

Modified atmosphere packaging of sweet cherries with biodegradable films

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Abstract

The effect of Modified Atmosphere Packaging (MAP) with biodegradable films (Film 1: 25 μm thickness; O_2 TR 3000 $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$; Film 2: 25 μm thickness O_2 TR 900 $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$) on preserving sweet cherry fruit quality during cold storage was evaluated. The biodegradable films were compared with a control film of polyethylene (25 μm thickness; O_2 TR 8000 $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$). Gas composition inside the packages, parameters related to quality (firmness, colour, Total Soluble Solids content, Titratable Acidity) and changes in bioactive compounds (total polyphenols, total anthocyanins and total antioxidant activity) were analyzed during 15 days of cold storage at 1°C. The data showed that the use of biodegradable films was useful to preserve quality of cherries through a delay in the changes in colour and the losses of firmness and acidity. Film 2, characterized by an high permeability to CO_2 and high barrier to O_2 provided the best results in terms of colour, acidity and firmness. With respect to anthocyanins content, phenolics contents and total antioxidant activity, differences existed among the three treatments (control, Film1, Film 2) but was detected any negative effect due to biodegradable films. The results suggest that biodegradable polymers could be used in packaging of sweet cherries without negative effects on final quality.

Keywords

Storage
organoleptic quality
bioactive compound
Sweetheart®
cherry

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Introduction

Cherries are a very perishable commodity, with a moderate respiration rate (10–20 $\text{mg CO}_2 \text{kg}^{-1} \text{h}^{-1}$ at 5°C) (Kader, 2011) and a short shelf life in a conventional cold storage in consequence of a high susceptibility to surface pitting, stem browning and decay. But Sweet cherries are also highly appreciated by the consumer due to their precocity and excellent quality. The main characteristics related to cherry fruit quality are colour, sweetness, sourness, firmness and stem colour. Sweet cherries also contain significant amounts of phytochemical components such as phenolic compounds, which are known to have positive effects on health (Kim *et al.*, 2005).

During storage and transport, cherry fruit soften and darken and postharvest technologies providing even a short extension of shelf life could have a profound effect on the marketing of fresh cherries. In recent years, the use of Modified Atmosphere Packaging (MAP) has been shown to lower respiration rates and delay ripening of fruits by altering the O_2 and CO_2 concentration in the bags to close to ideal MA conditions for cherries: 3-10% oxygen and 10-15% carbon dioxide at 0°C (Mitcham *et al.*, 2002). MAP can also prevent water loss and fruit shriveling

by maintaining a high humidity environment of 90-95% relative humidity. Other researches has also shown that MAP maintained green stems and fruit firmness, both of which are critical for marketing cherries in retail stores (Remón *et al.*, 2000; Kappel *et al.*, 2002; Padilla-Zakour *et al.*, 2004). However incorrect use of MAP or the use of an inappropriate MA film could result in anaerobic conditions leading to product spoilage (Rai *et al.*, 2002).

Sweet cherry has a higher tolerance to elevated CO_2 concentrations than most stone fruit crops (Porritt and Mason, 1965). High CO_2 concentrations were used to reduce losses from decay caused by many fungi in the fruit (De Vries-Paterson *et al.*, 1991). This feature makes cherries particularly suitable to MAP (Serrano *et al.*, 2005). Traditionally, a great quantity of plastic materials is used for packaging purposes but there is a growing pressure in fresh fruits and vegetables packaging sector to replace the petrochemical based packaging films with a more environmentally friendly biodegradable materials (Tharanathan, 2003). The use of biodegradable polymers for packaging offers an alternative and partial solution to the problem of accumulation of solid waste composed by synthetic inert polymers. Compostable and biodegradable polymeric materials

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are therefore under great attention by both academy and industry (Guralp and Sebnem, 2009), although biodegradable films are more expensive than petrochemical materials.

The aim of this paper was to evaluate the effect of MAP with biodegradable films on preserving sweet cherry fruit quality during cold storage (15 days). Gas composition inside the packages, parameter related to quality (firmness, colour, TSS, TA) and changes in bioactive compounds (total polyphenols, total anthocyanins and total antioxidant activity) were analyzed during 15 days of cold storage at 1°C.

Materials and Methods

Plant material

Sweet cherry fruit, cultivar Sweetheart[®], were obtained from an experimental farm in Piemonte (Italy). The cherries were hand-picked at commercial maturity (TSS 15°Brix; TA 56.9 meq/L). Fruit of uniform size (25-27 mm diameter, 8.5 g average weight), disease-free and without other defects were selected.

Fruit treatments

20 Kg of sweet cherries were selected based on homogeneous colour and size and distributed random into 40 lots of 500 g. Four lots were used to determine physicochemical properties at harvest (day 0) (Table 1). The remaining lots, divided into 3 batches (6 Kg/batch), were packaged with different films for the following MAP: Control, Film 1, Film 2. Control was an high-permeability film of PE (low density polyethylene), Film 1 and Film 2 were based on Mater-Bi[®], completely biodegradable bioplastics obtained from corn starch and biodegradable polymers (Novamont SpA, Novara, Italy).

The films properties were: control (25 µm thickness; O₂ TR 8000 cm³ m⁻² day⁻¹ atm⁻¹); Film 1 (25 µm thickness; O₂ TR 3000 cm³ m⁻² day⁻¹ atm⁻¹), film 2 (25 µm thickness O₂ TR 900 cm³ m⁻² day⁻¹ atm⁻¹). All bags were stored at 1°C and approximately 90% RH for 15 days.

Table 1. Quality characteristics of Sweetheart[®] cherries at harvest

TSS (°Brix)	15
TA (meqL ⁻¹)	56.95
pH	5.04
firmness (H)	52.98

Gas monitoring

The concentrations of oxygen and carbon dioxide inside the packages was monitored by sampling the headspace using a CANAL 121 (Vizag, Gas Analysis,

France). A sample of 0.5 ml was automatically withdrawn from the headspace atmosphere with a pin-needle connected to the injection system. Gases were analyzed with an infrared sensor for CO₂ level and an electrochemical sensor for O₂ level. The instrument was calibrated towards air. The O₂ and CO₂ concentration were quantified (three replications for each film type) every five days

Analysis of total soluble solids (TSS) and titratable acidity (TA)

Total soluble solids (TSS) and titratable acidity (TA) were determined at the beginning of the experiment and after storage (5, 10, 15 days) in triplicate form using juice extracted from a 500 g cherry sample (each film type) blended at high speed in a tissue homogenizer. Soluble solids content was determined by a digital refractometer (Atago refractometer model PR-32). Titratable acidity was measured by titrating 1:10 diluted juice using 0.1 N NaOH by an automatic titrator (Compact 44-00, Crisom).

Fruit firmness

Measurements of firmness were performed every five days on 30 fruits per treatment with hand-held Shore Durometer (T.R. Turoni, Italy) (Kappel *et al.*, 1996; Poovaiah and Nukaya, 1979).

Color measurement

Skin color was measured with a Minolta colorimeter (Chroma Meter Model CR-400, Minolta, Japan). The colorimeter was calibrated using a standard white reflector plate. CIELAB values L* a* b* were determined daily on the cheek area of 30 fruit per treatment (film type). L* indicates lightness, a* indicates chromaticity on a green to red axis and b* chromaticity on a blue to yellow axis. Chroma (C* = (a*²+b*²)^{1/2}) and hue angle (h = arctan b*/a*) were calculated using numerical values of a* and b*.

Anthocyanins content, phenolics content, total antioxidant capacity

For determination of the anthocyanin contents, phenolic contents and total antioxidant capacity, extracts were prepared by weighing 10 g of fresh berries into a centrifuge tube, adding methanol and homogenising the sample for 1 min. Extractions were performed under reduced light conditions. Tubes were centrifuged (3000 rpm for 15 min) and the clear supernatant fluid collected and stored at -26°C for further work. For identification and quantification, extraction was performed as three replicates.

Anthocyanin content was quantified according to the pH differential method by Cheng and Breen

(1991). Anthocyanins were estimated by their absorbance at 510 and 700 nm in buffer at pH 1.0 and pH 4.5, where $A = (A_{515} - A_{700})_{pH1.0} - (A_{515} - A_{700})_{pH4.5}$. Results were expressed as mg of cyanidin-3-glucoside (C3G) per 100 g of fresh berries.

Total phenolics were determined with Folin-Ciocalteu reagent by the method of Slinkard and Singleton (1977) using gallic acid as a standard. Absorption was measured at 765 nm. Results were expressed as mg gallic acid equivalents (GAE) per 100 g of fresh berries.

Antioxidant activity was determined using ferric reducing antioxidant power (FRAP) assay, following the method by Pellegrini *et al.* (2003) with some modifications. The antioxidant capacity of dilute berry extract is determined by its ability to reduce ferric iron to ferrous iron in a solution of TPTZ prepared in sodium acetate at pH 3.6. The reduction of iron in the TPTZ-ferric chloride solution (FRAP reagent) results in the formation of a blue-colored product (ferrous tripyridyltriazine complex), the absorbance of which is read spectrophotometrically at 593 nm 4 min after the addition of appropriately diluted berry extract or antioxidant standard to the FRAP reagent. Results were calibrated against a standard curve produced by addition of freshly prepared $FeSO_4 \times 7H_2O$ 100 - 1000 μM solutions. Results were expressed as mmol Fe^{2+}/kg of fresh berries.

Statistical analysis

Statistical analysis was performed using the STATISTICA 7.1 software package (Statsoft Inc., Tulsa, OK, USA). Experimental data were processed with the variance analysis (ANOVA) according to Tukey's Honestly Significant Difference (HSD) test at $P = 0.05$ to compare means between treatments and control. Sources of variation were treatments and storage.

Results and Discussion

Gas composition

During storage an increase in CO_2 and decrease in O_2 concentrations occurred inside the MAP packages. Final gas concentrations were affected by the type of film used. The highest concentration of CO_2 was reached, after 15 days, inside the packages with Film 1 (6.9%) (Figure 1). It could be explained by low CO_2 permeability of Film 1, which promotes CO_2 accumulation in the packages. The level of carbon dioxide increased rapidly in the last five days of storage, due to the respiration activity. This behavior occurs because the respiration activity is so high at elevated O_2 concentrations that the CO_2 generated

exceeds the quantity that can permeate. The lower concentrations of O_2 and CO_2 were found in packages with Film 2, characterized by an high permeability to CO_2 and high barrier to O_2 (Figure 1). These findings are in accordance with Guilbert *et al.* (1997), they found that some biopolymer-based packagings have impressive gas barrier properties especially against O_2 while they remain relatively permeable to CO_2 . Instead, final gas concentrations were no affected by the film used as Control.

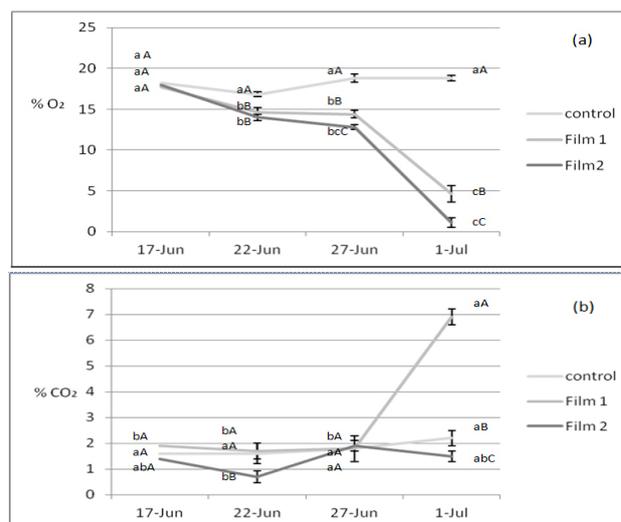


Figure 1. Changes in O_2 (a) and CO_2 (b) concentrations (%) inside MAP packages during storage ($1^\circ C$). Data are the mean \pm SE ($n = 3$). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively.

Fruit Quality

TSS remained unchanged during storage of control fruit while it increased slightly during storage under MAP condition (Film 1 and Film 2). No significant differences existed among control, Film 1 and Film 2 (Figure 2). By contrast total acidity (TA), decreased during storage for all film types. The use of film 2 delayed acidity losses and there were no statistic differences between values of acidity content measured at the start and at the end of storage period (Figure 3) although a slight decrease was observed. Cherry packaged with Film 1 and control fruit showed, after 15 days, TA values significantly lower (Figure 3). According to Diaz-Mula *et al.* (2011), the effectiveness of film appeared to be due to the low permeability to O_2 more than to the high concentration of CO_2 . Values of total acidity of control fruits were to be related to weight loss.

The firmness trend was the same for all samples. Firmness decreased at day 5 then increased in the following days (Figure 4) and the differences were significant. No significant differences were observed

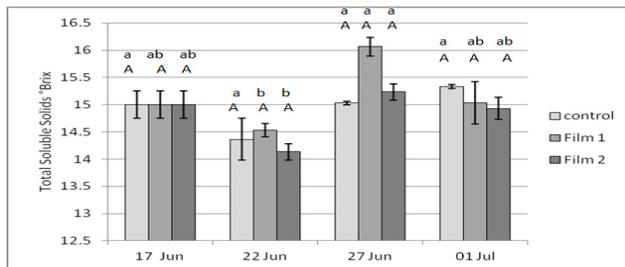


Figure 2. Total soluble solids (TSS) changes during storage of Sweetheart cherries under MAP conditions. Data are the mean \pm SE (n = 3). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively.

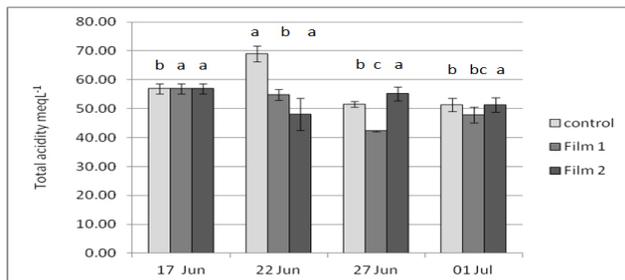


Figure 3. Total acidity (TA) changes during storage of Sweetheart cherries under MAP conditions. Data are the mean \pm SE (n = 3). Different following letters indicate significant differences ($P < 0.05$) during storage for each treatment

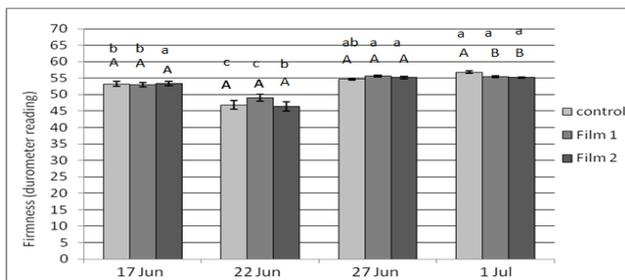


Figure 4. Fruit firmness changes during storage of Sweetheart cherries under MAP conditions. Data are the mean \pm SE (n = 30). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively

among treatments at day 5 and 10, instead at the end of storage control fruits showed the higher value of firmness. This increase in firmness may be attributed to moisture loss during storage, which corresponds to fruit drying and hardening characteristics (Chiabrando *et al.*, 2009). Similar results were reported by Pelayo *et al.* (2003) for strawberries and Basiouny and Chen (1988) for rabbiteye fruits. Increased flesh firmness has been reported for cherry by Mehereiuk *et al.* (1997) and Chen *et al.* (1981).

Lightness (L^*) and Hue angle (h) showed changes during storage. L^* value decreased in all treatments

and the differences found were significant. Film 2 showed almost always higher L^* values while control fruits the lower lightness (Table 2). Hue values increased significantly in all treatments, and were higher in fruits packaged with film 2, indicating that yellow tonality rose in cherry fruit during storage (Table 3). These effects have also been found by Bernalite *et al.* (2003) and Barret and Gonzales (1994) in cherry fruit, and could be attributed to the delay in anthocyanin biosynthesis induced by MAP (Diaz-Mula *et al.*, 2011).

Table 2. Lightness (L^*) changes during storage of Sweetheart cherries under MAP conditions. Data are the mean \pm SE (n = 30)

	17-Jun	20-Jun	23-Jun	26-Jun	29-Jun	1-Jul
control	36.85 ^{aA} \pm 0.58	31.7 ^{bB} \pm 0.78	30.62 ^{bcB} \pm 0.92	30.26 ^{bcC} \pm 0.80	28.1 ^{dA} \pm 0.74	29.12 ^{cdB} \pm 0.60
Film 1	38.48 ^{aA} \pm 0.75	33.78 ^{abB} \pm 0.84	32.39 ^{bcB} \pm 0.75	39.66 ^{aA} \pm 1.21	30.96 ^{bcB} \pm 0.84	30.7 ^{cdB} \pm 0.74
Film 2	38.82 ^{aA} \pm 0.94	37.88 ^{abA} \pm 1.14	35.99 ^{bcA} \pm 1.20	33.78 ^{cdB} \pm 1.07	34.89 ^{abA} \pm 1.20	34.69 ^{abA} \pm 0.99

Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively.

Table 3. Colour (Hue angle) changes during storage of Sweetheart cherries under MAP conditions. Data are the mean \pm SE (n = 30)

	17-Jun	20-Jun	23-Jun	26-Jun	29-Jun	1-Jul
control	25.43 ^{abA} \pm 0.44	27.79 ^{abB} \pm 0.70	29.65 ^{abB} \pm 0.59	28.31 ^{bc} \pm 0.58	29.07 ^{ab} \pm 0.59	28 ^{ab} \pm 0.59
Film 1	26.95 ^{ca} \pm 0.58	29.21 ^{bcAB} \pm 0.60	29.06 ^{bcB} \pm 0.63	34.97 ^{aA} \pm 0.76	30.94 ^{abB} \pm 0.60	28.85 ^{bcB} \pm 0.42
Film 2	27.18 ^{ba} \pm 0.78	30.59 ^{abA} \pm 0.72	31.68 ^{aA} \pm 0.64	31.26 ^{abB} \pm 0.69	32.39 ^{aA} \pm 0.60	30.74 ^{abA} \pm 0.60

Minor and capital letters show significant differences ($p < 0.05$) for each treatment and among treatments for each storage time respectively.

Several authors reported increases in anthocyanins during storage (Kalt *et al.*, 1999; Wang et Stretch 2001; Bernalite *et al.*, 2003), in our study it was not possible to observe similar increases, in fact, the differences found, mainly in control fruit, were not significant (Figure 5). Statistical variations instead were found for total phenolics content, in all treatments. Final values were statistically lower than the initial ones (Figure 6) without significant differences among the 3 treatments. During storage control fruit exhibited significant increases, regarding TAA, after 5 days, while the lower value was observed, at the end of storage period, in samples packaged with Film 2 (Figure 7). Almost no information exists on the effect of MAP on antioxidant activity of fruit in general and of cherry in particular, however Diaz-Mula *et al.* (2011b) obtained similar results on plums. The low increases observed during storage probably were due to the use of plastic films, however MAP did not impart any negative effect on TAA.

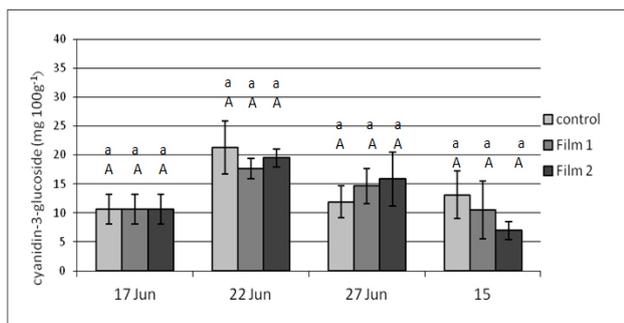


Figure 5. Changes in anthocyanins in Sweetheart cherries during storage under MAP conditions. Data are the mean \pm SE (n = 3). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively

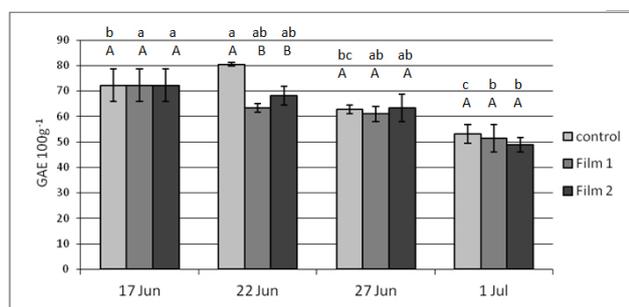


Figure 6. Changes in phenolics content in Sweetheart cherries during storage under MAP conditions. Data are the mean \pm SE (n = 3). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively

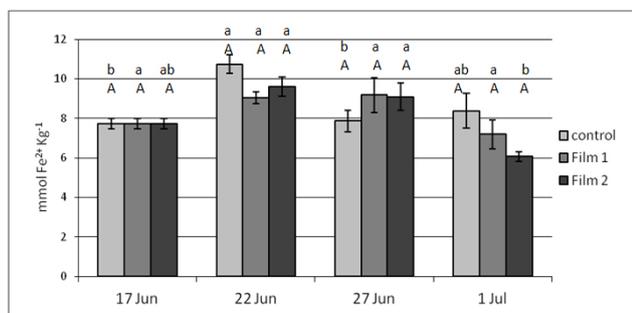


Figure 7. Changes in total antioxidant activity in Sweetheart cherries during storage under MAP conditions. Data are the mean \pm SE (n = 3). Minor and capital letters show significant differences ($p < 0.05$) during storage for each treatment and among treatments for each storage time respectively

Conclusion

In conclusion this work showed that the use of biodegradable films was useful to preserve quality of cherries through a delay in the changes in color and the losses of firmness and acidity. Film 2, characterized by an high permeability to CO₂ and high barrier to O₂ provided the best results in terms of color, acidity and firmness. With respect to anthocyanins contents,

phenolic contents and total antioxidant capacity, differences existed among the three treatments but was not detected any negative effect due to biodegradable films. Our results suggest that biodegradable polymers could be used in packaging of sweet cherries without negative effects on final quality.

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