نهمین کنگره ملی مهندسی ماشین‌های کشاورزی

(مکانیک بیوسیستم) و مکانیزاسیون

پردیس کشاورزی و منابع‌طبیعی دانشگاه تهران

۲ و ۳ اردیبهشت ۱۳۹۴ - کرج

Effect of Nano Biocomposite, Chitosan and carnauba wax Coating on Physical and Rheological Properties of Apple during Different Storage Condition

M. H. Movahednejad[1], M. H. Khoshtaghaz[2], S. Minaee[3], M. J. Zohouriyan Mehr[4]

1- Assistant Professor of Agricultural Machinery Engineering Dept., Shahrood University

2- Associated Professor of Agricultural Machinery Engineering Dept., Tarbiat Modares University

3- Associated Professor of Agricultural Machinery Engineering Dept., Tarbiat Modares University

4- Associated Professor of Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute

Corresponding Email: mhmovahed@yahoo.com

Abstract

In this paper, the effect of three coatings (carnauba wax, Chitosan and naocomposite) was compared with uncoated samples on Rheological and physical properties of apples during storage. These properties were water loss, firmness, elasticity module, and viscoelastic properties. The variations of Rheological and physical properties of apples during six months at two conditions of cold storage (2°C and 95% RH) and environmental storage (20°C and 45% RH) were evaluated. The results showed that minimum weight loss was happening in wax coating. In wax coating, Firmness was decreased lease than other coatings. it was also observed that the wax coating to other coating was much less change for elasticity module. Less strain on the wax coating was observed in all the storage time. The wax coating to other coating was in the higher level of energy.

Keywords: apple; nanocomposite; firmness; elasticity module; viscoelastic properties

1. Introduction

One of the most important tips to reduce waste garden products attends to postharvest issue like storage. In this context a number of factors in storage of garden products are effective. Among them will be mentioned temperature, humidity, atmospheric pressure and type of coating. One of Iran's most important agricultural export products are apples. Because of the high value export and high waste must pay close attention to their storage. Apple orchards under cultivation in Iran with 201.350 hectares, equal to 6.6 percent of apple cultivation in Asia and 2.4 percent of apple cultivation in the world are. Iran's annual production of 2,661,901 tons of apples and performance against 13.220 kg /ha 2.7 percent of apple production in Asia and 2.4 percent of world apple production is allocated to (Anonymous, 2009).

The main purpose of employing edible films and coatings is to provide a semi permeable barrier against gases and vapor and also as carriers of functional ingredients, including antimicrobial agents and antioxidants (Embuscado and Huber, 2009). Similarly, Zheng et al, reported a considerable improvement of the physical properties in nanocomposite prepared by gelatin and montmorillonite (Zheng, *et al.*, 2002). An appreciable increase in stability of Chitosan/layered nanocomposite was also reported (Weiss, *et al.*, 2006).

For improve the quality and physical properties of apples have used the edible coatings. In a study, The effect of alginate and gellan-based edible coatings on the shelf-life of fresh-cut Fuji apples was investigated by measuring changes in headspace atmosphere, color, firmness and microbial growth during 23 days of storage at 4 1C. The results showed that the firmness of uncoated apples pieces decreased from 10.19 to 5.30N during 23 days storage. Both alginate and gellan coating showed a beneficial result on firmness retention of apple wedges during the entire storage period. In addition, firmness deterioration is frequently associated with water content loss (Rojas-Grau, *et al.*, 2008). In the other study, Chitosan was used for coating the slice apples. Properties measured were included weight

loss, firmness, color. The results showed that the coating sample had more lightness than uncoating samples in during storage. Firmness also significantly was higher in the coating samples (Qi . *et al.*, 2010).
The aim of this paper to determine and compare quality and physical properties of apples with different coatings in different conditions of storage, then finds the best way to decrease losses in apple storage.

2. Material and Methods

2.1. Sample preparation and storage methods

Apples (Golden delicious) were prepared from the garden in Damavand. Apples stored in low (2 °C with 95% humidity) and environment temperature (20 ° with 40 % RH). Sampling was monthly in six months. Apple Properties per month (water loss, (ΔE), firmness, elasticity module, and visco-elastic properties) were evaluated.

2.2. Coatings Materials and Preparing

Three coatings in this study were used. The first edible coating was carnauba wax. This wax was made by international company (Zeta) from France. The others coating were Chitosan based and nano-composite of Chitosan-clay that produced in the laboratory. Chitosan used had low molecular weight with 85% deacetylation degree (Company Sigma-Aldrich). Clay was Bentonite and prepared from Khak Sefid of Ali Goodarz Company. The chitosan solutions were prepared dissolving the Chitosan (3% w/v) in a 2% (v/v) lactic acid solution using a magnetic stirrer during 3 hr at 60°C. Then adding 10% glycerol and 5% tween80 (w/w with Chitosan) to Chitosan solution. For nanocomposite, at first bentonite suspension was prepared by adding bentonite to 2% (v/v) lactic acid solution. Then Chitosan solution was added into pretreated bentonite suspensions (with 1-2 (w/w) ratio clay to chitosan). Then mixtures were stirred continuously for 24 hour at 60°C.
For Coating samples after washing and drying, covered with different coating. After that, the coating samples were maintained in environmental conditions for 24 hours to dry the coatings. After drying, according to different methods of storage, samples were divided.

2.3. Water Loss

Weight loss for 320 samples in 16 categories, 20 bits (two and four types of coverage and the maintenance of the tree) was determined. Their weight and color intensity was determined each month.

2.4. Firmness

Punch test was used to determine the stiffness of apple. In this test the loading speed 200 mm / min and the probe was 11 mm, round bottom. In each test, 5 samples were randomly selected. Then each sample was divided into two half and was placed under the jaw. In each test, a small amount of apple skin was removed **(**Belie *et al.*, 2000**)**

2.5. Elasticity Module

To determine the modulus of elasticity, compressive tests were used. Loading rate 2.5 mm / min was determined. The following equation was used to determine the modulus (ASAE Standard 2009).

$$E = \frac{0.338 {K_u}^{3/2} F(1-\mu^2)}{D^{3/2}} \left(\frac{1}{R_u} + \frac{1}{R_u'}\right)$$

2.6. Viscoelastic Properties

To determine the viscoelastic properties of apples used loading-lifting test. Loading and lifting rate 5 mm / min was chosen. Displacement was 3 mm. Properties obtained in this test consists of elastic and plastic strain, Hysteresis, Resilience and total energy (Guillermin, *et al.*, 2006)

2.7. Statistical Test

Factorial test base on completely randomized design with compound analyzed based on two experimental units (trees) were selected for statistical analysis of these experiments. Independent variables in the study included period time (six stage one month), storage conditions (two levels low temperature storage (S) and environment (I)) and coating (wax, chitosan, nanocomposite and without coating). Samples were taken from two trees. Dependent variables included apple properties such as water loss, color change (Δa, Δb, ΔL and ΔE), firmness, elasticity module, and visco-elastic properties. Then based on the data obtained used the software SPSS to measure analysis of variance and mean comparison (Duncan).

3. Results and discussion

3.1. Coating Properties

3.1.1. XRD test

According to Figure 1, 2θ was 7 ° for the nanocomposite films. Also based on this angle, the distance between layers of clay, was 15.85 Å. Based on Kabirian research and also in Darder's research distance between the layers of bentonite(clay), was 12 Å(Kabiri *et al.*, 2007; Darder *et al.*, 2003). Based on the above information, structure of film been produced was nano. Based on results from Darder's paper, distance of clay layers in the nano composite structure was 13.8 and 20 Å (Darder *et al.*, 2003).

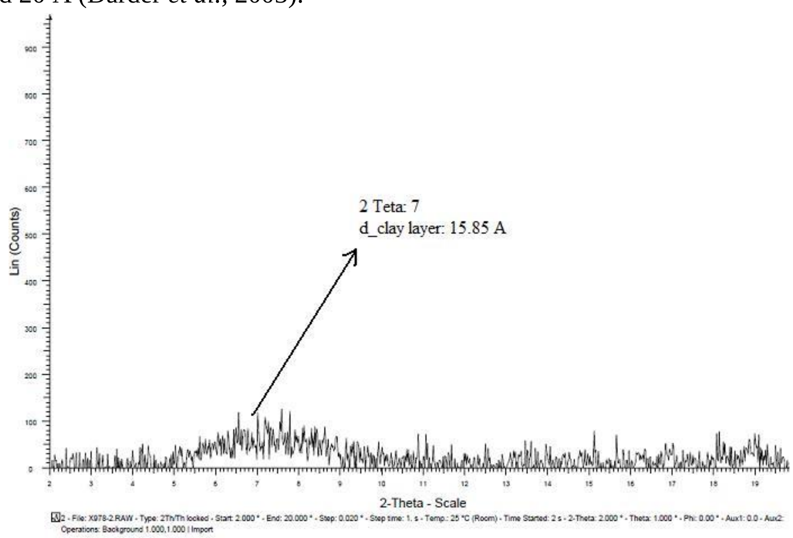
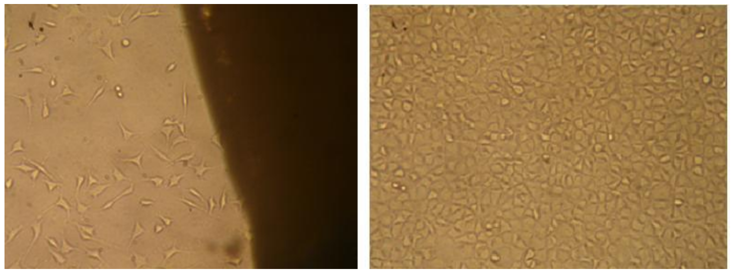


Figure 1: XRD diagram of sample clay nanocomposite chitosan (chitosan/clay 2 to 1)

3.1.2. Biocompatibility testing

Compared with the control sample and mouse cell with nanocomposite, cell activity was observed in the vicinity of the nanocomposite. Given the above results, a nanocomposite film can be considered biocompatible(figure 2).



a b

Figure 2: Image of cell Biocompatibility (a) growth control (b) nanocomposite

3.2. Physical properties

3.2.1. Water Loss

Due to the cold and environment storage results (figure 3, 4), minimal weight loss was happened in the wax coating. Two factors can impact on weight loss. The first occurred due to loss of moisture and the second factor was due to respiration and transpiration of product. In wax coating, because of lipid material had low permeability to moisture and oxygen, had the best performance to the nanocomposite coatings and chitosan. Weight losses in apples coated with wax were, respectively, 20.2 and 5.4% in environmental and cold storage. Compared with uncoated samples, respectively, 30 and 22% weight loss was reduced. In other coatings, because of more pores couldn't reduce the weight loss to uncoated sample. Olivas *et al.*, showed that a large increase in water loss occurred with uncoated apples. Uncoated apples lost around 20% of their weight, while coated apples with alginate lost about 7% of their weight(Olivas *et al.*, 2007). Bai *et al.*, reported Weight loss was least for fruit with candelilla wax coatings. The carnauba-shellac coating did not protect against weight loss better than shellac, probably because it contained such a high percentage of shellac, although carnauba wax coatings generally offer good protection(Bai *et al.*, 2003).

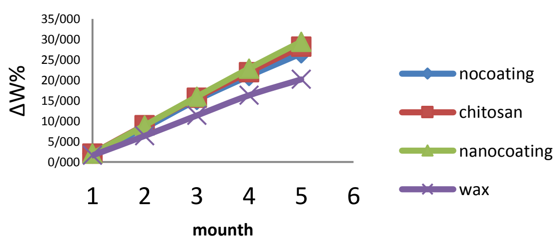


Figure 3: Changes in percentage weight loss of apples coated with nanocomposite, chitosan, carnauba wax, and the no coating during storage at 20˚C and 45% RH

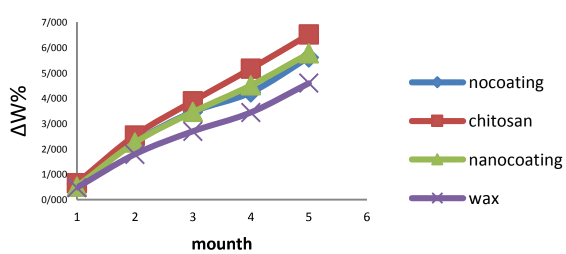


Figure 4: Changes in percentage weight loss of apples coated with nanocomposite, chitosan, carnauba wax, and the no coating during storage at 2˚C and 95% RH Mechanical Properties

3.2.2. *Firmness*

Trend of Firmness in the environment storage was descending except wax coating. Chitosan and nanocomposite coatings were very close. The wax coating on the second month slightly reduced then remained constant to forth month. After the forth month, the trend was descending and had steeper slope than the other coating (figure 5). In Cold storage, there was a different trend to environmental storage. Trend in all coatings were descending with very gentle slope downward (figure 6). Olivas *et al.*, showed that Firmness of coated apples remained practically constant regardless of the type of coating, while uncoated apples had a large decrease in firmness during storage(Olivas *et al.*, 2007). Bai *et al.*, reported the loss of firmness during storage was least for fruit without coatings. The firmness of ‘Delicious’,, declined to less than 44 N. firmness in delicious with carnauba and shellac wax were least at 43 and 47N(Bai *et al.*, 2003).

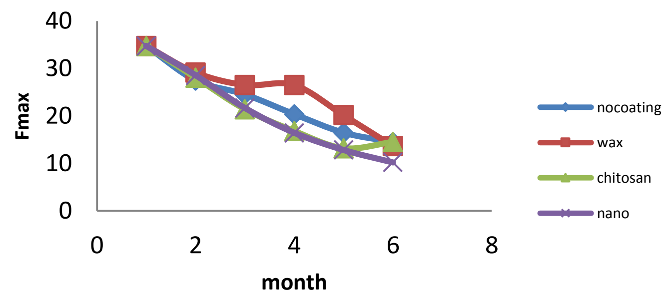


Figure 5: Changes in firmness of apples coated with nanocomposite, chitosan, carnauba wax, and the no coating during storage at 20˚C and 45% RH

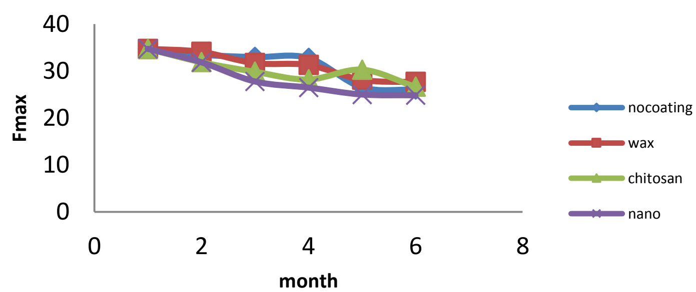


Figure 6: Changes in firmness of apples coated with nanocomposite, chitosan, carnauba wax, and the no coating during storage at 2˚C and 95% RH

3.2.3. *Elasticity Module*

Survey results were observed with the environmental conditions at the beginning from the first month to the second month, there was sharp drop in all coatings (figure 7).. After that, the trend remained relatively constant. The modulus of the wax coating is generally higher than other coating in the third and fourth month. In all coating, the modules in the fifth and sixth months reached a same level. It was also observed that the wax coating to other coating was much less change. In the fifth module distinguished from each other the highest and lowest values, respectively, to wax and nanocomposite coatings were about (figure 8). Varela *et al.*, reported elasticity module for golden delicious decreased from 2.45 to 1.4MPa at 14 days and for Graney apples from 4 to 2.25MPa at 14 days(Varela *et al.*, 2007).

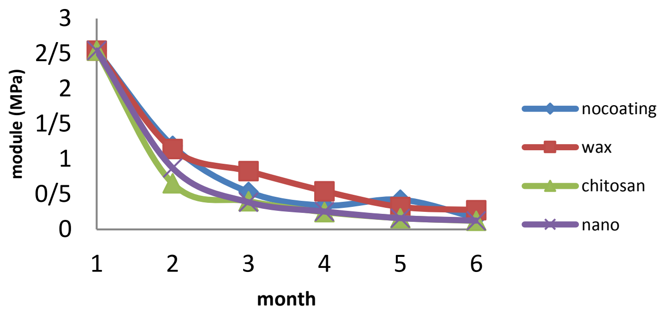


Figure 7: Changes in module of apples coated with nanocomposite, chitosan, carnoba wax, and the no coating during storage at 20˚C and 45% RH

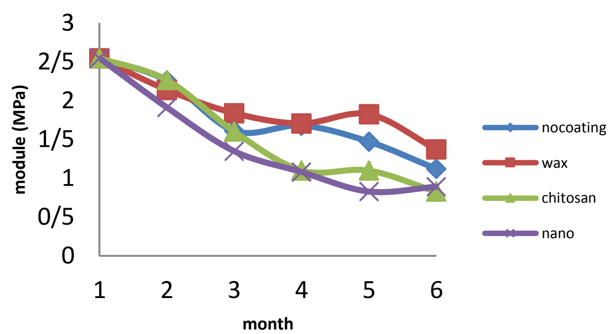


Figure 8: Changes in module of apples coated with nanocomposite, chitosan, carnoba wax, and the nocoating during storage at 2˚C and 95% RH

3.2.4. Viscoelastic Properties

3.2.4.1. Strain

According to the results observed in the elastic strain, was declined in environmental storage in all coatings. Despite the more drop in chitosan and nanocomposite coatings, changes in these coatings, from the third month were almost constant (table 1). Instead of less strain on the wax coating, drops downward trend was observed in all the storage time. In contrast, environmental storage, trend of strain in cold storage was approximately constant. This phenomenon was indicated that the elastic properties of apples reduced circumstances, but in cold storage was constant. Guillermin *et al.*, showed that elastic strain didn't change significant at 30 days(Guillermin *et al., 2006*).

3.2.4.2. P strain

Results were observed the plastic strain on the environment storage in all coatings showed the opposite trend to elastic strain. This trend was steeper in the beginning and from the fourth month was fixed for all coatings. A plastic property of apple with wax coating was lower than the other coatings. In contrast, in cold storage, the trend was approximately constant. This phenomenon was indicated that the plastic properties of apples were grown in environmental storage, but there was little change in cold storage (table 1).

3.2.4.3. Er

The study results, the elastic energy in the environment would follow the total energy. The trend of wax and nanocomposite coatings (from second month) was reduced with a gentle slope. After the third month, the wax coating had the highest energy and lowest energy was in chitosan coating (table 1). Guillermin *et al.*, who reported elastic energy decrease from 90 to 67N.mm/mm during the cold storage(Guillermin *et al., 2006*).

3.2.4.4. Eh

In the environmental storage, the trend in wax coating and uncoated sample was reduced with steep slope to third month and then the slope was declined. Trend of nanocomposite and chitosan coating was descending with steep slope to the second month and after the second month, the downward trend was observed with a gentle slope. in cold storage until the fourth month, a decline trend was visible. Most notable of the reduction was in the second and the third month. The remaining months of the gradient was gentle. The wax coatings and uncoated samples were compared with other coating had the same trend to forth month. In fifth month, wax coating was in the highest energy. Chitosan and nanocomposite coatings also had the same trend, especially from the fourth month (table 1).

Table 1: change of Viscoelastic properties during warm and cold storage with different coating

Factors		Mean							
		Warm Storage				Cold Storage			
Coating	Time	E_h	E_r	ε_p	ε_e	E_h	E_r	ε_p	ε_e
Nocoating	0	77.947^{a}	54.385^{a}	0.022^{d}	0.066^{a}	77.947^{a}	54.385^{a}	0.022^{d}	0.066^{a}
	1	43.211^{b}	31.355^{b}	0.038^{c}	0.055^{b}	73.267^{a}	49.172^{a}	0.029^{bc}	0.060^{a}
	2	15.531^{c}	8.342^{c}	0.051^{b}	0.043^{cd}	40.067^{b}	47.710^{a}	0.025^{cd}	0.063^{a}
	3	11.215^{cd}	5.709^{cd}	0.058^{a}	0.040^{d}	36.860^{b}	38.757^{b}	0.030^{bc}	0.064^{a}
	4	10.907^{cd}	6.361^{cd}	0.055^{ab}	0.044^{c}	38.782^{b}	27.434^{c}	0.037^{a}	0.059^{a}
	5	6.147^{d}	2.350^{d}	0.055^{ab}	0.039^{d}	33.165^{b}	32.455^{bc}	0.033^{ab}	0.062^{a}
Chitosan	0	77.947^{a}	54.385^{a}	0.022^{e}	0.066^{a}	77.947^{a}	54.385^{a}	0.022^{c}	0.066^{a}
	1	44.462^{b}	35.140^{b}	0.031^{d}	0.057^{b}	70.176^{a}	51.533^{ab}	0.024^{c}	0.063^{a}
	2	24.434^{c}	18.481^{c}	0.039^{c}	0.051^{c}	41.080^{bc}	45.982^{bc}	0.025^{bc}	0.063^{a}
	3	14.186^{d}	8.851^{d}	0.049^{b}	0.045^{d}	36.351^{c}	41.623^{cd}	0.026^{bc}	0.063^{a}
	4	8.983^{d}	3.968^{de}	0.050^{b}	0.040^{d}	46.756^{b}	35.349^{c}	0.034^{a}	0.057^{b}
	5	7.354^{d}	2.807^{e}	0.056^{a}	0.042^{d}	37.851^{bc}	40.493^{cd}	0.030^{ab}	0.061^{ab}
Nanocoating	0	77.947^{a}	54.385^{a}	0.022^{c}	0.066^{a}	77.947^{a}	54.385^{a}	0.022^{d}	0.066^{a}
	1	20.839^{b}	15.703^{b}	0.042^{b}	0.050^{b}	59.448^{b}	49.447^{ab}	0.025^{cd}	0.064^{a}
	2	11.490^{c}	5.180^{c}	0.055^{a}	0.044^{c}	37.657^{c}	44.036^{b}	0.027^{cd}	0.066^{a}
	3	7.436^{c}	2.636^{c}	0.057^{a}	0.036^{d}	25.425^{d}	28.681^{c}	0.031^{bc}	0.061^{ab}
	4	5.343^{c}	1.727^{c}	0.060^{a}	0.036^{d}	29.442^{cd}	23.608^{cd}	0.037^{a}	0.057^{bc}
	5	5.228^{c}	1.835^{c}	0.057^{a}	0.043^{c}	22.252^{d}	19.875^{d}	0.036^{ab}	0.055^{c}
Wax	0	77.947^{a}	54.385^{a}	0.022^{c}	0.066^{a}	77.947^{a}	54.385^{a}	0.022^{c}	0.066^{a}
	1	26.987^{b}	21.487^{b}	0.043^{b}	0.052^{b}	53.069^{b}	41.613^{b}	0.029^{ab}	0.060^{bc}
	2	14.013^{c}	7.461^{c}	0.053^{a}	0.044^{c}	31.426^{c}	39.667^{bc}	0.024^{bc}	0.065^{ab}
	3	8.372^{cd}	3.323^{d}	0.057^{a}	0.039^{d}	26.414^{c}	34.032^{cd}	0.026^{bc}	0.063^{ab}
	4	6.118^{d}	2.046^{d}	0.060^{a}	0.038^{d}	31.979^{c}	27.535^{d}	0.031^{a}	0.056^{c}
	5	5.345^{d}	1.903^{d}	0.055^{a}	0.044^{c}	25.027^{c}	27.282^{d}	0.030^{ab}	0.061^{abc}

4. Conclusion

Minimum weight loss was happen in coating. All coatings used decrease change of Δa to uncoated sample. The least change of Δb and ΔL was happened in wax and nanocomposite coating. Firmness was decreased lease than other coatings. It was also observed that the wax coating to other coating was much less change. Less strain on the wax coating, drops downward trend was observed in all the storage time. The wax coating to other coating was in the higher level of energy.

5. References

1. **Anonymous (2009).** Agriculture Database of FOA-STAT. Available at http:faostat.fao.org/faostat/form?collection=Production.Crops.Primary&Domain=Production&servlet=1&hasbulk=0&version=ext&language=EN.

2. **ASAE Standard** (2009). Compression Test of Food Materials Of Convex Shape. ASAE S368.4 DEC00.
3. **Bai J., Hagenmaier R. D., Baldwin E. A. (2003).** Coating selection for 'Delicious' and other apples. Postharvest Biology and Technology. 28 :381-390.
4. **Darder, M., Colilla, M., Ruiz-Hitzky, E. (2003).** Biopolymer-Clay Nanocomposites Based on Chitosan Intercalated in Montmorillonite. Chemistry Material. 15: 3774-3780.
5. **Embuscado M. E. and Huber K. C.** (2009). Edible Films and Coatings for Food Applications. Springer.
6. **Guillermin P., Dupont N., Le Morvan C., Le Que re J. M., Langlais C., Mauget J.C.** (2006). Rheological and technological properties of two cider apple cultivars. LWT. **39**: 995–1000.
7. **Kabiri, K., Mirzadeh, H., Zohouriaan-mehr, M. (2007).** Highly Rapid Preparation of a Bio-modified Nanoclay with Chitosan. Iranian Polymer Journal. 16(3): 147:151.
8. **Olivas G. I., Mattinson D. S., Barbosa-Cánovas G.V.** (2007). Alginate coatings for preservation of minimally processed 'Gala' apples. Postharvest Biology and Technology 45: 89–96
9. **Qi, H., Hu, W., Jiang, A. & Tian, M., (2010).** Extending shelf-life of Fresh-cut 'Fuji' apples with chitosan-coatings, Innovative Food Science and Emerging Technologies. In press: 10.1016/j.ifset.2010.11.001
10. **Rojas-Grau M. A., Tapia M. S., Martin-Belloso O. (2008)**. Using polysaccharide-based edible coatings to maintain quality of fresh-cut Fuji apples. LWT 41: 139-147.
11. **Varela P., Salvador A., Fiszman S.** (2007). Changes in apple tissue with storage time: Rheological, textural and microstructural analyses. Journal of Food Engineering 78 622–629.
12. **Weiss J. , Takhistov P. , McClements J.** (2006). Functional materials in food nanotechnology . J Food Sci 71 (9) : 107 – 116.
13. **Zheng JP , Li P , Ma YL , Yao KD (2002).** Gelatine/montmorillonite hybrid nanocomposite.I. Preparation and properties. J. Appl. Polym. Sci. 86 , 1189 – 1194

تاثیر سه پوشش نانوکامپوزیت، کیتوزان و واکس کارنوبا بر روی خواص فیزیکی و رئولوژی سیب طی شرایط مختلف انبارداری

چکیده

در این تحقیق اثر سه پوشش (واکس کارنوبا، کیتوزان و نانوکامپوزیت) در مقایسه با سیب های بدون پوشش بروی خواص فیزیکی و رئولوژی سیب در طی انباداری مورد بررسی قرار گرفت. خواص اندازه‌گیری شده شامل افت وزن، سفتی، مدول الاستیسیته و خواص ویسکوالاستیک بود. خواص فیزیکی و رئولوژی سیب طی دو شرایط انبارداری محیطی (۲۰ºC و رطوبت نسبی ۴۵٪) و سردخانه‌ای (۲ºC و رطوبت نسبی ۹۵٪) در مدت شش ماه اندازه‌گیری شد. نتایج نشان داد که کمترین افت وزن و کاهش سختی در طی مدت انبار داری در پوشش واکس رخ داد. میزان مدول الاستیسته در پوشش واکس کمتر تغییر کرده و کمترین تغییرات کرنش نیز در پوشش واکس مشاهده گردید. همچنین بیشترین انرژی نیز مربوط به همین پوشش بود.

کلمات کلیدی: سیب؛ نانوکامپوزیت؛ سفتی؛ مدول الاستیسیته؛ خواص ویسکوالاستیک