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ORIGINAL PAPER

Preparation and characterization of a bio-nano-polymer film for walnut packaging

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ABSTRACT

To apply the nanomaterial as a component in the packaging material structure, in this research, the carboxymethyl cellulose (CMC)/polyvinyl alcohol (PVA) films were prepared with three levels of nanoclay particles (0.5, 1 and 3%) using solution casting evaporation method. The effect of incorporation of nanoclay on mechanical, water vapor permeability and oxygen barrier properties of CMC/PVA-based film was investigated. The best result was obtained for the nanocomposite film containing 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 for the nanocomposite film with 3% nanoclay in terms of oil content, moisture content, acidity and peroxide indexes of walnut. According to the overall results, the CMC/PVA film reinforced with 3% nanoclay could be presented as a good candidate for the development of high barrier food packaging material against the diffusion of water vapor and oxygen. **Polyolefins J (2019) 6: 159-167**

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. The use of natural polymers in numerous forms is increasing in food packaging applications. Some weak properties of natural polymers may be improved through nanotechnology appliances [1-2]. Small amount of organo modified montmorillonite (MMT), commonly called nanoclay, has considerably improved the mechanical characteristics of pure polymers in both academic and industrial sectors [3]. The use of MMT has been very much considered because of its natural resources, high modulus, and high performance in enhancing mechanical properties. These layered materi-

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als exist in the form of the cumulative bonded with physical forces, accordingly that they can be exfoliated even to single nanolayers [4]. Natural MMT is hydrophilic and miscible with hydrophilic polymers [5-6]. Development of the polymer/clay nanocomposites is one of the revolutionary steps in the polymers technology [7-8]. Some researchers have proved potential of organoclays for starch-based polymer nanocomposites to improve the long-term mechanical properties over the unfilled formulations [8-10]. For example, physicochemical properties of starch/CMC/nanoclay films were studied by Almasi et al. [11]. Their study results showed that the MMT addition at content of 7% (w/w), caused to increase the ultimate tensile strength by more than threefold in comparison to that of 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, and 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 [12-14]. 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 [15]. 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 [16-18].

The present paper states a number of CMC/PVA/nanoclay films characteristics. Furthermore, some properties of walnuts packaged 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 [10]. Most varieties of walnuts have almost 54.2 to 72.2% (w/w) oil [20]. Nuts such as walnut have a suitable taste when they keep in the presence of low concentrations of oxygen [21]. For example, immersion of walnut in a CMC solution causes to prevent walnut from oxygen contacting and oxidation, thus, its shelf life increases [22].

EXPERIMENTAL

Materials

Walnut was prepared from 700 hectares Shahmirzad agro-industry, Semnan province, Iran. CMC glue with 6% moisture and 0.65 degree of substitution (DS) was purchased from agency of USK 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 with 4-9% moisture and 1.17 nanometer D001 was obtained from Southern Clay (USA). Glycerol was purchased from Merck Company agency (Iran).

Film preparation

Preparation of film is already specified [8, 14]. This method was modified for the conditions of this work. Thus, to produce CMC/PVA/nanoclay films, 5 g of CMC was dissolved in 200 ml distilled water with stirring on heater at 90°C and 750 rpm for 70 minutes. PVA at 10%v of CMC solution 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) was 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 85°C for 15 minutes. PVA was added into solution and stirring and heating was continued for 30 minutes. Two ml of glycerol (40 ml per 100g of CMC) was inserted to the solution and stirring and heating at 65°C was continued 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 0.8mm were peeled off and used for various testing.

Film characteristics

Mechanical Properties

According to ASTM D0882-02 [23], the mechanical test of prepared films was performed by a 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 films were considered.

Water vapor permeability (WVP)

WVP test of CMC/PVA/nanoclay films was done according to ASTM E-996-00 [24]. 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 were 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). Cups were then placed within the desiccator containing silica gel (0% relative humidity). Cups were weighed 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 Equation 1.

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

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

Oxygen permeability of films

The oxygen permeability of prepared films was carried out based on the amount of oxygen transmission from outside of films to the inside of the laboratory cups containing soybean oil. The amount of oxygen transmission was determined based on peroxide value of oil [25]. The higher peroxide value of oil means the higher oxygen transmission through the film. Thus, 10 grams of soybean oil were poured into the laboratory cups. Cups were completely sealed with the different treatments of prepared CMC/PVA/nanoclay films. Sufficient number of sealed cups and an unsealed cup (as a control) were placed inside an oven at 40°C, for 12 days. The peroxide value of soybean oil of cups was determined every four days in a period of 12 days based on standard method of Irannian National Standardization Organization [26].

Figure 1. WVP test for a film sample.

X-Ray Diffraction (XRD)

The XRD pattern of samples was studied using an X-ray 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 films, exactly in the parts that come into contact with the sealing machine. Films edges were then sealed using sealing machine. Walnut packed in CMC/PVA films without nanoclay was considered as a control sample. All samples were then placed at 25 °C, room temperature and relative humidity. Figure 2 shows the walnut packed in CMC/PVA/nanoclay films at environment conditions.

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

Figure 2. Walnut packaged in CMC/PVA/nanoclay films.

again after desiccating [27]. Moisture content was determined using Equation 2.

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

W_0 = Sample initial mass (g)
W_t = Sample 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 was 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 again. The oil content of samples was calculated according to Equation 3 [28].

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

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

Acid index
Acid index is the number of milligrams of potassium (sodium) 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 using Equation 4 [29].

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

V= Consumed volume of NaOH (ml)
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 Equation 5 [26].

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

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 the films and pure CMC/PVA samples was analyzed. Tensile strength (TS) of the films was improved from 11.54 to 25.01MPa, when the clay concentration was increased from zero to 3% [30]. This finding is consistent with those of Ray et al. (2004) [31] 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 creation of interfacial bonding between the molecules and the formation of ionic bonds between the clay and polymer compounds, in comparison with the pure polymer matrix. In the thermoplastic starch films prepared by reinforcing hydrophilic and hydrophobic nanoclays, the hydrophobic nanoclays increased the rigidity of the films but did not alter the TS [32]. Furthermore, the elongation-at-break of films decreased from 24.55 to 6.85% with increasing the clay content from 0 to 3%. This result seems to be in agreement with the re-

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

Day \ Films	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 ($P < 0.05$).

sults of Rhim and Ng (2007) [33] 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 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 least WVP to prevent moisture exchange between environment and food [5]. 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 [34]. Adding nanoparticles to the matrix reduces the penetration of water vapor molecules and provides a winding route for the passage of water molecules by increasing the coherence between the chains and decreasing pores (empty spaces).

In addition, it decreases the rate of penetration and thus reduces the WVP. However, the results of this research showed that the sample with 3% nanoclay had the lowest WVP. This result is consistent with those of Cyras et al. (2008)'s study [10]. The lowest WVP in 3% nanoclay sample may be due to the relatively strong interactions between the 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, and these changes are strongly associated with the dispersion of nanoclay in the polymer matrix [32]. In fact, the reasons for this conclusion can be attributed to existence of more coherent structure with high cohesion and free space in the polymer that is filled due to the addition of nanoparticles. In the other hand, clay fillers are less hydrophilic than the matrix resulting in 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 rancidity of lipids, contributing in the growth of microorganisms, etc. As it is shown in Table 1, the peroxide value (amount of active oxygen) 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 the peroxide index decreases.

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 [35]. This result is in agreement with the results of Ray et al. (2006) [36]. The results showed that CMC/PVA polymer chains could enter the space between the layers of nanoclay and distribute 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. Figures 3 and 4 show the XRD pattern for CMC/PVA films with 0% and 3% nanoclay.

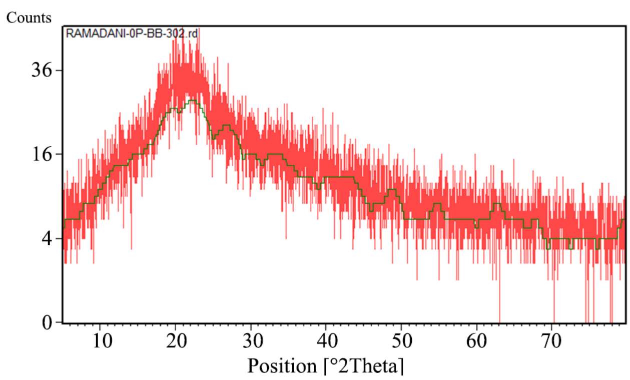

Figure 3. XRD pattern of CMC/PVA/0%nanoclay film.

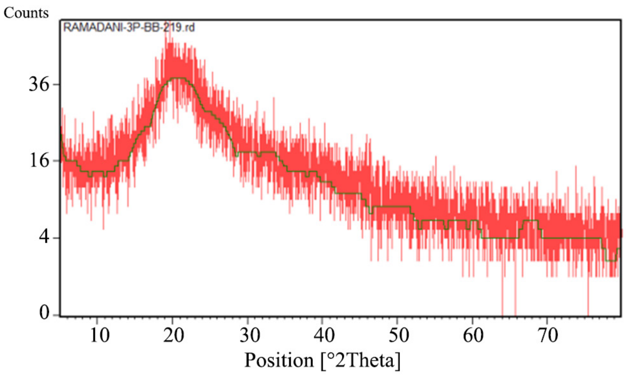

Figure 4. XRD pattern of CMC/PVA/3%nanoclay film.

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 [37]. 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 [38-39].

Oil content

The oil content was measured using the soxhlet extraction method based on dry weight. As it is shown in Table 3, the percentage of walnut oil is 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 days. There are not significant differences (P<0.05) between all samples containing 3%nanclay during 90 days storage. This result means that the walnut oil in the packaged film containing 3%nanoclay has changed less and has remained healthy.

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. However, as it can be seen in Table 4, the nanoclay percentage in the prepared films has great effect (P<0.05) on the acid value of walnuts.

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 are generated as well which results in the creation of undesirable odor and taste in foods containing oils and fats. Thus, the initial oxidation of oils can be evaluated using measurement of peroxide value [40]. 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. This presents a significant difference (P<0.05) com-

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 (P < 0.05).

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 (P < 0.05).

Table 4. Acidity index of packaged walnuts during 90 days.

Day \ Films	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 (P < 0.05).

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

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

Different letters in each column indicate the significant differences (P < 0.05).

pared with other samples that could be due to the presence of nanoparticles.

CONCLUSION AND SUGGESTIONS

This research is carried out to show how a type of biopolymer and nano-sized filler can be employed to form bio-nanocomposite film for packaging of walnut kernels. Thus, nanocomposite films were obtained from CMC/PVA as a matrix and nanocaly particles as a reinforcing material. The XRD results showed that nano-clay platelets are distributed throughout the matrix and films containing 3% nanoclay have the best performance. With increasing nanoclay loading in the specimens, the tensile strength and elongation percent increased and decreased, respectively. Water vapor permeability of samples decreased significantly by increasing nanoclay content in the films. Reducing peroxide index of samples was a sign of decreasing 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 samples packaged inside the CMC/PVA films. Moisture content of walnuts packaged in the films with 3% nanoclay decreased 0.44% compared to the samples packaged 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 walnut packaged in these films recommend that natural nano polymers are suitable for food packaging to overcome severe ecological problems associated with petrochemical-based packaging materials. The film with 3% nanoclay showed the best characteristics among other films tested, for this reason it could preserve the properties of walnuts well. However, it is felt that more research should be conducted on the use of higher levels of nanoclays in the CMC nanocomposite films. Furthermore, the influence of nanoclay particles migrated into the packaged product and its safety should be investigated.

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