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Characterization of a new biodegradable edible film based on semolina loaded with nano kaolin

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Abstract

Biodegradable packaging, such as edible coatings and films, is widely used because it is free from synthetic substances and does not lead to environment pollution. Therefore, this industry is continuously growing. This study aimed to prepare and characterize biodegradable films loaded with nano kaolin. Semolina protein films were prepared and plasticized with sorbitol/glycerol by the casting method. Nano kaolin with 0%, 1%, 2%, 3%, 4% and 5% (w/w) was added to the films before casting them. The films were dried at controlled conditions. The effects of the addition of nanoparticles were measured on water absorption capacity (WAC), density, ultraviolet transmittance, heat sealability, and film morphology. Results showed that the WAC and density of the films decreased by increasing the nano kaolin concentration. By contrast, the seal strength for the semolina film was increased by incorporating a low percentage of nano kaolin. The X-ray diffraction curves of the semolina film incorporated with kaolin exhibited broad reflection, thus indicating that the kaolin nanosize matches the transmission electron microscopy images. In summary, nano kaolin incorporation enhanced the physicochemical properties and heat sealability of semolina films, thereby indicating the potential application of these bionanocomposites to food-product packaging.

Introduction

Numerous food studies aim to discover and produce natural-based biopolymers that can be used in food packaging (Sorrentino *et al*., 2007; Ghanbarzadeh and Almasi, 2011) to prevent the pollution caused by packaging materials produced from petroleum derivatives, prevent the problems associated with different methods of decontamination, such as burying, burning, and recycling (Tharanathan, 2003; Ahmad *et al*., 2016), and avoid the hazards related to petroleum-derived raw materials used for packaging. These challenges and concerns are nonexistent in biopolymers, which are naturally biodegradable. Hence, the development of biodegradable materials is important to our society, and research on biodegradable materials with controlled properties presents a compelling topic for any food specialist (Gonzalez-Gutierrez *et al*., 2010; Ghasemlou *et al*., 2011).

Proteins, which are biopolymer materials known to form transparent films that can act as excellent oxygen barriers and provide certain mechanical properties, have received considerable attention for their potential as biodegradable films (Sothornvit *et al*., 2009). Protein films are renewable, economical, readily available, biodegradable, and highly safe. These proteins possess good film-forming properties and unique nutritional and/or health-protective functions (Zhang *et al*., 2005). Moreover, the unique capability of proteins to form networks and induce plasticity and elasticity is beneficial in preparing biopolymer-based packaging materials (Voon *et al*., 2012).

Most biodegradable polymers exhibit excellent properties that are comparable with those of petroleum-based plastics, but their applications are limited by certain poor properties, such as brittleness and high permeability. Thus, researchers have started to modify and enhance biopolymer properties. Nanotechnology is one of the most recent important technological advances in the field. The addition of low amounts of nanoparticles to biopolymers improves their mechanical, thermal, and barrier properties, thus allowing the use of polymers to various applications, particularly in food packaging (Rhim *et al*., 2005; Hedenqvist *et al*., 2006).

Nanofillers possess large specific surface areas

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and high surface energy, which engender strong interfacial interactions between polymer bonds and nanofillers, thereby significantly improving polymer properties (Kovacevic *et al*., 2008). Nanoclay is extensively used as functional filler in protein films because of their clay layer, which improves film properties (Sothornvit *et al.*, 2009). Kaolin nanoclay, a type of hydrated aluminosilicate, is used in a considerable number of industries because of its relatively low cost, availability, abundance, environmental friendliness, and versatility (Schwartz and Goodman, 1982; Ma and Bruckard, 2010). Furthermore, improvements in thermal stability and water susceptibility are observed in thermoplastic amylose/kaolin composites (Huang *et al.*, 2006).

Among the different types of proteins used as biodegradable materials in packaging (Khwaldia *et al.*, 2010), wheat is a valuable candidate for packaging applications because of its low price, biodegradability, renewability, good film-forming capability, and adhesive/cohesive properties (Türe *et al.*, 2013). Semolina flour is a type of wheat that has the high gluten content, which improves the nutritional properties of edible films (Quaglia, 1998; Jafarzadeh *et al*., 2015). Semolina is a rigid, translucent, light-colored grain with antioxidant activities. Semolina extracts can suppress radical-induced liposome lipid peroxidation and radical cation scavenging activity (Zielinski and Kozlowska, 2000). Semolina has excellent properties as edible film, and nano kaolin can reinforce its physicochemical properties; however, the heat sealability of semolina film has not been analyzed. The application of nano kaolin to semolina film is hypothesized to improve the sealability, water susceptibility, and morphology of the film. The proposed film can be utilized in the food-packaging industry, specifically in cheese packaging, because of its good antioxidant property. In the current study, nano kaolin was used as a filler to prepare semolina bionanocomposite films.

Materials and Methods

Materials

Semolina flour (14.2% protein, 18.5% gluten) was obtained from a local market in Tehran, Iran, and stored in a dry and cool place until use. Liquid sorbitol and glycerol were purchased from Liang Traco (Penang, Malaysia). Magnesium nitrate for humidity control was obtained from Sigma–Aldrich (Kuala Lumpur, Malaysia), and nano kaolin was obtained from Sigma Chemical Co. (St. Louis, MO, USA).

Preparation of nanobiocomposite films

Four grams of semolina flour was dispersed in 80 ml of distilled water (according to water or water/ethanol) at room temperature by simple magnetic stirring, and the pH of the dispersion was adjusted to 8 by using 1M of NaOH. Different percentages of kaolin powder (1%, 2%, 3%, 4% and 5%; w/w total solid) plus 2 g of a sorbitol and glycerol (3:1) mixture (previously reported by Abdorreza *et al*., 2011)were likewise dispersed in 20 ml of distilled water for 30 min, followed by sonication in an ultrasonic bath (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil).Dispersions of semolina flour and kaolin–plasticizer were then mixed by stirring for 1 h at a constant temperature of 90°C to allow gelatinization. Upon gelatinization completion, the solution was cooled to 40°C to 45°C. A portion (90 g) of each suspension was cast on Perspex plates and fitted with rims to yield a (16 × 16) cm^2 film-forming area. The films were then dried in an oven at 40°C for 24 h, peeled off, and kept at 25°C and 58% relative humidity (RH) until testing. The control films were prepared with the same plasticizers but without the addition of nanoparticles.

Determination of film thickness

The films were equilibrated at 25°C and 58% RH in a humidity chamber for two days. The thickness of the nanocomposite films was determined as the mean of measurements made at five random points. Measurements were obtained using a micrometer (Model No. 2046-08; Mitutoyo Tokyo, Japan).

Film density

Films with 2 cm × 3 cm dimensions were conditioned at 55% ± 3% RH and room temperature for 48 h. Film thickness was measured by averaging the five measurements for each of the three replicates. Nanofilm density is the ratio of film mass to its volume (the product of area and thickness).

Water absorption capacity

The water absorption capacity (WAC) of the bionanocomposite films was tested using a method modified by Kiatkamjornwong *et al.* (2000). Pieces of bionanocomposite films (2 cm × 3 cm) were first dehydrated over phosphorous pentoxide (0% RH) for a few days, and the dried films were placed into100 mL of deionized water and allowed to stand for 30 min for swelling. The swollen films were filtered, and the drained films were weighed. The amount of water retained by the films per dried weight of the films was calculated as WAC

Table1.Density property of semolina nanocomposite films

Nano kaolin(g/g dried semolina)	Density (g/cm3)
0.00	1.345±0.115[a]
0.01	1.290±0.095[a]
0.02	1.286±0.082[a]
0.03	1.248±0.009[a]
0.04	1.248±0.065[a]
0.05	1.057±0.095[b]

Different letters in each column represent significant difference among semolina films at the 5% level of probability

Heat seal strength measurement

The heatsealability of bionanocomposite films were determined according to the ASTM F-88-09 standard by using a TA.XT2 texture analyzer equipped with Texture Exponent 32 software V.4.0.5.0.

Optical properties

By using a UV-vis spectrophotometer model UV-1650PC (Shimadzu, Tokyo, Japan), we studied the transmittance of triplicate film samples at 200 and 800 nm. The bionanocomposite films were cut (60 mm long and 40 mm width) and directly placed in a spectrophotometer test cell. An empty glass plate was used as the reference.

Film morphology

A Siemens D5000 x-ray diffractometer was used to investigate the crystallinity of the semolina nanocomposite. Transmission electron microscopy (TEM; Phillips CM12) and energy-dispersive x-ray spectroscopy (EDX) measurement were conducted under15 kV incident electron energy.

Statistical analysis

ANOVA and Tukey's post hoc tests were used to evaluate the properties of semolina films at the 5% significance level. Statistical analysis was conducted using SPSS version 22.0.

Results and Discussion

Density and thickness

The film density decreased by increasing the percentage of nano kaolin and showed small variations (Table 1). The reduction in density might be attributed to the enhanced thickness (and volume) in relation to the increased nano kaolin content. The thickness of the films increased with increasing nano kaolin concentration from 0.14±0.02 to 0.17±0.005.

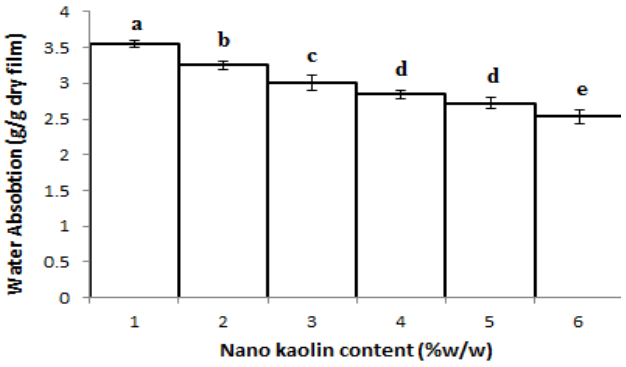

Figure1. WAC of semolina films and effects of nanokaolin on the WAC of the films in water at 25°C. The values are mean (n = 5) ± SD, and the bars with different letters are significantly different at a 5% level of probability

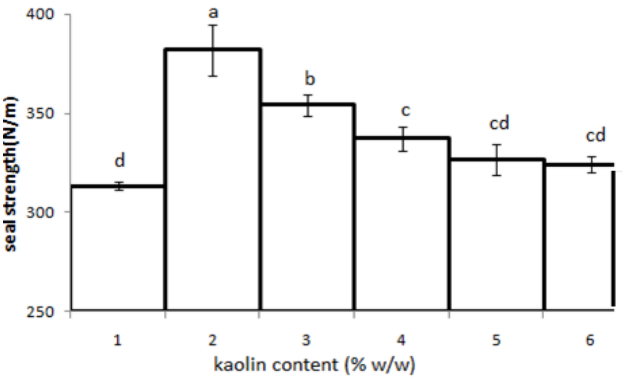

Figure 2. Effects of nanokaolin contents on the heat sealability of semolina nanocomposite films, the bars show mean (n=5) ± SD. The different letters on the bars represent the significant difference at a 5% level of probability among films

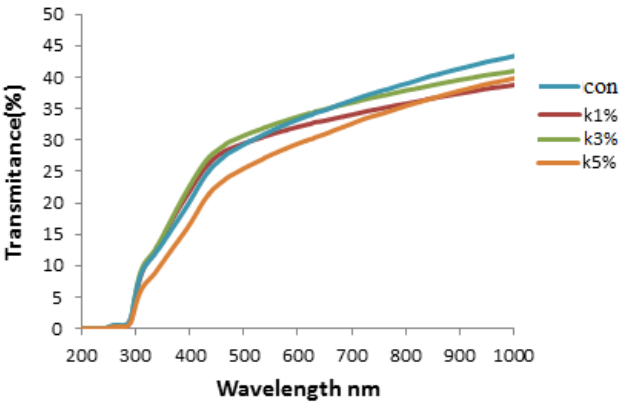

Figure 3.UV-vistransmittance spectra for semolina nanocomposite films

WAC

The WAC of the nano kaolin biocomposite films is given in Figure1. Introducing nano kaolin to semolina matrix significantly decreased the WAC of

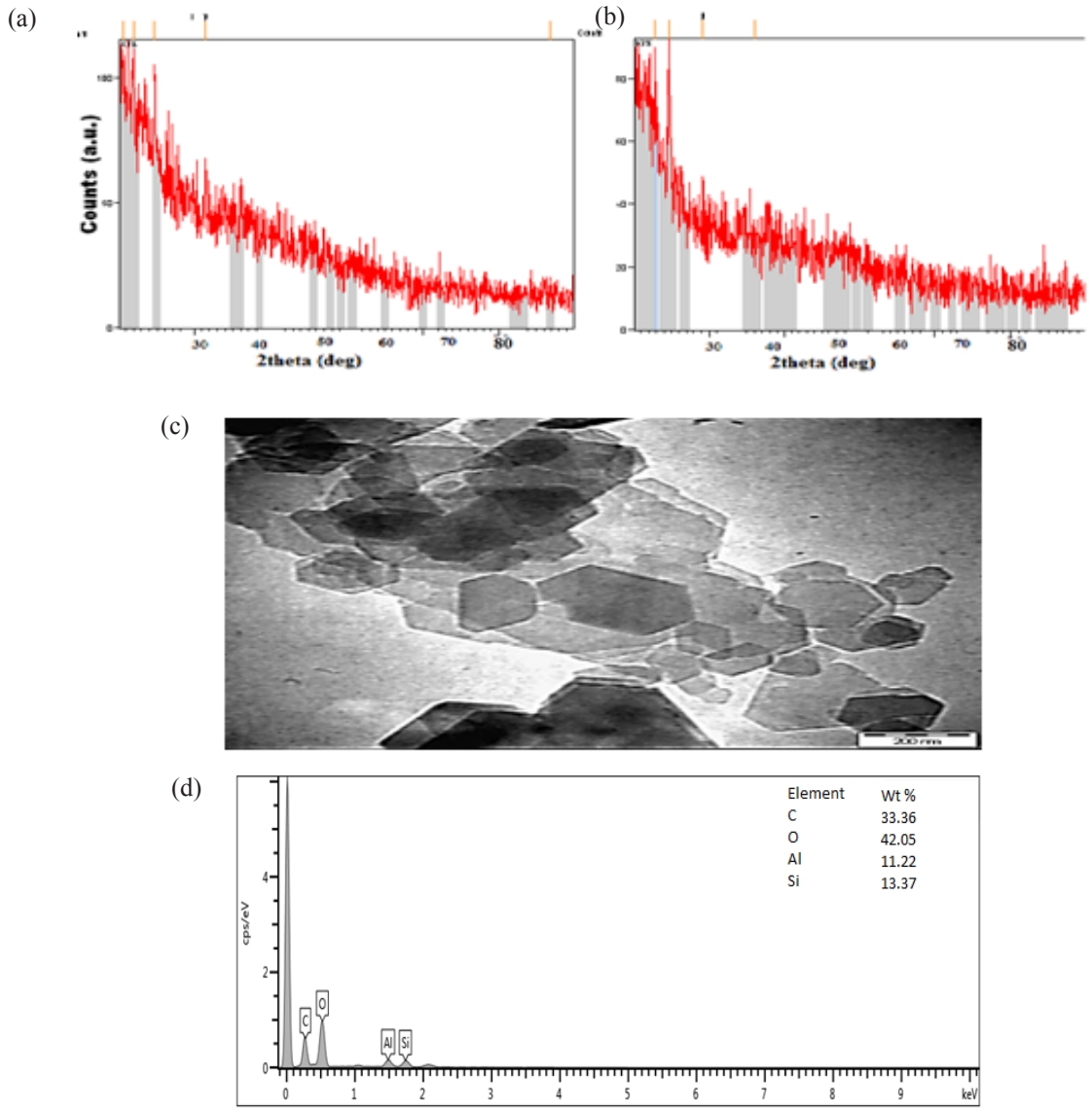

Figure 4. (a) XRD semolina film incorporation with 1% kaolin, (b) XRD semolina film incorporation with 4% kaolin, (c) TEM micrograph nanokaolin, and (d) EDX semolina incorporation with kaolin

the semolina film. This result might be related to the interactions between kaolin and semolina in the film structure. The final experimental results demonstrated that when the nanoparticle content of semolina films was high, considerable hydrogen bonds formed between the kaolin and matrix components (Tunc *et al*., 2010). Free water molecules do not interact as strongly with nanocomposite films as with composite films alone. This result is consistent with the results obtained by other researchers on nanobiocomposites (Tunç *et al*., 2010; Müller *et al.*, 2011).

Heat seal strength measurement

Heat sealability is an important factor in the use of films for packaging purposes. The final results on the seal strengths of semolina-based nanocomposite films prepared are revealed in Figure 2. The seal strength for semolina film was increased by incorporating a low percentage of nano kaolin. This enhancement was probably related to the improvement of hydrogen and other bonds on the surface by nano kaolin (Kim and Ustunol, 2001). However, the sealability of the films decreased with the addition of a great percentage of kaolin, which was likely caused by the reduction in moisture content and the flexibility of the films (Abdorreza *et al*., 2011).

Optical properties

These properties of the biopolymer films and their nanocomposite films were studied by measuring transmittance using a UV-vis spectrophotometer. The UV region was classified into three zones as follows: UVC (100 nm to 280 nm), UVB (280 nm to 320 nm), and UVA (320 nm to 400 nm) (Jafarzadeh *et al.,* 2017). UV transmittance was studied as a function of filler loading; thus, biocomposites were prepared

with kaolin contents ranging from 1wt.-% to 5 wt.-%. The results are shown in Figure 3.

Figure 3 indicates that the UV-vis transmission spectra at 250 nm to 300 nm wavelength were reduced by adding 5 wt.-% of nano kaolin to biopolyesters, whereas the biocomposite with 1, 2, and 3 wt.-% of kaolin contents showed a reduction in transmittance to approximately 0%. As a result, the decrease in the UV-vis transmittance was efficient for kaolin contents of 5 wt.-%.

Film morphology

The x-ray diffraction (XRD) method uses the scattered intensity of an x-ray beam on the sample to reveal information about the crystallographic structure, chemical composition, and physical properties of the material studied. This technique is widely used in material characterization because it is nondestructive and does not need elaborated sample preparations (Espitia *et al*., 2012). The films loaded with 1% and 4% of nano kaolin were analyzed using the XRD technique, as shown in Figures 4(a) and (b), respectively. The results showed the main characteristic peaks of kaolin nanoparticles (observed at 2 = 22.86°; 2 = 24.76°; 2 = 29.19°; 2 = 36.02°).The intensity of the main characteristic peaks of kaolin became high as the concentration of kaolin nanoparticles in matrix increased.

From the XRD patterns of nanocomposite films, the addition of nano kaolin affected the crystallinity of the matrix. In this way, the addition of kaolin nanoparticles resulted in sharp and strong peaks of the matrix, thus indicating that the crystallinity structure of films increased. The TEM images of kaolin nanoparticles are presented in Figure 4(c). The morphology of kaolin was hexagonal, and its size was narrowly distributed between 100 and 200 nm diameter. Figure 4(d) shows the EDX of the nano kaolin added to the biopolymer.

Conclusion

We incorporated nano kaolin into semolina film to manufacture bionanocomposites. The solution-casting method was used to prepare films, and the resulting films were characterized. The incorporation of nanoparticles enhanced the heat sealability properties of films made from semolina. The WAC of the films significantly decreased with the addition of nanoparticles and because of the improved water susceptibility property of the bionanocomposite films. The XRD patterns of the nanocomposite films revealed that nano kaolin affected the matrix crystallinity. The addition of nano kaolin to the matrix indicated great crystallinity and sharp and strong peaks of the nanocomposite films. These findings showed that under strict regulation, bionanocomposites based on nano kaolin may present potential applications in food-packaging industries.

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