0.24 ^{abD}
2	7.93 ± 1.10 ^{aA}	9.30 ± 0.64 ^{abA}	7.57 ± 0.26 ^{aA}	9.27 ± 0.88 ^{bcA}	2.09 ± 0.02 ^{abB}	1.77 ± 0.07 ^{aA}	2.02 ± 0.05 ^{abB}	2.05 ± 0.12 ^{abB}	86.85 ± 0.35 ^{cdA}	86.12 ± 0.24 ^{aA}	86.93 ± 0.39 ^{aA}	86.13 ± 0.62 ^{aA}
3	8.00 ± 0.37 ^{aA}	8.53 ± 0.09 ^{bcAB}	8.27 ± 0.76 ^{abA}	9.60 ± 0.43 ^{cdB}	2.16 ± 0.42 ^{bcA}	2.15 ± 0.08 ^{bcA}	1.93 ± 0.13 ^{abA}	1.78 ± 0.13 ^{abA}	86.34 ± 0.67 ^{bcA}	85.46 ± 0.85 ^{aA}	86.81 ± 0.34 ^{aA}	86.07 ± 0.35 ^{aA}
4	9.73 ± 0.05 ^{bcB}	9.20 ± 0.24 ^{cdAB}	8.63 ± 0.53 ^{abA}	9.87 ± 0.00 ^{cdB}	2.49 ± 0.40 ^{abB}	1.96 ± 0.04 ^{abA}	2.04 ± 0.03 ^{abB}	2.04 ± 0.17 ^{abAB}	86.79 ± 0.40 ^{cdA}	86.42 ± 0.53 ^{aA}	87.40 ± 0.23 ^{aA}	86.11 ± 0.11 ^{aA}
5	8.73 ± 0.42 ^{abAB}	9.20 ± 0.36 ^{cdB}	8.07 ± 0.54 ^{abA}	9.20 ± 0.16 ^{cdB}	2.02 ± 0.16 ^{abA}	1.90 ± 0.11 ^{abA}	1.94 ± 0.07 ^{abA}	2.01 ± 0.08 ^{abA}	87.23 ± 0.35 ^{cdB}	86.77 ± 0.23 ^{abB}	86.64 ± 0.12 ^{abB}	86.43 ± 0.33 ^{abA}
6	8.68 ± 0.04 ^{abA}	8.30 ± 0.61 ^{bcDA}	9.28 ± 0.29 ^{abA}	8.50 ± 0.75 ^{abA}	2.02 ± 0.24 ^{abB}	1.88 ± 0.09 ^{abAB}	1.82 ± 0.10 ^{abB}	1.80 ± 0.06 ^{abA}	87.28 ± 0.32 ^{abB}	87.37 ± 0.24 ^{abD}	86.67 ± 0.30 ^{abA}	86.71 ± 0.08 ^{abD}
7	8.67 ± 0.25 ^{abA}	7.57 ± 0.26 ^{abA}	9.60 ± 0.86 ^{abA}	9.53 ± 1.40 ^{abA}	1.59 ± 0.15 ^{abA}	2.02 ± 0.12 ^{abB}	1.86 ± 0.03 ^{abB}	1.97 ± 0.11 ^{abB}	87.56 ± 0.72 ^{abA}	87.55 ± 0.36 ^{abA}	87.65 ± 0.14 ^{abA}	87.05 ± 0.19 ^{abA}
8	9.87 ± 0.58 ^{cdB}	9.27 ± 0.58 ^{cdAB}	8.93 ± 0.24 ^{abA}	10.17 ± 0.26 ^{cdB}	2.00 ± 0.02 ^{abAB}	2.19 ± 0.02 ^{cdB}	1.87 ± 0.19 ^{abA}	1.87 ± 0.06 ^{abA}	85.01 ± 0.55 ^{abA}	85.35 ± 0.07 ^{abA}	85.66 ± 13.37 ^{abA}	85.26 ± 0.13 ^{abA}
9	9.60 ± 0.14 ^{bcA}	9.77 ± 1.02 ^{abA}	8.87 ± 1.16 ^{abA}	9.13 ± 0.37 ^{abA}	1.89 ± 0.21 ^{abA}	2.06 ± 0.07 ^{abA}	2.03 ± 0.04 ^{abA}	1.93 ± 0.13 ^{abA}	87.73 ± 0.21 ^{abA}	87.99 ± 0.04 ^{abA}	87.93 ± 0.35 ^{abA}	90.58 ± 3.83 ^{abA}
10	9.63 ± 0.45 ^{bcA}	7.63 ± 1.23 ^{abA}	7.73 ± 1.03 ^{abA}	9.57 ± 0.92 ^{abA}	2.39 ± 0.13 ^{bcA}	2.25 ± 0.39 ^{abA}	2.00 ± 0.08 ^{abA}	2.09 ± 0.09 ^{abA}	86.36 ± 0.19 ^{bcA}	90.35 ± 5.10 ^{abA}	87.78 ± 0.67 ^{abA}	87.14 ± 0.23 ^{abA}
11	9.67 ± 0.71 ^{bcC}	6.47 ± 0.71 ^{abA}	8.27 ± 0.41 ^{abB}	10.10 ± 0.36 ^{abC}	2.01 ± 0.22 ^{abA}	1.93 ± 0.01 ^{abA}	1.99 ± 0.16 ^{abA}	2.07 ± 0.14 ^{abA}	86.88 ± 0.41 ^{cdA}	86.44 ± 0.18 ^{abA}	86.44 ± 0.58 ^{abA}	86.42 ± 0.15 ^{abA}
Mean	8.99 ± 0.73 _B	8.56 ± 0.99 _A	8.46 ± 0.65 _A	9.44 ± 0.51 _C	2.08 ± 0.24 _B	2.01 ± 0.14 _{AB}	1.96 ± 0.08 _A	1.96 ± 0.11 _A	86.70 ± 0.82 _A	86.89 ± 1.42 _A	86.00 ± 3.48 _A	86.78 ± 1.37 _A
Sig.	*	**	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	**	n.s.	n.s.	*

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507 Table 8

508 Effect of storage period, from the fruits stored in the different films, on O₂ and CO₂ concentrations
 509 in red raspberries (cv. Erika), stored at 1 °C in the fridge

Day	O ₂ (%)			CO ₂ (%)		
	NA	NB	PET	NA	NB	PET
1	9.1 ± 0.9 ^{nsA}	17.3 ± 2.0 ^{nsB}	16.3 ± 1.6 ^{nsB}	9.6 ± 0.6 ^{nsB}	4.4 ± 2.0 ^{nsA}	5.9 ± 1.7 ^{nsA}
2	7.7 ± 1.8 ^{nsA}	17.7 ± 1.2 ^{nsB}	16.8 ± 1.0 ^{nsB}	11.7 ± 1.2 ^{nsB}	4.8 ± 1.8 ^{nsA}	5.3 ± 1.4 ^{nsA}
3	12.3 ± 4.4 ^{nsA}	14.2 ± 6.9 ^{nsA}	17.5 ± 1.2 ^{nsA}	9.3 ± 3.8 ^{nsA}	7.9 ± 5.9 ^{nsA}	4.4 ± 1.7 ^{nsA}
4	9.3 ± 8.5 ^{nsA}	14.3 ± 4.3 ^{nsA}	17.9 ± 0.6 ^{nsA}	12.1 ± 7.5 ^{nsA}	8.5 ± 4.5 ^{nsA}	3.8 ± 0.8 ^{nsA}
5	6.7 ± 8.8 ^{nsA}	15.7 ± 3.1 ^{nsA}	17.2 ± 1.1 ^{nsA}	13.0 ± 7.1 ^{nsA}	7.9 ± 4.4 ^{nsA}	4.9 ± 1.6 ^{nsA}
6	1.5 ± 0.8 ^{nsA}	19.4 ± 0.3 ^{nsC}	17.4 ± 1.1 ^{nsB}	18.0 ± 2.9 ^{nsB}	1.2 ± 1.0 ^{nsA}	4.8 ± 1.6 ^{nsA}
7	5.0 ± 3.9 ^{nsA}	19.8 ± 0.3 ^{nsB}	17.1 ± 1.6 ^{nsB}	15.6 ± 2.7 ^{nsB}	1.0 ± 0.6 ^{nsA}	5.2 ± 2.4 ^{nsA}
8	9.8 ± 4.0 ^{nsA}		16.8 ± 0.1 ^{nsA}	12.7 ± 3.4 ^{nsA}		5.6 ± 3.4 ^{nsA}
9	7.2 ± 2.3 ^{nsA}		15.3 ± 9.8 ^{nsA}	14.4 ± 12.2 ^{nsA}		8.0 ± 1.2 ^{nsA}
10	2.0 ± 1.0 ^{nsA}		15.9 ± 2.5 ^{nsB}	20.8 ± 3.4 ^{nsB}		7.5 ± 1.8 ^{nsA}
11	1.0 ± 1.2 ^{nsA}		16.6 ± 0.5 ^{nsB}	19.8 ± 3.6 ^{nsB}		6.5 ± 1.6 ^{nsA}
12	2.4 ± 0.9 ^{nsA}		16.7 ± 1.3 ^{nsB}	19.8 ± 0.7 ^{nsB}		6.4 ± 0.7 ^{nsA}
13	2.6 ± 0.3 ^{nsB}			21.0 ± 7.1 ^B		
14	4.8 ± 0.28 ^{nsB}			20.3 ± 0.91 ^B		
Mean	5.81 ± 3.58	17.31 ± 2.35	16.72 ± 0.76	15.58 ± 4.29	4.56 ± 3.32	5.91 ± 1.43
Stg.	n.s.	n.s.	n.s.	n.s.	*	n.s.

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511 Table 9

512 Variance analyses on the different parameters, taking into consideration film effect, day or month
 513 effect and the interaction. ** (P< 0.01); * (P<0.05); n.s. (not significant).

Parameter	Refrigerated fruits			Frozen fruits		
	Film	Days	Film*Days	Film	Months	Film*Months
Length (cm)	**	**	**			
Diameter (cm)	**	**	**			
Weight (g)	**	*	**			
L*	n.s.	*	**	n.s.	n.s.	n.s.
a*	**	**	**	*	**	**
b*	**	**	**	n.s.	**	n.s.
SSC (°Brix)	**	n.s.	n.s.	*	n.s.	**
Titratable Acidity (% citric acid)	n.s.	n.s.	**	n.s.	n.s.	*
Moisture (%)	**	n.s.	**	n.s.	**	n.s.
O ₂ (%)	**	n.s.	*			
CO ₂ (%)	**	n.s.	*			

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