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Preparation and Characterization of a Bionanopolymer Film for Packaging Applications (a Case Study: Walnut Packaging)

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Abstract

The carboxymethyl cellulose (CMC)/polyvinyl alcohol (PVA) film were prepared by adding three levels of nanoclay particles (0.5, 1 and 3%) using solution casting evaporation method. The incorporation of nanoclay on mechanical, water vapor permeability, and oxygen barrier properties of CMC/PVA-based film was investigated. The best result was obtained through the nanocomposite film contain 3% nanoclay. In the next step, the CMC/PVA/nanoclay films were employed for walnut packaging. After 90 days storage in the environmental condition, the optimum result was found through the nanocomposite film with 3% nanoclay in terms of oil content, moisture content, acidity and peroxide indexes of walnuts. According to the overall results, the reinforcement of CMC/PVA film with 3% nanoclay could be introduced as a good candidate for the development of high barrier food packaging material against the diffusion of water vapor and oxygen permeability.

Keywords: Film, Nanocomposite, Packaging, Properties, Walnut

Introduction

Nowadays, most materials used for food packaging are petrochemical-based and non-biodegradable, leading to environmental pollution and severe ecological problems. Using natural polymers in numerous forms are increasing in food packaging applications. Some weak properties of natural polymers may be improved through nanotechnology appliances (De Azeredo, 2009; Tajeddin, 2015). Organo modified montmorillonite (MMT), commonly called nanoclay, could be considerably improved the mechanical characteristics of pure polymers by adding of its small amount as reinforcement in both academic and industrial sectors (Chan, Lau, Wong, Ho, & Hui, 2011). Using MMT is a great interest because of its natural source, high modulus of clay platelets, and low content to achieve the proper mechanical properties. These layered materials exist in the form of the cumulative bonded with physical forces, accordingly that they can be exfoliated even to single nanolayers (Majdzadeh Ardakani, Navarchian, & Sadeghi, 2010). The natural MMT is hydrophilic and is miscible with hydrophilic polymers (Park, Lee, Park, Cho, & Ha, 2003;Ray & Bousima, 2005). Development of the polymer/clay nanocomposites is one of the revolutionary steps in the polymers technology (Ray, 2010; Taghizadeh & Sabouri, 2013). Some researchers have proved potential of organoclays for starch-based polymer nanocomposites to improve the long-term mechanical properties over the unfilled formulations (Chivrac, Gueguen, Pollet, Ahzi,

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Makradi, & Averous, 2008; Cyras, Manfredi, Ton-That, & Vazquez, 2008; Taghizadeh & Sabouri, 2013). For example, physicochemical properties of starch/CMC/nanoclay films were studied by Almasi, Ghanbarzadeh, & Entezami (2010). Their study results showed that the MMT addition at content of 7% (w/w), caused to increase in ultimate tensile strength by more than threefold in comparison to starch/CMC biocomposites.

However, a nanocomposite film was produced based on nanoclay particles, in this research. Carboxy methyl cellulose (CMC) and polyvinyl alcohol (PVA) were used as matrices. Glycerol also was applied as plasticizer. It is noteworthy that CMC can be used in the biocomposite films production due to its polymeric structure and high molecular weight (Debeaufort & Voilley, 1994; Ma, Chang, & Yu, 2008; Taghizedeh, Abbasi, & Nasrolahzadeh, 2011; Taghizadeh, Sabouri, & Ghanbarzadeh, 2013). In addition, PVA, as a water-soluble polymer, has been widely used as a matrix for the preparation of nanocomposites. The main reason is due to its easy process ability, high optical clarity and biocompatibility (Lee, Mohan, Kang, Doh, Lee, & Han, 2009). Glycerol is one of the most well liked plasticizers used in the films and coatings preparation by reason of its stability and compatibility with the hydrophilic nature of the biopolymer chains. The main advantage of this plasticizer is a high boiling point, lack of odour, water solubility and miscibility with those components (Chillo, Flores, Mastromatteo, Conte, Gershenson, & Del Nobile, 2008; Galus, Uchanski, & Lenart, 2013; Vanin, Sobral, Menegalli, Carvalho, & Habitante, 2005).

The present paper states a number of CMC/PVA/nanoclay films characteristics. Furthermore, some properties of packaged walnuts in the prepared films during its storage time discuss in this article. Walnut is a very nutritious and its composition varies depending on its variety (Mitrovic, Stanisavijevic, & Gavrilovic, 1997). Most varieties of walnuts have almost 60% oil (Prasad, 1994). Nuts such as walnut have a suitable taste when they keep in the presence of low concentrations of oxygen (Jensen, Sørensen, Brockhoff, & Bertelsen, 2003). For example, immersion of walnuts in a CMC solution can be prevented from oxygen contacting and walnut oxidation, thus, its shelf life increases (Baldwin, 2006).

Materials and methods

Materials

Walnut was prepared from 700 hectare Shahmirzad agro-industry, Semnan province, Iran. CMC glue with 6% moisture was purchased from agency of USK (Uğur Selüloz Kimya) company (Turkey) in Iran. CMC (average molecular weight of 41,000, practical grade) and PVA were purchased from Tetrachem agency (Iran). MMT (Cloisite Na+), as nanoclay particles were arranged from Southern Clay (USA). Glycerol was purchased from Merck company agency (Iran).

Film preparation

To produce CMC/PVA/nanoclay films, 5 g of CMC was dissolved in 200 ml distilled water with stirring on heater at 90ºC and 750 rpm for 70 minutes. PVA at 10%v of CMC was dissolved in the 60ml of distilled water by heating at 90°C for 40 minutes. MMT in concentrations of 0.5, 1, and 3% (based on the weight of CMC) dispersed in 100ml of distilled water, followed by ultrasonic in a water bath for 10 minutes. CMC and MMT solutions were then mixed under strong magnetic stirring on heater at 85ºC for 15 minutes. PVA was added into solution and stirring heating was continued for 30 minutes. Two ml of glycerol (40 ml per 100g of CMC) was inserted to the solution and stirring heating was remained at 65ºC for 20 minutes. Films were then cast into Petri dishes and dried at room temperature and relative humidity for 18 hours. The dried films with average thickness of 0.8 mm were peeled off and used for various testing.

Film characteristics

Mechanical Properties

According to the ASTM D0882-02 (Anon, 2002), mechanical test of prepared films was performance by an universal testing machine (Model Zwick, England) in laboratory conditions (temperature 25°C and 50% relative humidity). The cross-head speed was set at 60 mm/minute. The specimens were placed vertically in the grips of the testing machine. Tensile Stress (TS) and elongation at break (E) of the CMC/PVA/nanoclay composites were considered.

Water vapor permeability (WVP)

WVP of films was done according to ASTM E-996-00 (Anon, 2000). This test is based on gravimetric method. To perform this test, glass cups with an inner diameter of 3 cm and a height of 5.3 cm was used. To create 100% relative humidity, 8 ml of distilled water was poured inside each of the cups and cups were covered with the prepared film (Figure 1).

Fig 1. WVP test for a film sample

Cups were then placed within the desiccator containing silica gel (0% relative humidity). Cups were weighing every two hours until weight difference between two consecutive weighing remained constant. Due to weight changes over time, the water vapor transmission rate through the film (the amount of WVP) was calculated according to the following Eq.:

$$\textbf{WVP}= \frac{\Delta m \times d}{A \times \Delta t \times \Delta P} \quad \textbf{(1)}$$

WVP = Water vapor permeability of samples (g/m.s.Pa)
Δm = Weight loss of the cup (g)
A= Exposed surface (7.06 $\times 10^{-4}$ m^2)
Δt= Time (s)
d= Film thickness (m)
ΔP= Partial pressure difference between the inside and outside of the cup (3.179 $\times 10^{-3}$ Pa)

Oxygen permeability of films

Oxygen permeability of films was performed accordance of the work of Ou, Wang, Tang, Huang, & Jackson (2005), with slightly modified based on peroxide value of oxidation monitoring of soybean oil without antioxidants. Thus, 10 grams of this oil was poured into the laboratory cups. Cups were completely sealed with the prepared films. Sealed Cups and an unsealed cup (as a control) were placed inside an oven at 40 °C, for 12 days. The peroxide value of oil samples was determined every four days in the period of 12 days.

X-Ray Diffraction (XRD)

The XRD pattern of samples was studied using an Xray diffractometer (Model Xpert-philips, Pw 3040/60, MI, USA). The 2θ range was from 0 to 80° with a velocity of 5°/min.

Walnut Packaging

Walnuts were packed in the prepared CMC/PVA/nanoclay films. Three grams of CMC glue were then mixed with 15 ml of distilled water and were used around the film, exactly the parts that come into contact with the sealing machine. Films edges were then sealed using sealing machine. Packed walnut in the CMC/PVA films without nanoclay was considered as a control. All samples were then placed at 25 °C, room temperature and relative humidity. Figure 2 shows the walnut packed in the CMC/PVA/nanoclay films at environment conditions

Fig 2. Packaged walnut in the CMC/PVA/nanoclay films

Packaged walnut properties

Moisture content

To measure the moisture content of walnuts, the Petri dishes after drying in an oven and cooled in desiccators were weighed. A few grams of walnuts was then weighed and put in the dishes and their weight was recorded. The containers were placed in an oven at 105 °C for 24 hours. Petri dishes were then weighed again after desiccating (Anon, 2005). Moisture content was determined by calculating the weight difference according to the Eq. 2.

$$\text{Moisture content (\%)} = [(W_0 - W_t)/W_0] \times 100 \qquad (2)$$

W_0 = Samples initial mass (g)
W_t = Samples final mass (g)

Oil content

The oil content was measured using the soxhlet extraction method based on dry weight. For this purpose, the balloon device was dried in oven at 103 ± 2°C until reach to a constant weight. It was then weighed. About 15 grams of crushed walnuts were poured on a filter paper and placed on the thimble of the extractor device. The weighed balloon was filled to 2/3 of its volume by hexane as a solvent. The balloon was heated at 45 °C while there was a steady flow of cold water. By continuously touching and penetration of solvent into the thimble, the fat present in the sample dissolved. After full extraction of fat, hexane was collected from the balloon. The balloon was then heated in the oven at 103 ± 2°C until reach to a constant weight and weighed agian. The oil content of samples was calculated according to following Eq. (Hamilton & Rossell, 1986):

$$\text{Fat\%} = [(W_1 - W_2) \times 100] / W \qquad (3)$$

W_1= Initial balloon weight (g)
W_2= Final balloon weight (g)
W= Sample weight (g)

Acidity index

Acid index is the number of milligrams of potassium hydroxide required to neutralize free fatty acids contained in 1 gram of fats. To determine the amount of acid index of walnuts, 4 grams of sample were poured in the 100 ml Erlenmeyer flask and weighed. 2 ml of ethanol (ethylic alcohol) was added to it. After shaking Erlenmeyer flasks, 2 drops of phenolphthalein were added to the solution and was titrated with NaOH, 0.01 N. The first appearance of pink durable color (lasting 30 seconds) was the end point of titration. Acid value was calculated from the following Eq.:

$$\text{Acid value} = (N \times V \times 56.1)/W \qquad (4)$$

V= Consumed volume of NaOH
N= Normality of NaOH
W= Sample weight (g)

Peroxide Index

To measure the peroxide index, the oil extracted was solved in 30 ml mixture of acetic acid-chloroform (2:3 v/v) solution. 0.5 ml saturated potassium iodide was added to the mixture and shaked vigorously for one minute. 30 ml of distilled water was then added to the mix, after one minute. Thorough mixing, the solution was titrated with sodium thiosulfate 0.01 N until the bright yellow was observed. After that, 0.5 ml of 1% starch was added to the mixture to appearance dark blue color. Titration was continued to remove the blue color and get the bright color. Peroxide value was calculated according to the following Eq.:

$$\text{Peroxide value} = (V \times N \times 1000)/W \qquad (5)$$

V= Consumed thiosulfate volume

N= Normality

W= Sample weight (g)

Statistical Analysis

Data were analyzed by one-way analysis of variance (ANOVA) through Minitab 16 software. Differences with a probability value of $p < 0.05$ were considered significant.

Results and discussion

Films properties

Mechanical Properties of films

The mechanical behavior of obtained films was analyzed as well as pure CMC/PVA samples. Tensile strength (TS) of the films was improved from 11.54 to 25.01MPa, when the clay concentration increased from zero to 3% (Tajeddin & Ramedani, 2016). This finding is consistent with those of Ray, Pouliot, Bousmina, & Utracki (2004) who found the same result. The significantly increase in the TS of films as increasing of clay particles is ascribed to the uniform distribution of clay particles in the polymer structure and create interfacial bonding between the molecules and the formation of ionic bonds between clay and polymer compounds, in comparison with the pure polymer matrix. In the prepared thermoplastic starch films by reinforcing hydrophilic and hydrophobic nanoclays, the hydrophobic nanoclays increased the rigidity of the films but did not alter the TS (Müller, Laurindo, & Yamashita, 2012). Furthermore, the elongation at break of films decreased from 24.55 to 6.85% with increasing in the clay content (from 0 to 3%). This result seems to be in agreement with the results of Rhim & Ng (2007) who added some type of modified clay to achieve a reduction in the percent of elongation. The ratio of stress to strain in the linear region, elastic modulus increases from 36.2 to 184.14 MPa with increasing in the clay content.

Water vapor permeability (WVP)

WVP is one of the important properties of food packaging polymers, especially biopolymers. Packing materials should as far as possible, have at least WVP to prevent moisture exchange between environment and food (Park, Lee, Park, Cho, & Ha, 2003). The presence of moisture and water vapor is the one of the main reasons for the reactions in food spoilage. Polymers permeability is directly affected by hydrophilic or hydrophobic nature of compounds, process and production of polymer, polymer type and amount of additives, presence of pores and cracks, and the polymer structure (Vasconez, Flores, Campos, Alvarado, & Gerschenson, 2009). Adding nanoparticles to the matrix reduces the penetration of water vapor molecules and provide a winding route for the passage of water molecules by increasing the coherence between the chains and decrease pores (empty spaces).

In addition, it decreases the rate of penetration and thus reduces the WVP. However, the results of this research showed that sample content 3% nanoclay has the lowest WVP compared to the control. This result is consistent with those of Cyras, Manfredi, Ton-That, & Vazquez (2008)'s study. Reducing WVP of 3% nanoclay sample may be due to the relatively strong interactions between matrix and filler in the film containing 3% nanoclay. Muller et al. (2012) also concluded that the blending of nanoclays with thermoplastic starch modifies the WVP properties, these changes are strongly associated with the dispersion of nanoclay in the polymer matrix. In fact, the reasons for this conclusion can be attributed to be existent of more coherent structure with high cohesion and free space in the polymer that fill due to the addition of nanoparticles. In the other hand, clay fillers are less hydrophilic than that of the matrix in resulted the reduction of permeability of the films.

Oxygen permeability

Besides of the moisture permeability, impermeability to the oxygen is another important property of polymers for food packaging. Oxygen is an important factor to create the reactions such as oxidation and rancidities of lipids, contributing in the growth of microorganisms. As it is shown in Table 1, the peroxide value for a concentration of 3% nanoclay film is much lower than other treatments. It is related to the presence of clay nanolayers that create a circuitous route and subsequently prevented from the rapid diffusion of oxygen molecules. Thus, the amounts of oxygen reduce for the oxidation process and consequently decrease the peroxide index.

Table 1. Peroxide value (mEq g of peroxide /1kg oil) of prepared films and determination of its permeability to oxygen

Films / Day	CMC/PVA	CMC/PVA+ 0.5%C	CMC/PVA+ 1%C	CMC/PVA+ 3%C
0	0 ± 0.00 [a]	0 ± 0.00 [a]	0 ± 0.00 [a]	0 ± 0.00 [a]
4	1.82 ± 0.08 [a]	1.77 ± 0.02 [a]	1.63 ± 0.02 [ab]	1.42 ± 0.09 [b]
8	1.92 ± 0.04 [a]	1.86 ± 0.04 [a]	1.78 ± 0.04 [ab]	1.66 ± 0.03 [b]
12	2.9 ± 0.09 [a]	2.44 ± 0.07 [b]	2.02 ± 0.06 [c]	1.72 ± 0.04 [d]

Different letters in each column indicate the significant differences in the statistical level of 95% (α=0.05)

X-ray diffraction (XRD) analysis

The XRD results of prepared films showed that the diffraction peak is not observed for the clay that means the incorporation of CMC/PVA and nanoclay in the film is a kind of layered (Tang, 2008). This research result is in agreement with the results of Ray, Quek, Easteal, & Chen (2006). The results showed that CMC/PVA polymer chains could enter the space between the layers of clay nano-layers and mixing thoroughly distributed throughout the matrix. The average distance between particles containing clay nanocomposite films has decreased and the number of interactions between the matrix and the filler has increased.

Properties of packaged walnuts

Moisture content

The moisture content of the walnuts kernel should not be more than 6%. Packaging material should be impermeable to oxygen to maintain for more than a few months (Tajeddin, 2004).

Table 2. Moisture content (%) of packaged walnuts during 90 days

Films / Day	CMC/PVA	CMC/PVA+ 0.5%C	CMC/PVA+ 1%C	CMC/PVA+ 3%C
0	1.19 ± 0.00 [a]	1.19 ± 0.00 [a]	1.19 ± 0.00 [a]	1.19 ± 0.00 [a]
30	1.68 ±0.1 [a]	1.51 ± 0.06 [ab]	1.35 ± 0.04 [bc]	1.29 ± 0.05 [c]
60	1.97 ± 0.19 [a]	1.73 ± 0.14 [ab]	1.68 ± 0.05 [ab]	1.47 ± 0.05 [b]
90	2.12 ± 0.11 [a]	1.97 ± 0.21 [a]	1.87 ± 0.2 [a]	1.63 ± 0.19 [a]

Different letters in each column indicate the significant differences in the statistical level of 95% (α=0.05)

As it is shown in Table 2, there is a significant difference ($P < 0.05$) between the moisture of samples during 90 days storage. The highest moisture content (2.12%) is belonged to walnuts packaged in the CMC/PVA/0% nanoclay films and the lowest moisture content (1.63%) is for sample containing 3% nanoclay, at 90th day.

This result is probably related to the nanoclay role that creates a barrier against the diffusion of gases and water vapor (Tang, Alavi, & Herald, 2008; Adam & Beall, 2009).

Oil content

The oil content was measured based on dry weight. As it is shown in table 3, the percentage of walnut oil was 69.26% in the first day of storage. It decreases from 69.26 to 58.85% for CMC/PVA films to 65.86% for CMC/PVA/3% nanoclay films after 90 th days. There is not significant differences (P<0.05) between all samples content 3% nanclay during 90 days storage. This result means that the walnut oil in the packaged film contains 3% nanoclay has changed less and has remained healthy.

Table 3. Oil content of packaged walnuts during 90 days

Films / Day	CMC/PVA	CMC/PVA+ 0.5%C	CMC/PVA+ 1%C	CMC/PVA+ 3%C
0	69.26 ± 0.00 [a]	69.26 ± 0.00 [a]	69.26 ± 0.00 [a]	69.26 ± 0.00 [a]
30	63.9 ±2.47 [b]	65.31 ± 1.62 [ab]	66.96 ± 2.03 [ab]	68.69 ± 0.77 [a]
60	61.40 ± 1.68 [b]	63.32 ± 0.04 [ab]	65.07 ± 3.13 [ab]	67.36 ± 1.32 [a]
90	58.85 ± 0.55 [c]	62.37 ± 1.76 [b]	63.41 ± 1.4 [ab]	65.86 ± 1.02 [a]

Different letters in each column indicate the significant differences in the statistical level of 95% (α=0.05)

Acidity index

Acid index shows the quality, purity, freshness or musty of fats and oils. Edible fatty substances have a certain amount of free fatty acids that may be increase due to foods spoilage or hydrolysis. Percentage of nanoclay amount in the prepared films was affected significantly (P<0.05) on the acid value of walnuts (Table 4).

Table 4. Acidity index of packaged walnuts during 90 days

Films / Day	CMC/PVA	CMC/PVA+ 0.5%C	CMC/PVA+ 1%C	CMC/PVA+ 3%C
0	0.88 ± 0.00 [a]	0.88 ± 0.00 [a]	0.88 ± 0.00 [a]	0.88 ± 0.00 [a]
30	1.76 ±0.39 [a]	1.29 ± 0.32 [ab]	1.09 ± 0.22 [ab]	0.90 ± 0.17 [b]
60	1.97 ± 0.17 [a]	1.59 ± 0.35 [a]	1.38 ± 0.39 [a]	1.22 ± 0.45 [a]
90	2.81 ± 0.67 [a]	2.18 ± 0.67 [a]	1.72 ± 0.64 [a]	1.34 ± 0.57 [a]

Different letters in each column indicate the significant differences in the statistical level of 95% (α=0.05)

Peroxide Index

Peroxide value is the amount of oxygen that can be reacted with oil or fat. In fact, this value is the amount of present peroxide in oil in terms of mEq g peroxide per 1000 grams of oil. Whenever peroxide produces volatile aldehydes, ketones and fatty acids generate as well which results in the creation of undesirable odor and taste in foods content of oils and fats. Thus, the initial oxidation of oils can be evaluated using measurement of peroxide value (Chakrabarty,2003).

Table 5. Peroxide index (mEq g peroxide/1kg oil) of packaged walnuts during 90 days

Films / Day	CMC/PVA	CMC/PVA+ 0.5%C	CMC/PVA+ 1%C	CMC/PVA+ 3%C
0	[a] 0.00 ±3.33	[a] 0.00 ±3.33	[a] 0.00 ±3.33	[a] 0.00 ±3.33
30	[a] 0.83 ±5.98	[ab] 0.64 ±5.16	[ab] 0.41 ±4.46	[b] 0.34 ±3.94
60	[a] 0.68 ±7.42	[ab] 1.27 ±6.66	[ab] 0.72 ±5.63	[b] 1.09 ± 4.35
90	[a] 0.07 ±9.05	[ab] 0.67 ±8.66	[ab] 0.68 ±6.98	[b] 0.34 ±6.31

Different letters in each column indicate the significant differences in the statistical level of 95% (α=0.05)

Table 5 shows the peroxide index for different treatments within 90 days storage. The amount of peroxide is 3.33 mEq g peroxide/1kg oil at the first day. The highest amount of peroxide is observed in the control sample (CMC/PVA) with 9.05 mEq g peroxide/1kg oil at 90th day. Thus present a significant difference ($P<0.05$) compared with other samples could be due to the presence of nanoparticles.

Conclusion

Common materials used for food packaging are nonbiodegradable which do not agree with growing requests in society for sustainability and environmental safety. Therefore, numerous biopolymers have been developed to expand biodegradable food packaging materials. However, using biopolymers has been limited due to their poor mechanical and barrier properties. These properties can be improved usage reinforcing nanomaterials or fillers to create composites. This article stated how a type of biopolymer and nano-sized filler employed to form bio-nanocomposite film and packaged for walnut kernels as a case study. Thus, nanocomposite films were obtained from CMC/PVA as a matrix and nanocaly particles as a reinforcing material in this research. XRD results showed that nano-clay layers are distributed throughout the matrix and films containing 3% nanoclay have proper mixing. With increasing nanoclay loading in the specimens, the tensile strength and elongation percent increase and decrease, respectively. Water vapor permeability of samples decreased significantly by increasing of nanoclay content in the films. Reducing peroxide index of samples was a sign of decreasing of oxygen permeability of films due to the presence of nanoclay in the composites. The prepared CMC/PVA/nanoclay films were then used for walnut packaging. It was found that the amount of oil in the sample with packaging containing 3% nanoclay was declined to 3.4% within 90 days storage, while it was 10.41% for packaged samples inside the CMC/PVA films. Moisture content of packaged walnuts in the films containing 3%nanclay decreased 0.44% compared to packaged samples inside the CMC/PVA films at the end of storage period. On the whole, the results of various tests on prepared films as well as packaged walnut in these films recommend that using natural nano polymers are suitable for food packaging to overcome severe ecological problems associated with petrochemical-based packaging materials. For the reason that, the prepared film containing 3%nanoclay was the most significant feature of the films as well as it preserved very well properties of walnuts. However, it is suggested that more research should be done on the use of higher levels of nanoclays in the CMC nanocomposite films and confirmed its optimum. Furthermore, the effect of nanoclay particles migrate into the packaged product and its safety be monitored.

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