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Effect of $Ca(NO_3)_2$ coating on chemical and mechanical properties and bruise susceptibility of Golden Delicious and Red Delicious apples during storage

M. Jafarian[1*], H. Emami[2] and J. Baradaran Motie[3]

[1] Department of Mechanical Engineering of Agricultural Machinery, Faculty of Agricultural Engineering & Veterinary, Technical and Vocational University (TVU), Tehran, Iran

[2] Department of Mechanical Engineering, Islamic Azad University, Khomeinishahr Branch, Khomeinishahr, Iran

[3] Department of Biosystem Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

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ABSTRACT

Effect of coating with calcium nitrate in three concentrations (0.0, 0.5, and 1.0 wt%) on chemical and mechanical properties, and impact behaviour of two apple cultivars (Golden Delicious (GD) and Red Delicious (RD)) during time (0, 2, and 4 months) was studied. Moisture content, pH, titratable acidity, °Brix, organoleptic properties, modulus of elasticity (E), yield stress, yield strain, and toughness were measured. The effect of impact loads was determined by measuring bruise volume (BV) and bruise susceptibility (BS). The results showed that pH and °Brix significantly increased, while titratable acidity, E, yield strain, toughness, and BV decreased during storage time. As $Ca(NO_3)_2$ concentration increased, titratable acidity, E, yield strain and yield stress increased and pH decreased ($P < 0.05$). Highest and lowest values for °Brix were observed in GD treated with 1.0% $Ca(NO_3)_2$ after four months (13.31) and GD treated with 0.5% $Ca(NO_3)_2$ at the first day (10.65), respectively. Maximum E was obtained in GD treated with 1.0% $Ca(NO_3)_2$ on the first day (2130 kPa) and this sample also showed the lowest BS after four months of storage (2.82 mL J^{-1}), while the uncoated GD had the highest BS on the first day (7.11 mL J^{-1}).

* Corresponding author. Tel.: +98 9153865474. E-mail: m.jafarian@ut.ac.ir

KEYWORDS

apple, impact, modulus of elasticity, yield strain, brix, titratable acidity

1. INTRODUCTION

The harvested agricultural products are subjected to chemical and mechanical changes causing fruit damage and quality loss (Grotte et al., 2001). Apple, *Malus domestica*, is mainly produced in European countries and is considered as an important horticultural crop in Iran (Masoudi et al., 2007). Respiration rises during the ripening of the fruit and may continue even after harvesting. Post-harvest damages and loss of apple fruit present economic and environmental challenges. Storage conditions might be controlled and the fruit could be coated to preserve its quality after harvest (Taghizadeh et al., 2016; Yang et al., 2018).

During harvest, transport, and storage, apple fruit experiences static and dynamic loads possibly causing damage (Van Zeebroeck et al., 2007). The dynamic loading may be a single impact, which may occur during harvesting as they are dropped into the picking buckets, or a vibration, which may occur during transportation (Van Zeebroeck et al., 2007). Impact caused by dynamic forces when transporting and handling apple fruit can result in more significant bruise damage, since dynamic forces are higher in occurrence and magnitude than static forces (Mohsenin, 1986).

Calcium, which is the primary mineral influencing fruit quality, enhances apple storage time and postpones its ripening. High levels of calcium content cause easier fruit handling and transportation (Conway et al., 2002). Treatment of apple by calcium and gradual permeating of calcium through cell walls leads to a harder texture and protects the fruit against microorganisms by reducing loss of pectin compounds in ripening (Conway et al., 2002). Calcium salts are used in combination with browning inhibitors as firmness agents in a wide variety of fruit and vegetables (Raybaudi et al., 2015).

This study aimed to investigate the effect of calcium nitrate ($Ca(NO_3)_2$) coating on chemical, organoleptic, mechanical properties and impact behaviour of two apple cultivars during storage time.

2. MATERIALS AND METHODS

All chemicals used in the experiments were purchased from Merck Co. (Germany).

2.1. Treatments

The intact apple fruits were selected from two most common cultivars in Iran, Golden Delicious (GD) and Red Delicious (RD), provided by the Department of Agriculture, Isfahan, Iran. After harvest and before experiments, a total of 20 fruits for each treatment were kept under the same conditions of temperature (3 °C) and relative humidity (87 ± 3%) for 24 h. Samples were then immersed in calcium nitrate solutions of 0.0, 0.5, and 1.0 wt% for 10 min. After drying in open air, the fruits were transferred to 3 °C cold room of RH = 87 ± 3% for 4 months. Control samples (without $Ca(NO_3)_2$ coating) were kept under the same conditions. Experiments were performed at two and four months of storage. Treatments were named by cultivar name abbreviation (RD or GD) succeeded by $Ca(NO_3)_2$ concentration (00, 05, or 10) and storage time (0, 2, or 4), respectively.

2.2. Chemical properties

Moisture, ash, and total soluble solids (°Brix) contents, pH, and titratable acidity were determined according to AACC approved methods 11th edition No.44-16, 08-01, 02-31.01 and 02-52.01, respectively (AACC, 2010).

2.3. Sensory properties

Sensory properties, including overall acceptability, were evaluated by 20 trained panellists according to a 7-point hedonic scale.

2.4. Mechanical properties

Mechanical properties of apple samples were determined using a uniaxial compression test. Cylindrical samples (10 mm diameter and 15 mm height) were prepared according to the method proposed by Masoudi et al. (2007).

A universal testing machine (Hounsfield H25KS, USA) was employed for compression test according to ASABE (2005) standard S368.4 with a loading rate of 25 mm min^{-1}. The resultant Force-Displacement curve was used to calculate the apparent modulus of elasticity (E), yield stress (σ), yield strain (ε), and toughness (Eqs. (1–3)):

$$E = \frac{FL}{A(\Delta L)} \tag{1}$$

where F is the force applied on the sample (N), L is initial length (mm), A is the cross-section area of the sample (mm^2), and ΔL is the change in length (mm). The values for F and ΔL were obtained from the curve at 50% yield stress.

$$\sigma = \frac{4F}{\pi d^2} \tag{2}$$

where F is the force applied on the sample at yield point (N), and d is the sample diameter (mm).

$$\varepsilon = \frac{\Delta L}{L} \tag{3}$$

Toughness (J cm^{-3}) was calculated as the area below the Force-Displacement curve in the elastic region (fracture energy; in J), obtained from universal testing machine software, divided by the sample volume (cm^3) (Mohsenin, 1986).

2.5. Impact test

A pendulum impact tester (Fig. 1A) was used for impact experiments. Impact energy (J) was obtained from Eq. (4) according to Halliday et al. (2001):

$$\mathrm{IE} = \mathrm{mgh}(1 - \cos\theta) \tag{4}$$

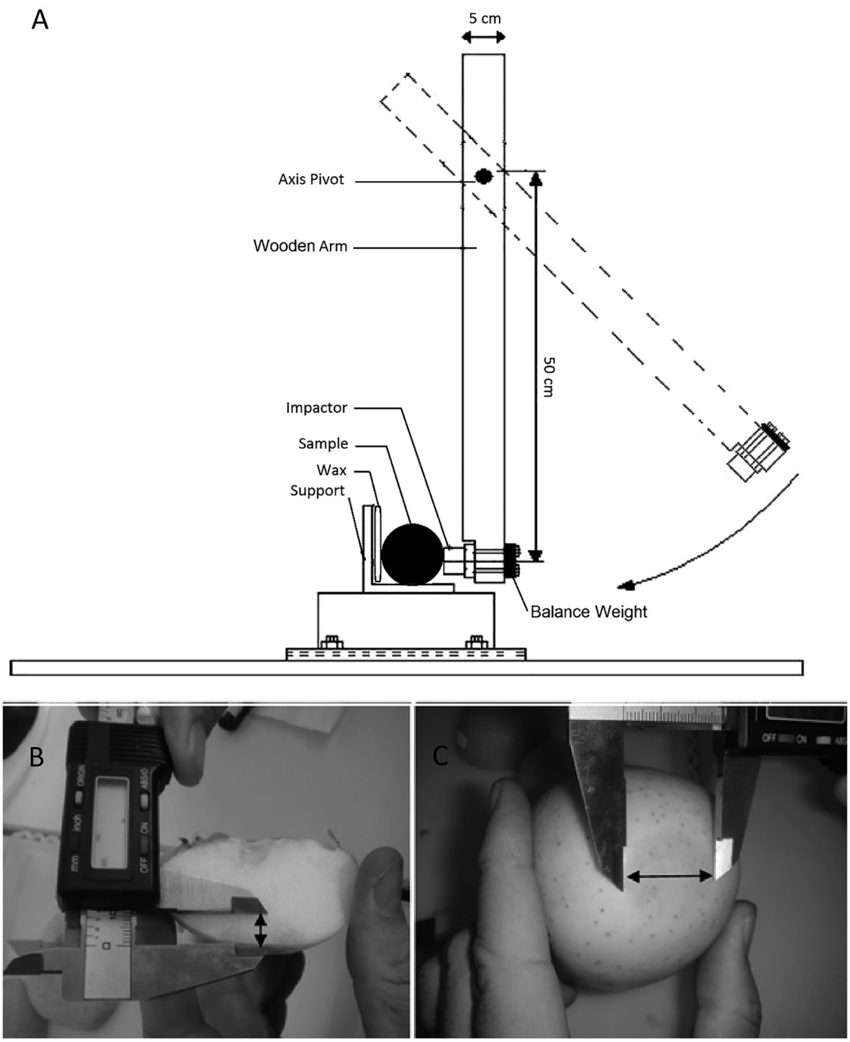

Fig. 1. Schematics of impact tester apparatus (A), measurement of damage depth (B), and diameter (C)

where m is pendulum mass (kg), g is the acceleration of gravity (m s^{-2}), h is the distance between pendulum centre of rotation and centre of mass (m), and θ is the pendulum angle (in degrees).

A spherical impactor (radius of curvature = 30 mm) was used with a release angle of 50° from a height of 230 mm. It has an impact energy of 420 mJ, equal to the energy applied to an apple falling from a 230 mm height (Lewis et al., 2007).

2.6. Damage measurement

To have bruises developed and more apparent, apple fruits were kept at 4 °C refrigerator for 48 h after impact. The fruit was then peeled and the largest diameter of damaged area (d) was measured using a digital calliper (Fig. 1B). Damage depth (h) was measured by cutting the fruit as shown in the picture (Fig. 1C).

Bruise volume (BV) was calculated as follows:

$$BV = \frac{\pi}{6} hd^2 \tag{5}$$

Finally, dividing bruise volume by impact energy, bruise susceptibility was obtained (Eq. (6)) (Studman, 1997):

$$BS = \frac{BV}{1000 \times IE} \tag{6}$$

where BS is bruise susceptibility (mL J^{-1}).

2.7. Statistical analysis

A completely randomised factorial design was used to study the interaction of calcium nitrate concentration, storage time, and cultivar (3 × 3 × 2) on chemical and mechanical properties of apple fruit. SPSS v. 22 statistical software was used to analyse the data. Analysis of Variance (ANOVA) method was applied to find significant differences among results. The means of results were compared using Duncan's Multiple Range Test at significance level of 5%. Each experiment was conducted in 20 replications.

3. RESULTS AND DISCUSSION

3.1. Chemical experiments

The average moisture content of RD and GD measured at the first day was 84.32 ± 1.12 and 85.41 ± 1.83 (wb%), respectively. The average reported for the cultivars planted in Iran is 85% (Masoudi et al., 2007). Total ash content was 2.38 and 2.46% for RD and GD, respectively. The results of chemical analysis of the apple samples are presented in Table 1.

The pH of fruit samples increased during storage time (Fig. 2). The highest and lowest pH values were observed in RD054 and GD050, respectively. Apple pH is lower immediately after harvest, due to the presence of organic acids, which convert into other compounds such as sugars during respiration and ripening process, leading to increased pH (Dris and Niskanen, 1999). Moreover, pH declined for each cultivar as the concentration of $Ca(NO_3)_2$ increased. Increment of calcium in the fruit inhibits organic acids conversion into sugars (Dris and Niskanen, 1999). It has been reported that RD indicates higher pH compared to GD, which is consistent with our results (Dris and Niskanen, 1999).

The titratable acidity values measured for different samples indicated descending trend during storage time (Table 1). The highest level was seen in GD000 and the lowest in RD04. It could be due to the fact that organic acids disappear gradually after harvest, during aging and ripening (Chardonnet et al., 2003). The results also revealed the effect of $Ca(NO_3)_2$ treatment on titratable acidity increment. Calcium ion stimulates organic acids and generates ionic equilibrium against cations, which enhances titratable acidity of the samples (Mika et al., 1983).

°Brix level of RD was higher than that of GD (Table 1 and Fig. 2). It increased during storage time for all concentrations. Brix increases as ripening goes on during storage (Jan et al., 2012).

Table 1. Chemical properties of apple samples coated with $Ca(NO_3)_2$ during storage

Treatment	pH	Titratable acidity (g L^{-1})	°Brix
GD000	3.94 ± 0.088	0.66 ± 0.155	10.85 ± 0.39
RD000	4.06 ± 0.062	0.53 ± 0.060	11.66 ± 0.82
GD002	3.97 ± 0.088	0.45 ± 0.074	11.51 ± 0.38
RD002	4.07 ± 0.046	0.45 ± 0.061	12.61 ± 0.89
RD004	3.93 ± 0.108	0.42 ± 0.042	12.88 ± 0.91
GD004	4.06 ± 0.095	0.31 ± 0.039	12.41 ± 0.59
RD050	3.81 ± 0.075	0.63 ± 0.125	10.65 ± 0.48
GD050	4.00 ± 0.041	0.52 ± 0.076	11.19 ± 0.56
RD052	3.91 ± 0.142	0.59 ± 0.107	11.53 ± 0.56
GD052	4.02 ± 0.046	0.44 ± 0.042	11.84 ± 0.57
RD054	3.94 ± 0.104	0.43 ± 0.072	12.84 ± 1.09
RD054	4.08 ± 0.065	0.35 ± 0.049	12.41 ± 0.62
GD100	3.84 ± 0.110	0.65 ± 0.126	10.97 ± 0.52
RD100	4.02 ± 0.046	0.48 ± 0.065	11.48 ± 0.64
GD102	3.86 ± 0.122	0.51 ± 0.095	11.22 ± 0.63
RD102	3.99 ± 0.078	0.46 ± 0.054	11.63 ± 1.03
GD104	3.91 ± 0.079	0.43 ± 0.062	13.31 ± 0.87
RD104	4.04 ± 0.067	0.34 ± 0.037	12.51 ± 0.73

GD: Golden Delicious; RD: Red Delicious; the first two digits represent $Ca(NO_3)_2$ concentration (0.0, 0.5, and 1.0); the third digit represents storage time (0, 2, and 4 months).

Highest and lowest °Brix levels were measured in GD104 and GD050, respectively. By increasing $Ca(NO_3)_2$ concentration to 0.5%, °Brix levels declined and then increased at the concentration of 1.0%. Since increased °Brix results in fruit ripening and aging, a lower concentration of $Ca(NO_3)_2$ is recommended to postpone ripening process. Yang et al. (2018) reported less weight loss and respiration rate for sweet potato roots with wax-based coating.

3.2. Sensory evaluation

According to sensory results RD100 had the highest overall acceptability (Fig. 3). Moreover, storage time was the only factor with a significant effect on overall acceptability. It seems that during storage and ripening, due to increment of the fruit porosity, mouthfeel score and consequently overall acceptability declined. According to Yang et al. (2018), coating resulted in preserved quality and desirable sensory properties of sweet potato roots during storage.

3.3. Mechanical properties

The modulus of elasticity values we obtained for apple cultivars in this study (Table 2) lay in the range of moduli reported for different apple varieties (Mohsenin, 1986). Increased $Ca(NO_3)_2$ concentration leads to more considerable turgor pressure and consequently higher E (Cybulska et al., 2011). In different $Ca(NO_3)_2$ concentrations, E declined during storage time. However, it increased as the $Ca(NO_3)_2$ concentration increased. It was due to the formation of Ca bridge in pectin, which enhances textural strength (Cybulska et al., 2011). Furthermore, E was lower for

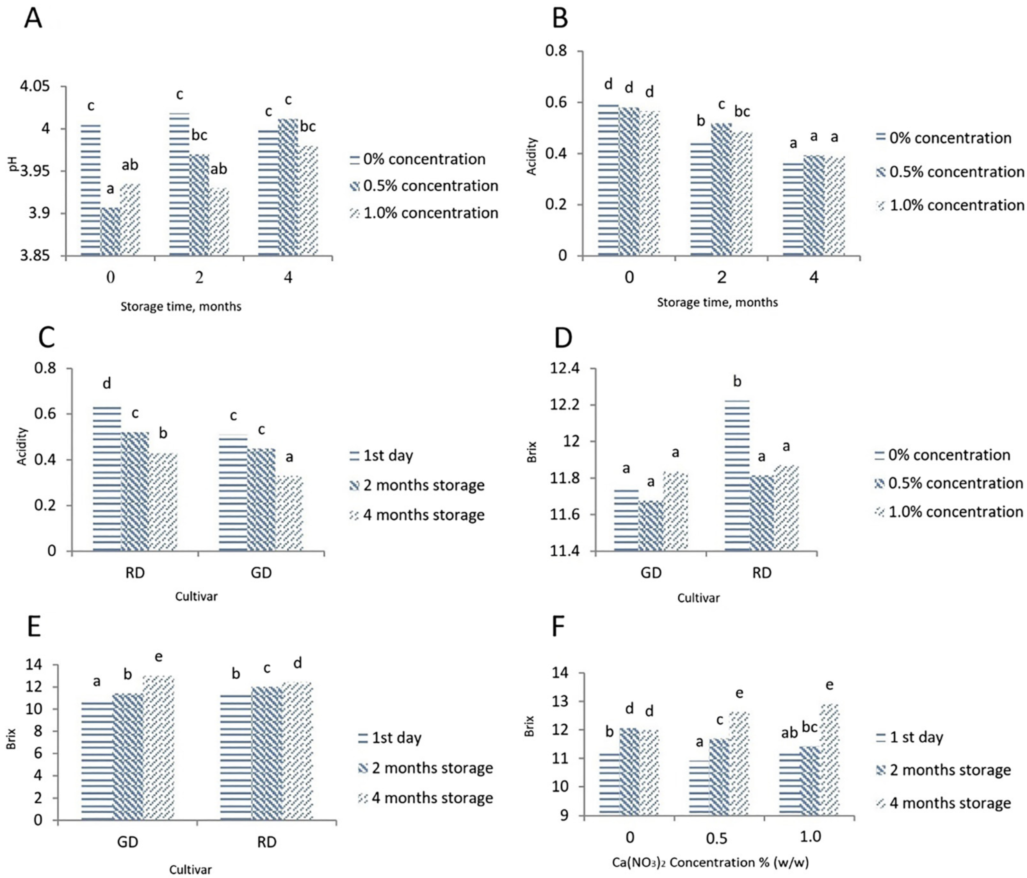

Fig. 2. Interaction of: (A), (B), and (F) storage time and $Ca(NO_3)_2$ concentration, (C) and (E) storage time and cultivar, and (D) cultivar and $Ca(NO_3)_2$ concentration on chemical properties of apple fruits. Different letters in columns represent significant difference at the 5% level

RD compared to GD. Masoudi et al. (2007) reported decreasing E for GD during a 6-month storage and an initially increasing E for RD within the first 2 months, succeeded by a decrement afterwards. Primary reason for this phenomenon is dissolving of middle lamella pectin, which causes adhesion of cells (Conway et al., 2002).

Yield stress was significantly influenced by storage time for both apple cultivars. However, the yield stress of RD was consistently lower than that of GD. Moreover, σ showed an increment as $Ca(NO_3)_2$ concentration increased for three storage times. The same result was reported by Masoudi et al. (2007).

Elasticity of Golden Delicious apple was higher and consequently indicated more significant strain than RD, leading to less damage within larger deformations (Table 2). The result was in agreement with that of Masoudi et al. (2007). The strain change pattern showed that ε increased

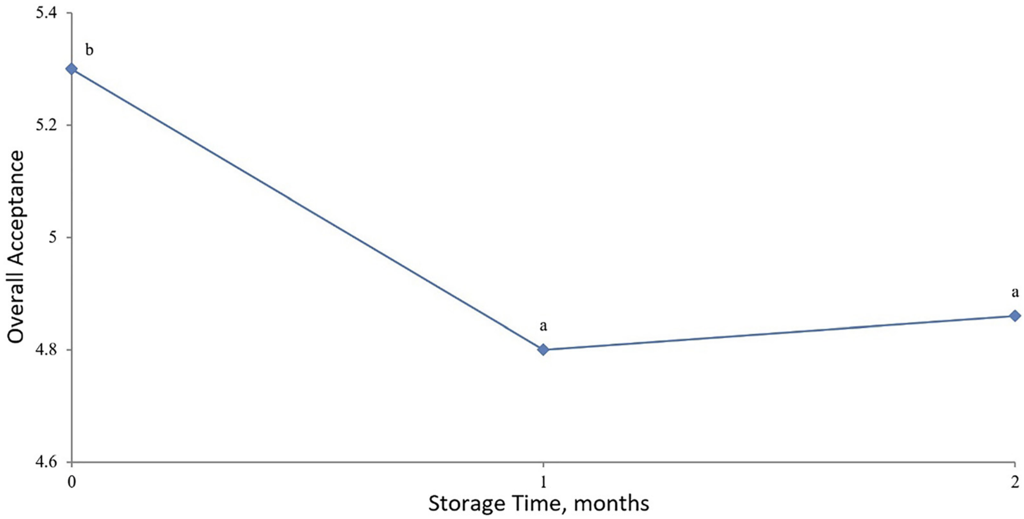

Fig. 3. Overall acceptability change of apple samples during storage. Different letters represent significant difference at the 5% level

Table 2. Mechanical and damage properties of apple samples coated with $Ca(NO_3)_2$ during storage

Treatment	E (MPa)	Toughness (kJ m^{-3})	Yield Stress (MPa)	Yield Strain (%)	BV (mm^3)	BS (mL J^{-1})
GD000	1,856 ± 356	5.631 ± 1.9	0.136 ± 0.025	7.38 ± 1.12	2,984 ± 698	7.11 ± 1.66
RD000	1,952 ± 416	18.10 ± 6.7	0.277 ± 0.066	14.33 ± 2.69	2,281 ± 624	5.43 ± 1.48
GD002	1,419 ± 379	4.38 ± 1.513	0.107 ± 0.022	8.12 ± 3.21	2,182 ± 493	5.19 ± 1.17
RD002	1,880 ± 466	10.58 ± 3.23	0.201 ± 0.0289	11.10 ± 2.31	1,996 ± 691	4.75 ± 1.64
RD004	1,753 ± 508	7.40 ± 3.30	0.157 ± 0.050	9.04 ± 1.64	1,607 ± 373	3.83 ± 0.88
GD004	1,482 ± 312	18.13 ± 3.11	0.178 ± 0.30	12.01 ± 2.06	1,859 ± 406	4.43 ± 0.96
RD050	1,880 ± 385	7.81 ± 1.934	0.159 ± 0.029	8.61 ± 1.09	1,867 ± 566	4.45 ± 1.34
GD050	2,015 ± 341	17.18 ± 3.6	0.279 ± 0.047	14.12 ± 2.03	1,634 ± 467	3.89 ± 1.11
RD052	1,674 ± 489	7.616 ± 3.4	0.153 ± 0.048	9.25 ± 1.53	1,364 ± 320	3.25 ± 0.76
GD052	1,885 ± 295	12.21 ± 3.7	0.213 ± 0.037	11.35 ± 1.41	1,706 ± 371	4.06 ± 0.88
RD054	1,324 ± 421	4.744 ± 1.4	0.104 ± 0.024	8.34 ± 1.89	1,194 ± 495	2.84 ± 1.18
RD054	1,824 ± 380	10.12 ± 3.6	0.188 ± 0.044	10.43 ± 1.62	1,314 ± 537	3.13 ± 1.28
GD100	1,884 ± 361	8.878 ± 1.1	0.149 ± 0.033	7.94 ± 1.06	1,584 ± 313	3.77 ± 0.74
RD100	2,130 ± 353	28.81 ± 4.7	0.292 ± 0.045	13.88 ± 1.59	1,540 ± 449	3.66 ± 1.33
GD102	1,828 ± 451	5.471 ± 2.4	0.136 ± 0.039	7.52 ± 1.52	1,463 ± 321	3.48 ± 0.76
RD102	2,049 ± 509	15.5 ± 1.78	0.217 ± 0.037	10.92 ± 1.97	1,559 ± 327	3.71 ± 0.78
GD104	1,548 ± 257	8.946 ± 3.2	0.157 ± 0.037	10.67 ± 4.79	1,184 ± 294	2.82 ± 0.72
RD104	1,767 ± 422	12.7 ± 4.08	0.197 ± 0.032	11.46 ± 1.89	1,354 ± 364	3.22 ± 0.87

GD: Golden Delicious; RD: Red Delicious; the first two digits represent $Ca(NO_3)_2$ concentration (0.0, 0.5, and 1.0); the third digit represents storage time (0, 2, and 4 months).

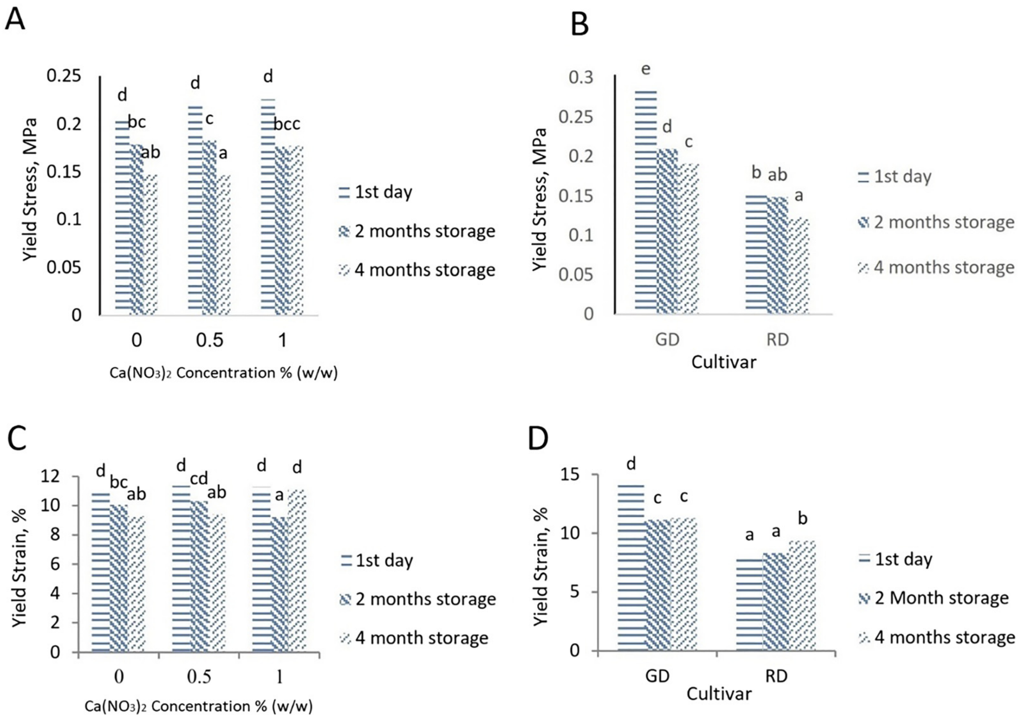

Fig. 4. Interaction of: (A) and (C) storage time and cultivar and (B) and (D) storage time and $Ca(NO_3)_2$ concentration on mechanical properties of apple fruits. Different letters in columns represent significant difference at the 5% level

by an increment of $Ca(NO_3)_2$ concentration. Chardonnet et al. (2003) attributed their similar results to the accumulation of Ca in the cell membrane.

For the control samples, no significant difference was observed between yield strains after 2 and 4 months, yet the ε value before storage was significantly higher (Fig. 4). At 0.5% concentration, yield strain decreased during storage. The descending yield strain corresponded to the results reported by Masoudi et al. (2007) for RD and Granny Smith cultivars during 3 months of storage. The apples treated by $Ca(NO_3)_2$ of 1.0% concentration revealed an increase in ε after 4 months, while it decreased in the first 2 months. Masoudi et al. (2007) reported similar results for RD without coating. Effect of cultivar was significant on yield strain during storage. Furthermore, GD always indicated a higher yield strain compared to RD. Different sensory brittleness of the two cultivars confirmed the results (Cybulska et al., 2011).

For both apple cultivars, toughness reduced significantly at the first 2 months and increased slightly during the second (Fig. 5). Previous studies have confirmed that the energy needed to cause bruise decreases at the beginning of storage time and increases after one month (Mohsenin, 1986; Masoudi et al., 2007). It seems that overall reduction of the measured parameters

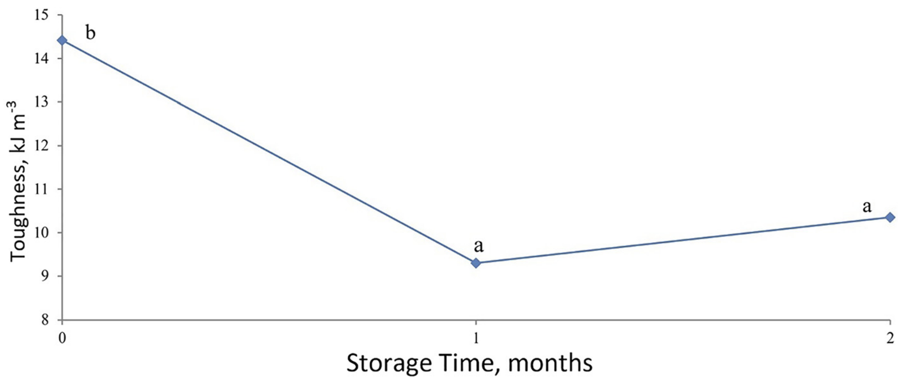

Fig. 5. Toughness change of the apple samples during storage. Different letters represent significant difference at the 5% level

observed during storage time resulted from ripening and conversion of increasing amounts of starch into sugar. Abbott and Lu (1996) also stated that ripening significantly affected the mechanical properties of apple fruit.

3.4. Impact force and bruising

3.4.1. Bruise volume. Damage diameter and depth declined as the $Ca(NO_3)_2$ concentration increased.

At different $Ca(NO_3)_2$ concentrations, BV decreased during storage time (Table 2). Furthermore, increment of $Ca(NO_3)_2$ concentration led to reduced BV. The largest and the smallest BV were obtained for GD000 and GD054, respectively. Coating was shown to significantly reduce BV for both cultivars. However, no significant difference was observed between the concentrations of 0.5% and 1.0% (Fig. 6). The volume also decreased significantly after 2 and 4 months of storage for RD and GD. Fruit turgor pressure change during storage, and consequent decrement of surface stress caused by mechanical impact, could reduce BV.

3.4.2. Bruise susceptibility. For different concentrations, BS decreased during storage (Table 2). The BS value for RD and GD obtained by Javadi et al. (2010) was 8.2 and 6.6, respectively. The higher values reported by them could be due to different impact energy, plant growth environment, and testing conditions. Moreover, BS decreased for samples treated with higher $Ca(NO_3)_2$ concentrations. The highest BS was observed in GD000 and the lowest in GD104. The interactions of cultivar and $Ca(NO_3)_2$ concentration and also cultivar and storage time on BS were significant (Fig. 6). For both cultivars, coating concentrations of 0.5% and 1.0% significantly reduced BS. In the case of time storage, BS obtained for GD showed considerable decrease after 2 and 4 months of storage. However, BS decreased after 4 months for RD and no significant difference was observed between BS on the first day and the 2^{nd} month.

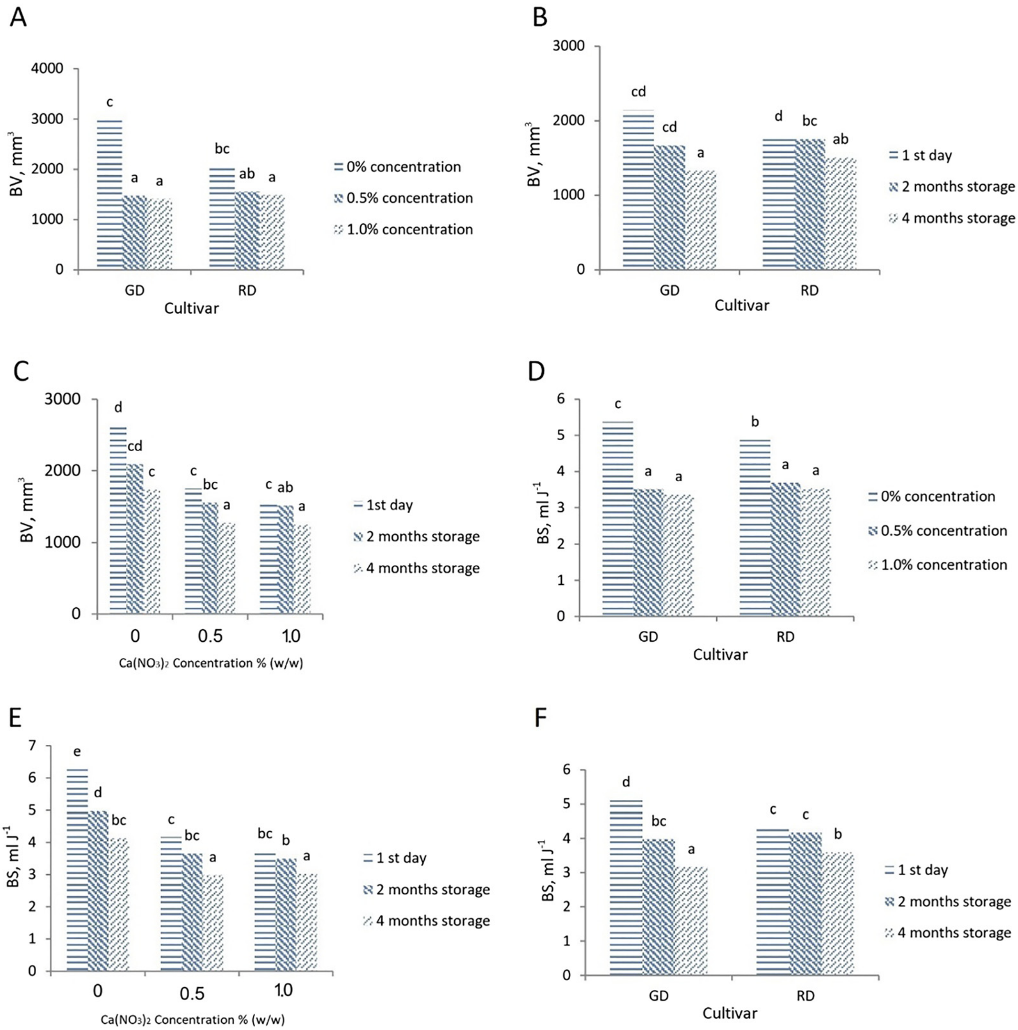

Fig. 6. Interaction of: (A) and (D) cultivar and $Ca(NO_3)_2$ concentration, (B) and (E) storage time and cultivar and (C) and (F) storage time and $Ca(NO_3)_2$ concentration on bruise parameters of apple fruits. Different letters in columns represent significant difference at the 5% level

4. CONCLUSIONS

Coating with $Ca(NO_3)_2$ of different concentrations and storage time was shown to significantly affect pH, titratable acidity, °Brix, modulus of elasticity, yield stress, and bruising parameters of two apple cultivars (Golden Delicious and Red Delicious). Thereby, °Brix and E increased and BV and BS decreased as the concentration increased. Storage time significantly reduced the overall acceptability of apple fruits. The 1.0% $Ca(NO_3)_2$ treated sample showed the lowest BS, while the control (0.0% $Ca(NO_3)_2$) specimen had the highest. A comparison of the results obtained for the two cultivars indicated that GD could better sustain its desirable properties during storage than RD.

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