

Fresh-cut apple: effect of CaCl_2 dips on firmness and quality

G. Giacalone and V. Chiabrando

Università di Torino, Department DISAFA, Via Leonardo da Vinci 44, 10095, Grugliasco (TO), Italy.

Abstract

The marketing of fresh-cut produce has increased rapidly due to the increased consumer demand for fresh and convenient foods. However, they have increased perishability and shorter shelf-life as compared with intact fruit. Firmness loss in fresh-cut apple is the main problem associated with quality loss, even under cold storage. Fresh-cut 'Golden Delicious', 'Granny Smith' and 'Scarlet Spur' apples were sliced, dipped in calcium chloride and in anti-browning solutions, packed and stored for five days at 4°C. Changes in headspace atmosphere, firmness and sensory quality were measured during storage. A significant reduction in the rates of O_2 depletion and CO_2 production was observed in all the samples. Treatments had beneficial effects on maintaining flesh firmness and reducing cut surface browning. The soluble solids content generally increased during fresh-cut storage, but without significant differences between treated slices and controls. The firmness and quality attributes of the treated samples up to five days of storage, showed no significant differences compared with the fresh apple, so they would be commercially acceptable at least until day five of storage.

Keywords: ready to eat, shelf-life, surface browning, storage

INTRODUCTION

Minimal processing has been defined as a combination of procedures, such as washing, sorting, trimming, peeling, and slicing or chopping, that do not affect the fresh-like quality of the food. The ready-to-eat fruits and vegetable market has rapidly grown in recent years due to the health benefits associated with these foods because of busy lifestyles, increasing purchasing power, and increasingly health-conscious consumers. Nevertheless, because the tissue integrity of fruit is more easily altered during processing, ready-to-use commodities are more perishable than the original materials. The deterioration of the fruits after minimal processing, resulting from wound-induced biochemical and physiological changes associated with water loss, respiration, and cut-surface browning, is accompanied by microbiological spoilage (Kader, 2002).

Minimally processed apples have a shorter shelf-life than their whole counterparts because they are more sensitive to enzymatic browning and tissue softening, which are stimulated by wounding of the tissue. Enzymatic browning of apples is caused by the action of polyphenoloxidase (PPO), which catalyses oxidation of phenolic compounds to the corresponding o-quinone in wounded tissues (Gacche et al., 2006). Color changes in fresh-cut fruit have been extensively reported (Eissa et al., 2006; İyidoğan and Bayindirli, 2004; Lozano-de-Gonzalez et al., 1993) and most of the time browning has been considered the limiting factor of the shelf-life of minimally processed fruit. A range of treatments have been applied to extend the shelf life of fresh-cut apples including the use of natural browning inhibitors (Buta et al., 1999; Luo and Barbosa-Canovas, 1996; Rojas-Graü et al., 2006), salt and chemical treatments (Aguayo et al., 2010; Arias et al., 2008; Cocci et al., 2006; Gil et al., 1998; Varela et al., 2007; Zuo and Lee, 2004), edible coating agents and reduced oxygen atmospheres (Pérez-Gago et al., 2006; Rocculi et al., 2004; Rojas-Graü et al., 2007; Soliva-Fortuny et al., 2001). A key approach used to avoid browning in apples has been the use of reducing agents, often with the addition of calcium chloride, in combination with modified atmospheres and low temperature storage. Calcium salts, particularly CaCl_2 , are used as

firming agents in a wide variety of whole, peeled, and fresh-cut fruits (Garcia and Barrett, 2002; Luna-Guzmán and Barrett, 2000). Firming and resistance to softening resulting from addition of Ca^{2+} have been attributed to the stabilization of membrane systems and the formation of Ca-pectates, which increase the rigidity of the middle lamella and cell wall to increased resistance to polygalacturonase attack on the peptic substances of the middle lamella and cell wall and to improved turgor pressure (Mignani et al., 1995).

The aim of this work was to evaluate the influence of different antibrowning treatments and CaCl_2 dip on the changes in headspace atmosphere, firmness and sensory quality that occurred in minimally processed apples during storage.

MATERIALS AND METHODS

Fruit processing

The apples ('Golden Delicious', 'Granny Smith' and 'Scarlet Spur') were harvested at commercial maturity, and stored at 4°C before processing. For 'Golden Delicious' and 'Granny Smith' three kinds of samples were compared during the 5 days cold storage period: 1) apple slices dipped in ascorbic acid (1%, w/v) and calcium chloride (1%, w/v) (Sigma-Aldrich Co., Steinheim, Germany), 2) apple slices dipped in citric acid (1%, w/v) and calcium chloride (1%, w/v) (Sigma-Aldrich Co., Steinheim, Germany), and 3) untreated apple slices as control. In 'Scarlet Spur' only ascorbic acid treatment (1) was evaluated.

The fruit was peeled, cored and cut into 5-mm-thick slices using a hand-operated apple corer and slicer. Apple slices were dipped for 2 min in the different solutions in a product/solution ratio of 1:2 according to previously used protocols (Cocci et al., 2006; Soliva-Fortuny et al., 2001, 2005). The control sample was processed in the same way but apple slices were dipped in water. The excess of solution was blotted off, and 30 slices were randomly selected and packaged in polypropylene plastic bags (UNIMEC packaging systems). The packages were heat-sealed and were stored at 4°C in darkness for five days.

Gas composition

The concentrations of oxygen and carbon dioxide inside the packages were monitored daily by sampling (0.5 mL) the headspace using a CANAL 121 (Vizag, Gas Analysis, France). A syringe was inserted into the package through a rubber seal placed on the film. Gases were analysed with an infrared sensor for CO_2 level and an electrochemical sensor for O_2 level. The instrument was calibrated using air. Results were expressed as % O_2 and % CO_2 inside the bags.

Color measurement

Color values of the cut apple surface were directly measured with a colorimeter (Minolta ChromaMeter, Model CR-400, Minolta, Tokyo, Japan). The results were expressed in the CIELAB ($L^*a^*b^*$) color space. L^* defines the lightness and a^* and b^* define the red-greenness and blue-yellowness, respectively. The instrument was calibrated using a standard white reflector plate. Fifteen slices per treatment were measured. Two readings were made on each replicate by changing the position of the apple pieces.

Quality measurements

Fruit firmness was tested using a TA-XT2i Texture Analyzer® (Stable Micro System) equipped with a 5 kg load cell. Fruit was sampled directly from the storage room, warmed for 3 h and then the measurements were made using a 6 mm probe (CYLINDER STAINLESS, Stable Micro System). The probe penetrated 3 mm into the sample at a crosshead speed of 3 mm s⁻¹ (Cocci et al., 2006). Force max (N) of penetration was calculated.

The total soluble solids content (TSS) was determined in the juice from 15 fruits with a digital refractometer Atago PR-101 (Atago, Japan) at 20°C and results expressed as °Brix. Titratable acidity (TA) was determined by titration with 0.1 N NaOH up to pH 8.1, using 10 mL of diluted juice in distilled H₂O and results were expressed as meq L⁻¹.

Statistical analysis

Data were analyzed by analysis of variance using statistical procedures of the STATISTICA ver. 6.0 (Statsoft Inc., Tulsa, OK, USA). The sources of variance being anti-browning treatments. Tukey's test HSP (honestly significant differences) was used to determine significant differences among treatment means. Means values were considered significantly different at $P \leq 0.05$.

RESULTS AND DISCUSSION

'Golden Delicious'

1. Gas composition.

The changes in attributes of packaged apples may be related to the changes in O_2 and CO_2 levels in the package. Apple slices passively modified the internal atmosphere, CO_2 partial pressure increased while O_2 levels progressively decreased throughout storage. Gorny (1997) concluded that a reduction of O_2 levels to near 0% is required to inhibit polyphenol oxidase (PPO) mediated browning of many fresh-cut fruit products. In the $CaCl_2$ treated 'Golden Delicious' the O_2 concentration of 18% at day 0 declined to 4-6% after five days without significant differences between treatments and control. The CO_2 production increased immediately after packaging and up to 8% at the end of the storage period for all the treatments. The atmosphere generated in the packs was somewhat extreme in that the CO_2 levels were high (>8% at the end of storage), although the low O_2 (<6%) did avoid the anaerobic limit (since no alcohol off-flavours were detected).

2. Color measurement.

Browning was evaluated throughout a period of five days using colorimetric measurements. Many authors describe browning using both L^* value and a^* value as a good indicator of darkening of the sample and resulting from oxidative browning reactions or from increasing pigment concentrations (Arias et al., 2008; İyidoğan and Bayindirli, 2004; Rojas-Graü et al., 2006). The lightness of fresh-cut 'Golden Delicious' apples not treated (control) decreased from 78.4 to 71.4 during five days of cold storage, while the L^* values of fresh-cut slices treated with antibrowning agents were maintained quite constant (free of darkening) over the entire storage time (the values range from 78.4 to 76). A same reduction was also reported by Soliva-Fortuny et al. (2001) in 'Golden Delicious' apple and by Raybaudi-Massilia et al. (2007) in 'Fuji' apple. Therefore, the treatment of 'Golden Delicious' apple slides with the acidic formulations had a significant effect ($P \leq 0.05$) in inhibiting browning during storage at 4°C.

3. Quality measurements.

The treatments of 'Golden Delicious' apple slices with the $CaCl_2$ formulations had no significant effect ($P \leq 0.05$) on the improvement in firmness during storage at 4°C (Table 1). Firmness of $CaCl_2$ treated pieces was not different from untreated samples after three and five days of storage. Also, no significant differences ($P \leq 0.05$) were noticed in the total soluble solids content of cut apple between treatments during storage (Table 2). Citric acid/ $CaCl_2$ treated slices, probably due to acidic treatment, exhibited the highest initial level of titratable acidity. The acidity levels were generally maintained during storage in all the samples.

'Granny Smith'

1. Gas composition.

O_2 slowly declined throughout the storage in a similar way for all the treatments (3% at five days). In the control, a slightly lower % of O_2 was recorded, probably due to a more rapid metabolism in control apple slices. In contrast, the CO_2 production was slightly lower in apple slices treated with ascorbic acid/ $CaCl_2$; this treatment probably slows down the

metabolism of the apple slices during storage.

Table 1. Firmness of fresh-cut apples dipped in calcium chloride solutions and stored at 4°C.

Cultivar/ Treatments	Days of storage			
	0	1	3	5
Golden Delicious				
Control	17.93	19.57 a	20.85	19.44
Asc. ac./CaCl ₂	17.93	18.24 b	18.75	18.28
Citric ac./CaCl ₂	17.93	17.88 b	18.59	17.63
		*	n.s.	n.s.
Granny Smith				
Control	24.22	21.21	20.71 b	22.37 a
Asc. ac./CaCl ₂	24.22	21.43	20.88 b	19.06
Citric ac./CaCl ₂	24.22	21.63	23.45 a	19.72 bc
		n.s.	*	*
Scarlet Spur				
Control	19.55	19.88	22.74	19.48
Asc. ac./CaCl ₂	19.55	21.68	18.94	21.07
		n.s.	n.s.	n.s.

Measurements were made with the Texture Analyzer after equilibrating to 20°C. Each data point is the average of 30 determinations. Means having * are significantly different ($p \leq 0.05$).

Table 2. Total soluble solid (TSS), titratable acidity (TA) and pH of fresh-cut apples dipped in calcium chloride solutions and stored at 4°C.

Cultivar/ Treatments	TSS (°Brix)		TA (meq L ⁻¹)		pH	
	Days of storage		Days of storage		Days of storage	
	1	5	1	5	1	5
Golden Delicious						
Control	11.10	11.10	24.91 c	36.27 ab	4.72 a	4.04 a
Asc. ac./CaCl ₂	10.40	10.80	37.77 b	34.93 b	3.78 b	3.87 bc
Citric ac./CaCl ₂	10.60	10.60	46.83 a	43.82 a	3.64 b	3.79 c
	n.s.	n.s.	*	*	*	*
Granny Smith						
Control	11.90	12.03 a	115.89 a	99.15 b	3.34 ab	3.38
Asc. ac./CaCl ₂	11.60	10.7 b	109.22 ab	100.34 b	3.35 a	3.36
Citric ac./CaCl ₂	11.40	11 b	101.04 b	105.07 a	3.35 a	3.33
	n.s.	*	*	*	*	n.s.
Scarlet Spur						
	TSS/°Brix		TA (meq L ⁻¹)		pH	
Control	9.60	10.7	14.12	14.23 b	6.21	5.62
Asc. ac./CaCl ₂	9.10	10.5	13.49	21.34 a	5.59	5.3
	n.s.	n.s.	n.s.	*	n.s.	n.s.

Means having * are significantly different ($p \leq 0.05$).

2. Color measurement.

The L* value of fresh-cut 'Granny Smith' slices decreased with time in storage. After five days of storage at 4°C, fresh-cut apple treated with citric acid/CaCl₂ resulted in the best maintenance of L* values followed by the ascorbic acid/CaCl₂ treatment and control (77.5, 76 and 66.8, respectively). Fresh-cut slices under acidic treatments presented the best visual appearance and fewer symptoms of browning. Kim et al. (1993) reported that a rapid decrease in L* values of fresh-cut apples can be due to enzymatic browning caused by tissue damage. The consequence is an enhanced contact between enzymes and substrates that led

to a loss of quality of fresh-cut produce. Lozano-de-Gonzalez et al. (1993) suggest that the browning in apple slices could be attributed to the consumption of substrates by PPO. The lower the L^* values, the higher the browning potential and the relative PPO activity.

3. Quality measurements.

The highest firmness values were obtained with citric acid/ CaCl_2 after three days of storage (Table 1). Control samples seemed to hold firmness better than other treatments over five days of storage.

Reduced respiration rate measured in MAP were associated in lower changes in pH, titratable acidity and total soluble sugars. A decline in titratable acidity (Table 2) of apple slices was noticed with storage time and the decrease in acidity might be due to the increased respiration following peeling and cutting. The titratable acidity values were significantly different between treatments and control. At one day of storage, control had the highest acidity and the citric acid/ CaCl_2 the lowest. In contrast at the end of the storage period (5 days) the trend was opposite: citric acid/ CaCl_2 apple slices showed the highest acidity, the control and ascorbic acid/ CaCl_2 treated slices showed significantly lower values. There was consistent effect of citric acid treatment on reducing loss of acidity during storage.

'Scarlet Spur'

1. Gas composition.

The O_2 production was slightly lower in ascorbic acid/ CaCl_2 (5.7%) compare with control samples (8%) and the CO_2 production was similar in the two treatments (8.5% at the end of the storage period). There was no consistent effect of CaCl_2 treatment on the resulting atmospheres in the bags.

2. Color measurement.

The color changes of fresh-cut 'Scarlet Spur' slices were determined by changes in lightness (L^*). The L^* value decreased (darkening increased) with time in all the samples. An ANOVA test showed significant differences ($P \leq 0.05$) after one day of storage between apple slices treated with antibrowning agent (ascorbic acid) and control (73 and 72, respectively) suggesting a fast darkening from the early hours of storage. The change in the L^* value was due to the slight browning on the surface of the slices probably due to the consumption of substrates by PPO (Lozano-de-Gonzalez et al., 1993).

3. Quality measurements.

Firmness of calcium chloride treated pieces was not different from untreated samples (Table 1). The treatment with the CaCl_2 formulations had no significant effect ($P \leq 0.05$) on the improvement in firmness during storage at 4°C . No significant changes ($P \leq 0.05$) were observed in the soluble solid content and pH (Table 2). The fact that the ascorbic acid/ CaCl_2 dip presented the lowest TSS and relatively low pH at the end of storage could suggest the efficacy of Ca formulation in suppressing the respiration rate of minimally processed apple, and the ripening process.

Literature cited

- Aguiayo, E., Requejo-Jackman, C., Stanley, R., and Woolf, A. (2010). Effects of calcium ascorbate treatments and storage atmosphere on antioxidant activity and quality of fresh-cut apple slices. *Postharvest Biol. Technol.* 57 (1), 52–60 <https://doi.org/10.1016/j.postharvbio.2010.03.001>.
- Arias, E., Gonzalez, J., Lopez-Buesa, P., and Oria, R. (2008). Optimization of processing of fresh-cut pear. *J. Sci. Food Agric.* 88 (10), 1755–1763 <https://doi.org/10.1002/jsfa.3276>.
- Buta, J.G., Moline, H.E., Spaulding, D.W., and Wang, C.Y. (1999). Extending storage life of fresh-cut apples using natural products and their derivatives. *J. Agric. Food Chem.* 47 (1), 1–6 <https://doi.org/10.1021/jf980712x>. PubMed

- Cocci, E., Rocculi, P., Romani, S., and Dalla Rosa, M. (2006). Changes in nutritional properties of minimally processed apples during storage. *Postharvest Biol. Technol.* 39 (3), 265-271 <https://doi.org/10.1016/j.postharvbio.2005.12.001>.
- Eissa, H.A., Fadel, H.H.M., Ibrahim, G.E., Hassan, I.M., and Elrashid, A.A. (2006). Thiol containing compounds as controlling agents of enzymatic browning in some apple products. *Food Res. Int.* 39 (8), 855-863 <https://doi.org/10.1016/j.foodres.2006.04.004>.
- Gacche, R.N., Shete, A.M., Dhole, N.A., and Ghole, V.S. (2006). Reversible inhibition of polyphenol oxidase from apple using L-cysteine. *Indian J. Chem. Technol.* 13, 459-463.
- Garcia, E., and Barrett, D.M. (2002). Preservative treatments for fresh-cut fruits and vegetables. In *Fresh-cut Fruits and Vegetables*, O. Lamikanra, ed. (Boca Raton, FL, USA: CRC Press), p.267-303.
- Gil, M.I., Gorny, J.R., and Kader, A.A. (1998). Responses of 'Fuji' apple slices to AA treatments and low-oxygen atmospheres. *HortScience* 33, 305-309.
- Gorny, J.R. (1997). A summary of CA and MA requirements and recommendations for the storage of fresh-cut (minimally processed) fruits and vegetables. Paper presented at: Seventh International Controlled Atmosphere Research Conference: Fresh-Cut Fruits and Vegetables and MAP, *Postharvest Horticulture Series No. 19* (Davis, CA, USA: University of California at Davis).
- İyidoğan, N.F., and Bayindirli, A. (2004). Effect of L-cysteine, kojic acid and 4-hexylresorcinol combination on inhibition of enzymatic browning in Amasya apple juice. *J. Food Eng.* 62 (3), 299-304 [https://doi.org/10.1016/S0260-8774\(03\)00243-7](https://doi.org/10.1016/S0260-8774(03)00243-7).
- Kader, A.A. (2002). Quality parameters of fruit and vegetable products. In *Fresh-cut Fruits and Vegetables*, O. Lamikanra, ed. (Boca Raton, FL, USA: CRC Press), p.11-19.
- Kim, D.M., Smith, N.L., and Lee, C.Y. (1993). Quality of minimally processed apple slices from selected cultivars. *J. Food Sci.* 58 (5), 1115-1117 <https://doi.org/10.1111/j.1365-2621.1993.tb06127.x>.
- Lozano-de-Gonzalez, P., Barrett, D.M., Wrolstad, R.E., and Durst, R.W. (1993). Enzymatic browning inhibited in fresh and dried apple rings by pineapple juice. *J. Food Sci.* 58 (2), 399-404 <https://doi.org/10.1111/j.1365-2621.1993.tb04284.x>.
- Luna-Guzmán, I., and Barrett, D.M. (2000). Comparison of calcium chloride and calcium lactate effectiveness in maintaining shelf stability and quality of fresh-cut cantaloupes. *Postharvest Biol. Technol.* 19 (1), 61-72 [https://doi.org/10.1016/S0925-5214\(00\)00079-X](https://doi.org/10.1016/S0925-5214(00)00079-X).
- Luo, Y., and Barbosa-Canovas, G.V. (1996). Preservation of apple slices using ascorbic acid and 4-hexylresorcinol. *Food Sci. Technol. Int.* 2 (5), 315-321 <https://doi.org/10.1177/108201329600200505>.
- Mignani, I., Greve, L.C., Ben-Arie, R., Stotz, H.U., Li, C., Shackel, K., and Labavitch, J. (1995). The effects of GA₃ and divalent cations on aspects of pectin metabolism and tissue softening in ripening tomato pericarp. *Physiol. Plant.* 93 (1), 108-115 <https://doi.org/10.1034/j.1399-3054.1995.930116.x>.
- Pérez-Gago, M.B., Serra, M., and Del Rio, M.A. (2006). Colour change of fresh-cut apples coated with whey protein concentrate-based edible coatings. *Postharvest Biol. Technol.* 39 (1), 84-92 <https://doi.org/10.1016/j.postharvbio.2005.08.002>.
- Raybaudi-Massilia, R.M., Mosqueda-Melgar, J., Sobrino-Lopez, A., Soliva-Fortuny, R., and Martin-Belloso, O. (2007). Shelf-life extension of fresh-cut "Fuji" apples at different ripeness stages using natural substances. *Postharvest Biol. Technol.* 45 (2), 265-275 <https://doi.org/10.1016/j.postharvbio.2007.02.006>.
- Rocculi, P., Romani, S., and Dalla Rosa, M. (2004). Evaluation of physico-chemical parameters of minimally processed apples packed in non-conventional modified atmosphere. *Food Res. Int.* 37 (4), 329-335 <https://doi.org/10.1016/j.foodres.2004.01.006>.
- Rojas-Graü, M.A., Sobrino-Lopez, A., Soledad Tapia, M., and Martin-Belloso, O. (2006). Browning inhibition in fresh-cut 'Fuji' apple slices by natural antibrowning agents. *J. Food Sci.* 71 (1), S59-S65 <https://doi.org/10.1111/j.1365-2621.2006.tb12407.x>.
- Rojas-Graü, M.A., Raybaudi-Massilia, R.M., Soliva-Fortuny, R.C., Avena-Bustillos, R.J., McHugh, T.H., and Martín-Belloso, O. (2007). Apple puree-alginate edible coating as carrier of antimicrobial agents to prolong shelf-life of fresh-cut apples. *Postharvest Biol. Technol.* 45 (2), 254-264 <https://doi.org/10.1016/j.postharvbio.2007.01.017>.
- Soliva-Fortuny, R.C., Grigelmo-Miguel, N., Odriozola-Serrano, I., Gorinstein, S., and Martín-Belloso, O. (2001). Browning evaluation of ready-to-eat apples as affected by modified atmosphere packaging. *J. Agric. Food Chem.* 49 (8), 3685-3690 <https://doi.org/10.1021/jf010190c> PubMed
- Soliva-Fortuny, R.C., Ricart-Coll, M., and Martin-Belloso, O. (2005). Sensory quality and internal atmosphere of fresh-cut Golden Delicious apples. *Int. J. Food Sci. Technol.* 40 (4), 369-375 <https://doi.org/10.1111/j.1365-2621.2004.00934.x>.

Varela, P., Salvador, A., and Fiszman, S.M. (2007). The use of calcium chloride in minimally processed apples: a sensory approach. *Eur. Food Res. Technol.* 224 (4), 461-467 <https://doi.org/10.1007/s00217-006-0344-7>.

Zuo, L., and Lee, J.H. (2004). Effects of anti-browning agents on the quality of minimally processed apple cubes. *Food Sci. Biotechnol.* 13 (1), 40-45.