Potential application of chitosan-clay coating on some quality properties of lemon during storage

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Abstract: Lemon is cultivated in many countries including of Iran as lemon is one of the most important citrus fruits. Because of its split skin and very juicy properties, the quality of lemon fruits is affected by means of some environmental factors during storage. In this study, the effect of chitosan-clay nano-composite coating on some quality properties of lemon was investigated during cold storage. Nano-structural feature of prepared chitosan-clay was approved by X-ray diffraction (XRD). The chemical and mechanical properties of coated and uncoated samples including of total soluble solid (TSS), titratable acid (TA), and firmness, shear and punch forces were measured after 0, 21, 42 and 63 days. Coated samples showed significant differences in ($p<0.05$) the lowest value of TSS and punch force, and the highest value of TA, firmness and peel shear forces. Furthermore, coated samples had the lowest weight loss during storage. Based on the results of present research, the quality properties of lemon fruit samples were improved using coating of chitosan-clay nano-composite during storage.

Keywords: chitosan-clay, chemical properties, mechanical properties, nano-composite, lemon fruit

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1 Introduction

Considering the annual production of citrus fruits is more than 2.7 million tones, it have occupied first place among horticultural crops in Iran (FAO, 2013) and lemon is the third important citrus species after orange and mandarin with about 0.6 million tones production (FAO, 2013). Lemon as a subtropical fruit has high commercial worth on the international fruit markets. Because of its the split skin and very juicy properties, the shelf life of lemon fruits is affected by some environmental factors during storage (Chien et al., 2007). Similar to the deciduous fruits, lemon fruits are not held in the cold storage and must be harvested with delay from the tree. On the other hand, it is usually maintained on the tree until transfer to market. However, under special circumstances such as low physical disorders, controlled humidity and environment, application of coating materials and employing of ethylene in cold storage, the shelf life of these fruits can be improved (Miller, 1946).

Product quality maintaining during storage is one of the introduced applications of nanotechnology in the agricultural sciences (Chaudhry et al., 2008, Chen et al., 2006, Das et al., 2009, Moraru et al., 2009, Moraru et al., 2003, Dasgupta et al., 2015). Nano-coating has been showed considerable potential in the fruit shelf life increasing (De Azeredo, 2009). In recent years, many layers and edible coatings were commonly used for fruit and fresh vegetables (Baldwin, 2007, Arnon et al., 2015). Corn starch coating at different concentrations (1%, 2%, 3%, 4%, 5% and 6%) was used to study the storage life and post-harvest quality of Assam lemon fruits (Ghosh et al., 2015). They suggested that coating with 4% corn starch was found very effective in the fruit maintaining. Khoshtaghaza and Taghinezhad (2016) studied the effect of particle nano-coating on quality properties of Thomson orange during storage. According to their results, nano-coating increased orange resistance to fungal diseases and retained peel color and texture inner strength

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of fruit during storage.

Chitosan is a non-toxic, natural and biodegradable polysaccharide (Sajomsang, 2010). It is derived from chitin and well known as an anti-fungicide (Devlieghere et al., 2004). Chitosan film has been used as coating of crops such as mandarin, strawberries and fresh fruits (Fornes et al., 2005, Ribeiro et al., 2007, Kerch, 2015). Chien et al. (2007) indicated that coating of citrus (*Murcott tangor*) by chitosan, with significant antifungal activity, increased postharvest quality and shelf life of fruits. Chitosan-clay components of applications have valuable advantages such as delaying in the moisture losses, reducing in the evaporation and breathing rate, and changing in the material tissue properties (Muzzarelli et al., 1990; Sajomsang, 2010).

Based on the aforementioned considerations, the purposes of this study were: a) to investigate the potential application of edible coating (chitosan-clay) on some quality attributes of Lemon during storage, b) to evaluate the kinetic parameters of weight loss.

2 Material and methods

2.1 Fruit samples

Sweet lemon's fruits (20 kg) were purchased randomly from a citrus orchard in Sari, Iran. The samples immediately brought into the laboratory for storage after necessary treatments.

2.2 Lemon fruit coating with chitosan- clay

Chitosan with low molecular weight (43 KD) was bought from Sigma Aldrich Company. Clay was purchased from Sefid Sang Aligoodarz Company in Iran. Chitosan-clay solution was prepared by dissolving 20 g chitosan and 10 g clay in 50 ml of glacial acetic acid, 900 mL distilled water, 1 g tween80 and 0.1 M NaOH (Casariego et al., 2009). The fruits were washed with tap water and then dried in the shade for 120 minutes. The fruits were dipped in chitosan-clay solution by hand. The surface coating of fruits was dried and stored at 8°C±2°C and 75%-80% of relative humidity for 63 days. Experiments were carried out at four storage times (0, 21, 42 and 63 days) with coated and uncoated samples and the chemical and mechanical properties of lemon fruit were measured at these times in triplicate.

2.3 The XRD characterization

The structure of chitosan-clay nano-composite was evaluated by XRD measurement. The XRD instrument (Siemens, D500, Germany) was applied using Ni-filtered Cu-Kαradiation with diffraction angle (2θ) from 2 to 20 degree, scan rate of 1.2° m^{-1} and step size of 0.02.

2.4 Chemical properties

After peeling and removal of seed, juice was extracted from the pulp through a mechanical juice extractor and strained. The chemical parameters of fruit juice such as TSS (%) and TA (%) of lemon juice were measured. TSS was determined by digital refractometer (model Atago- ATC- 20 E, made in Japan) in the range of 0%-20% (Sánchez-Moreno, 2002). TA was estimated by the method described by Sánchez-Moreno (2002).

2.5 Mechanical properties

The mechanical properties of samples were measured using Instron machine (Hounsfield Co., England, and Model 4400). The mechanical test was conducted at a cross-head speed of 60 mm m^{-1}. Furthermore, six replications were performed for each treatment and the average of the measured forces was calculated (Singh and Reddy, 2006).

For compression test, the samples were placed on the flat plate and pressed with a movable plate and a 500 N load cell fixed parallel to the base. The movable plate was shifted 35 mm from the contact point (Churchill et al., 1980, Singh and Reddy, 2006). Passable axis from fruit stem was perpendicular to the movement direction (Churchill et al., 1980). The force at rupture (first breaking) was recorded as the firmness force in each run.

For punch test, the samples were placed on a flat plate and punched with a steel rod 4.8 mm in diameter connected to the load cell of Instron. Steel rod was penetrated 10 mm in fruit (Singh and Reddy, 2006).

The shear test was conducted on 12 peel pieces with 6 cm^2 surface area. Peel piece was placed between two aluminum plates. Each plate had a 2.6 cm diameter hole in the central. Steel pins held the plates in place. A cylindrical knife-edges cutter 2.54 cm in diameter attached to the load cell of Instron was used to shear the peel pieces (Fidelibus et al., 2002).

For weight losses test, the fruit was weighted periodically by digital scale with an accuracy of 0.001 gr (Model GE2102).

2.6 Weight loss

To determine the weight loss of Lemon, three repetitions were performed for every treatment and every repetition contained five fruits. The same fruits were evaluated for weight loss during the 61 days storage period. Weight losses percentage is calculated according Equation (1):

$$\text{Weight losses percentage} = \frac{(\text{fruit weight before test} - \text{fruit weight after test})}{\text{fruit weight before test}} \times 100 \quad (1)$$

2.7 Statistical analysis

A full-factorial design was used to experimental analysis. The obtained data were analyzed by SPSS software (Version 15; SPSS Inc., Chicago, IL, USA). Tukey's test was used to determine the differences between means at a confidence level of 95%. All experiments were performed in triplicate and mean values were reported with standard deviations.

3 Results and discussion

3.1 XRD analysis of chitosan-clay nano- composites

Nano structure of chitosan-clay nano-composite was approved by XRD analysis. Figure 1 showed a sharp peak at 2θ=7° (i.e., d-spacing of 15.85 Å). This conclusion was in agreement with the results of (Darder et al., 2003). They reported that the interlayer spacing of clay particles and chitosan-clay nano-composite were 12 and 20 Å, respectively. So, the insertion of clay into the chitosan increased the d-spacing of clay particles.

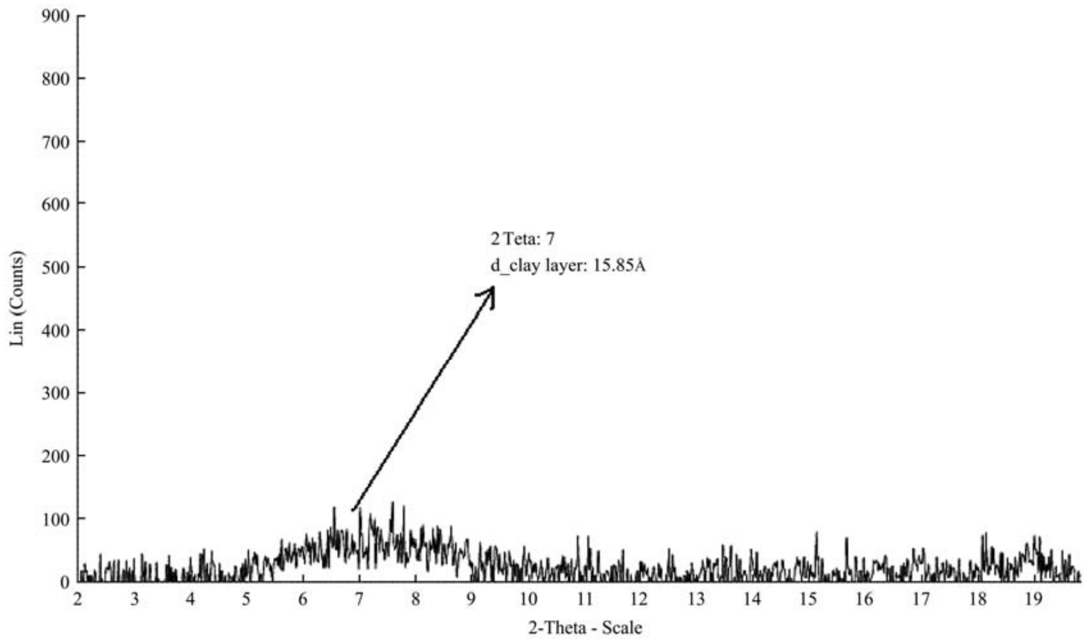
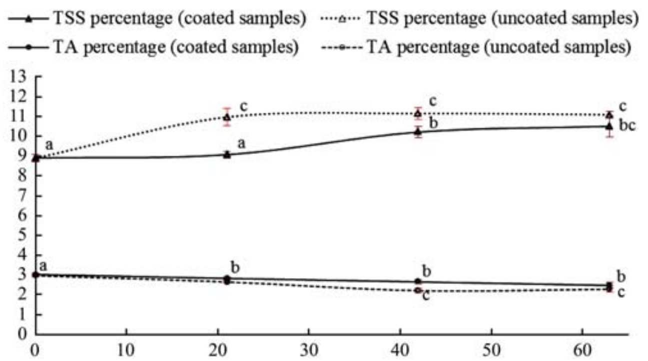


Figure 1 The XRD spectra of chitosan-clay nano-composites

3.2 Chemical properties

Amount of TSS of lemon fruit juice for coated and uncoated samples during storage was showed in Figure 2. TSS of lemon fruits increased by chitosan-clay nano-composite coating and there was a significant difference of TSS values in coated and uncoated samples. These findings were in agreement with the reported observations by Ghosh et al. (2015). Zareei et al. (2005), which resulted that the TSS values of fruit juice in cold storage were lower than local storage because of moisture protection in cold storage. The loss of soluble solids during the storage period was as natural as sugars which are the primary constituent of the soluble solids content of a product, consumed by respiration and used for the metabolic activities of the fruits (Özden and Bayindirli, 2002). TSS values were about 8.83% to 11.07% in the uncoated fruits. It was higher than the coated samples (from 8.83% to 10.67%). So lemon fruits with chitosan-clay coating may have the lowest respiration and moisture loss. Therefore, coated treatment by using of chitosan- clay has protected the fruit quality.

The TA values of the lemon juice for coated and uncoated samples were also shown in Figure 2. The TA of coated and uncoated samples decreased during storage between 2.97% to 2.5% and between 2.97% to 2.33%, respectively. According to Figure 2, the TA values for coated samples were higher than uncoated samples. The low level of TA in uncoated samples as compared to coated samples suggested that the chitosan-clay coating delayed ripening by providing a transparent coating around the fruit. It is also considered that coatings reduce the rate of respiration and may therefore delay the utilization of organic acids (Yaman and Bayoındırlı, 2002, Finidokht et al., 2013). Furthermore, decreasing of the TA values during storage was in agreement with the reported observations by Finidokht et al. (2013). TA and TSS of fruit juice was decreased and increased during storage, respectively (El-Zeftawi, 1976). So, the coated samples had lower TA than uncoated ones due to high TSS.



Note: The same letter over column shows that the mean amount had no significant difference (p<0.05) based on Tukey's test. The error bars represent standard error of the means.

Figure 2 TSS and TA of coated and uncoated samples of lemon in chitosan-clay nano-composite during cold storage (day)

3.3 Mechanical properties

By placing the fruit axis perpendicular to the orientation of the plate movement, the mechanical properties such as firmness, punch and cutting force were measured. The firmness force values of lemon fruits for coated and uncoated samples were shown in Figure 3a. The firmness force decreased during storage for coated and uncoated samples. These findings were in agreement with the data reported by Singh and Reddy (2006) for oranges. Equation (2) and Equation (3) showed the relationships between the fruit firmness (F (N)) and storage time (t (s)) for coated samples and uncoated samples, respectively.

$$F = -0.1115t + 260.76 \qquad R^2 = 0.93 \tag{2}$$

$$F = -1.5756t + 252.07 \qquad R^2 = 0.91 \tag{3}$$

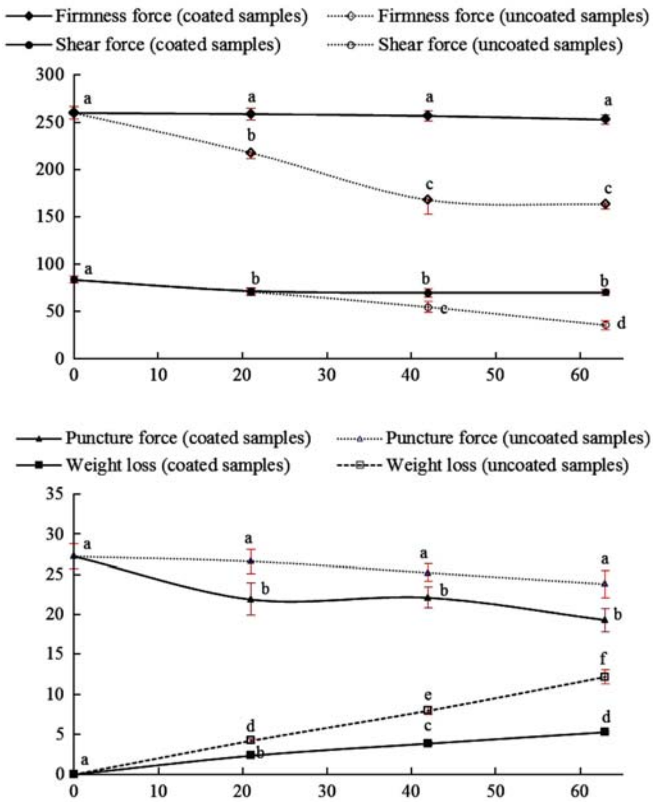
The firmness force for the coated lemons (260.13 to 252.98 N) was measured significantly higher than uncoated samples (260.13 to 165.18 N) during storage. Consequently, fruit softening was also delayed at the coated fruit (Singh and Reddy, 2006) and when storage was prolonged, coating will be more effective in maintaining of lemon firmness.

Punch forces of coated and uncoated lemon fruits were shown in Figure 3b. The values of punch force decreased from 27.64 to 25.34 N and from 27.64 to 20.88 N for uncoated and coated samples, respectively. No significant differences (p>0.05) was observed in punch force for uncoated fruits but it changed significantly (p<0.05) at the first three weeks of storage for coated samples. The punch force of coated samples was significantly lower than uncoated samples. The similar results were also explained by Singh and Reddy (2006).

Peel shear force data of lemon fruits during storage were also displayed in Figure 3a. The value of peel shear force for uncoated sample was significantly (p<0.05) less than coated ones. Intercellular spaces resulted in less cell wall material per volume of tissue and less contact area between cells. Both factors could cause the tissue to be less resistant to shear stress (Harker et al., 2010). Therefore, uncoated samples had the lowest stiffness because of less contact area between cells.

3.4 Weight loss

A comparison of the weight loss of all treated fruits exhibited the weight loss in all samples significantly increased in Figure 3b. The lowest weight loss was related to coated samples (5.28%) and control samples showed higher trend in weight loss than coated samples, which is in agreement with the results of Nabifarkhani et al. (2015). Weight loss was caused by evaporation of water from the fruit (Amarante et al., 2001). Undoubtedly, lower weight loss of coated samples in comparison with uncoated samples contributed to maintaining better quality of fruit during storage.



Note: The same letter over column shows that the mean amount had no significant difference (p<0.05) based on Tukey's test. The error bars represent standard error of the means.

Figure 3 Mechanical properties (firmness force (N), shear force (N), puncture force (N) and weight loss (%)) of coated and uncoated samples of lemon in chitosan-clay nano-composite during cold storage (day)

4 Conclusions

Investigation of chemical properties of lemon fruits showed that applied treatment (chitosan-clay coating) had the higher TA and lower TSS as compared to uncoated ones. Also loss of fruit weight reduced significant differences (p<0.05) in the coated samples. Furthermore, studying of the mechanical properties revealed that coated samples had the highest firmness, peel shear forces and the lowest punch force. Finally, this study suggested that coating of chitosan-clay extended the shelf life and preserved the quality during storage. The investigation of chitosan-clay coating in a range of food systems is still needed study for successful application to agricultural products. Also, in future research, coating of chitosan-clay can be used to investigate the appearance of fruits and fungi growth.

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