Fabrication and characterization of novel semolina-based antimicrobial films derived from the combination of ZnO nanorods and nanokaolin

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Abstract This study aimed to provide novel biopolymer-based antimicrobial films as food packaging that may assist in reducing environmental pollution caused by the accumulation of synthetic food packaging. The blend of ZnO nanorods (ZnO-nr) and nanokaolin in different ratios (1:4, 2:3, 3:2 and 4:1) was incorporated into semolina, and nanocomposite films were prepared using solvent casting. The resulting films were characterized through field-emission scanning electron microscopy and X-ray diffraction. The mechanical, optical, physical, and antimicrobial

properties of the films were also analyzed. The water vapor permeability of the films decreased with increasing ZnO-nr percentage, but their tensile strength and modulus of elasticity increased with increasing nanokaolin percentage. The UV transmittance of the semolina films were greatly influenced by an increase in the amount of ZnO-nr. The addition of ZnO-nr: nanokaolin at all ratios (except 1:4) into semolina reduced UV transmission to almost 0%. Furthermore, the ZnO-nr/nanokaolin/semolina films exhibited a strong antimicrobial activity against *Staphylococcus aureus*. These properties suggest that the combination of ZnO-nr and nanokaolin are potential fillers in semolina-based films to be used as active packaging for food and pharmaceuticals.

Keywords Biodegradable packaging · Zinc oxide nano rod · Nano kaolin · UV transmittance · Antimicrobial activity

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Introduction

In order to fulfill customers' need as well as the requirements of the industry, food packaging has been developed based on such biodegradable polymers as structural polysaccharides, lipids, proteins, gums, polyesters and their complexes. Being safe for consumers, minimal environmental impact has been considered for this type of food packaging. As reported by Siracusa et al. (2008), the demand of consumers for a safe and environment friendly material to be used in food packaging has led to the combination of biopolymer and functional nanostructures as a potentially encouraging substitute to the conventional plastics. Such functional features of biopolymers as their mechanical properties and hindrance against oxygen, light

and water vapor plays the main role in their selection in food packaging uses. These properties are determinant since oxygen, light and water vapor exert adverse influences on the quality and life of the food and the shelf used (Turhan and Sahbaz 2004). As one of the significantly favored elements in edible films' development, protein-based films have been encouraging. This is attributed to their nutritive values (Gennadios et al. 2004), their hindrance against oxygen, as well as their mechanical properties (Sothornvit et al. 2009).

According to Khwaldia et al. (2010), concerning the use of biodegradable materials in food packaging, this industry has exploited a diverse types of proteins. Having such favorable properties as being cheap, renewable, biodegradable, adhesive/cohesive as well as favorable film forming have turned the wheat protein to become among the valuable candidate in food packaging purposes (Türe et al. 2013). As a type of wheat, semolina flour is characterized by having a high gluten content of various flours (Quaglia 1988) through the usage of which the edible films' nutritional features can be improved. As mentioned by Onyeneho and Hettiarachchy (1992), semolina grains possess such properties as being translucent, extremely hard, and light-colored. In addition, semolina extracts exert antioxidant activities by suppressing radical-induced liposome lipid peroxidation and scavenging radical cations.

Nanobiocomposites are promising for the development of new and innovative materials, such as films, because they enhance the ductile properties of biopolymers in applications requiring flexibility. As maintained by Cushen et al. (2012), regarding food packaging purposes, the health, quality of the food stuff as well as wealth can potentially be enhanced by the application of nanotechnologies. Moreover, the concern over the impact of the produced residues on the environment would also be diminished to a great extent. Although there has been encouraging results, nanobiocomposites with adequate properties for food packaging remain to be developed (Jiménez and Ruseckaite 2012). Antimicrobial materials for food packaging are currently a research hotspot (Martínez-Abad et al. 2012). Recent studies have explored the applications of ZnO in the food packaging industry because of the potent and broad-spectrum antimicrobial properties (Li et al. 2009; Espitia et al. 2013; Arfat et al. 2015), large surface to volume ratio, chemically alterable physical property, increased surface reactivity, and mechanical and electrical properties of this compound (Sharon et al. 2010). In addition, ZnO is a heat stable and generally recorded as safe substance approved by the Food and Drug Administration (FDA 2011). Regarding such applications as pharmaceutical materials, pigments, coating materials and cosmetics, ZnO has been extensively utilized as useful filler in UV absorbers (Kumar and Singh 2008;

Li et al. 2009). As maintained by Shahrom and Abdullah (2006), the important factors in nanoparticles' basic properties include their morphology, size, composition, shape and the crystallinity of the particles. Additionally, there is also an UV absorption ability exhibited by ZnO nanorods (ZnO-nr) (Lin et al. 2009).

Due to the clay layer of nano clays, they have also been commonly used as practical and helpful filler in protein films. This layer results in the decrease in water permeability (WVP) as well as the increase of the film's strength (Sothornvit et al. 2009). As a hydrated aluminosilicate, several industries have applied the natural mineral kolin nanoclay. This is due to their such favorable properties as their low cost, wide range of application, availability, abundance and being environmentally friendly (Ma and Bruckard 2010; Jafarzadeh et al. 2016). Thermoplastic amylose/kaolin composites display high thermal stability, as well as mechanical and heat-sealing properties (Su et al. 2010) given their inherent properties, ZnO-nr and nanokaolin have been considered as reinforcements in biopolymers.

The current research aimed to produce and characterize high-performance semolina-based nanobiocomposites of ZnO-nr and nanokaolin for food packaging applications. Semolina films incorporated with the combination of ZnO-nr and nanokaolin were evaluated for such properties as their barrier, mechanical, physicochemical, and microbial characteristics.

Materials and methods

Materials

Semolina flour with the 18.5% gluten and 14.2% protein was used in the study. It was purchased from Tehran, Iran from the local market and was put in a cool dry storage until the test. The liquid sorbitol of the study was purchased from Penang, Malaysia, from the LiangtracoSdn. Bhd. Moreover, the food-grade glycerol was also obtained from Penang, Malaysia, from the SIM Company Sdn. The magnesium nitrate used to control humidity was purchased from Malaysia, Kuala Lumpur, from Sigma-Aldrich. The process of catalyst-free combust-oxidized mesh expressed by Shahrom and Abdullah (2007) was applied to synthesize ZnO-nr. Lastly, the nanokaolin used in the experiment was purchased from the USA, from the sigma Chemical Co. (St. Louis, MO).

Preparation of nanobiocomposite films

Keeping at the room temperature, semolina flour (4 g) was disseminated in distilled water (80 mL, based on water) by

the magnetic stirring. The dispersion pH was also attuned to 8 with 1 M NaOH to increase the protein solubilisation. Similarly, 20 mL of distilled water was used to disperse various ratios of the combination of ZnO-nr and nanokaolin powder (1:4, 4:1, 3:2, and 2:3, w/w of the total solid) and 2 g mixture of glycerol and sorbitol (1:3) for 30 min. Using an ultrasonic bath, the dispersion was followed by the sonication of the materials (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil). The dispersions obtained (semolina flour, ZnO-nr, nanokolin and plasticizer) were mingled. This was followed by stirring them at 90 °C for 1 h. For the preparation of nanocomposite films, the homogenous mixtures were poured into plates. At the room temperature, the solvents were then let to evaporate for 24 h.

The humidity chamber was kept in a controlled condition of the temperature and relative humidity of 25 °C and 58% respectively and the films were dried in the chamber under the mentioned conditions. A control film was also provided under the similar condition. However, no nanoparticles were added to the control film. The dried nanocomposite films were first peeled and then kept for the test at the temperature and relative humidity of 25 °C and 58% respectively.

Characterization studies

Determination of film thickness

The films were equilibrated at 25 °C and 58% RH in a humidity chamber for 2 days. The thickness of the nanocomposite films was determined as the mean of measurements obtained at five random points. Measurements were obtained using a micrometer (Model No. 2046-08; Mitutoyo Tokyo, Japan).

WVP

WVP tests for the nanobiocomposite films were performed gravimetrically in accordance with the ASTM Standard Method E96-05 (ASTM 2005).

Mechanical properties

At the temperature and RH of 25 °C and 58% respectively for 48 h, the minimum number of seven films of 10 cm × 2.5 cm were placed in an environment test chamber (SangWoo Co., Korea). The films' TS (MPa), elongation at break [EB (%)] and the Young's modulus were measured through the usage of a texture analyzer (TA-XT2, Stable Micro System, Surrey, UK). These measurements were in accordance with the ASTM

Standard Method D882-10 (ASTM 2010). The crosshead speed and the initial grip separation were set to 0.5 mm/s and 50 mm respectively.

Optical properties

We studied the transmittance and absorbance of the films (in triplicate) at 200 and 800 nm by using the UV–Vis spectrophotometer model UV-1650PC (Shimadzu, Tokyo, Japan). Biofilms were sectioned (60 mm × 4 mm) and directly placed in a spectrophotometer test cell. An empty glass plate served as the reference.

In consideration of the latest consumer promotions and the complexities created by the demands for food products, new techniques that ensure the quality of packaging are necessary.

Film morphology

In order to do the field-emission scanning electron microscopy, gold was used to vacuum coat the samples of conditioned nanobiocomposite. A Leo Supra VP field-emission scanning electron microscope was employed for the visualization of the nanocomposite films' surface microstructure (Carl-Zeiss. SMT, Oberkochen, Germany). The used microscope was prepared with an Oxford INCA 400 energy dispersive spectrometer.

The crystallinity of the semolina nanocomposite films was investigated using a Phillips CM12 transmission electron microscope and a Siemens D5000 X-ray diffractometer. In addition, energy-dispersive X-ray spectroscopy was conducted under 15 kV incident electron energy.

Antimicrobial assay

The antimicrobial activity of the nanocomposite film was evaluated using the agar diffusion method as described by Maizura et al. (2007). The test for zone of inhibition on solid media was applied to determine the antimicrobial effects of the films against common food borne pathogens and spoilage bacteria, such as the Gram-positive *Staphylococcus aureus*.

Statistical analysis

The mean value of the mechanical, barrier, physical and antimicrobial characteristics of the semolina films, prepared at the 5% level of significance, was evaluated by exploiting ANOVA as well as Tukey's post hoc tests. SPSS version 22.0 was used for doing these statistical analyses.

Results and discussion

Thickness

The different ratios of the nanocomposite (ZnO/kaolin) films based on semolina did not show significant influence on film thickness. *T* test results showed a significant difference ($p < 0.05$) in the mean thickness of the nanocomposite films (0.16 ± 0.05 mm) and control film (0.14 ± 0.01 mm). The thickness of the nanocomposite films significantly increased ($p < 0.05$) with increasing solid content compared with that of the control semolina film.

Optical properties

Favorable optical properties are important for food packaging because protection against light is a basic requirement to preserve food quality. Protein-based films possess excellent UV barrier properties because of their high content of aromatic amino acids that absorb UV light efficiently (Ramos et al. 2013). The UV barrier property of packaging films is desirable to prevent UV light-driven lipid oxidation, discoloration of packed food stuffs, and eventual loss of nutrients (Ramos et al. 2013). The UV region is classified into three zones: UVC (100–280 nm),

UVB (280–320 nm), and UVA (320–400 nm). The properties of the biopolymer films and their nanocomposite films were studied by measuring absorbance using a UV–Vis spectrophotometer, and the results are shown in Fig. 1. The control biopolymer films showed no absorption peaks within 290–400 nm. However, the films blended with ZnO-nr/kaolin revealed a clear absorption peak, and the nanocomposite film with additional ZnO-nr exhibited a higher absorption peak. The ZnO/kaolin film at 4:1 and 3:2 ratios exhibited high intensity absorption peaks at UVA (320–400 nm) with no significant differences between these two ratios. In addition, the intensity absorption peaks in the 1:4 and 2:3 ZnO/kaolin films decreased and slightly shifted to a higher wavelength region.

Figure 1 shows the UV transmission in the control and nanocomposite films. The control films exhibited a relatively high transmittance within the UV range. The addition of ZnO-nr/kaolin completely prevented UV transmission. The addition of ZnO-nr/kaolin at all ratios (except 1:4) into semolina reduced UV transmission to almost 0%. Similarly, Nafchi et al. (2014) reported that adding 5% ZnO-nr into starch film reduces UV transmission to almost 0%. These findings suggest the applicability of ZnO-nr/kaolin-reinforced biopolymer films as UV-blocking films and heat insulators in the packaging industry.

Fig. 1 UV–Vis absorbance and transmittance spectra for semolina nanocomposite films at 25 °C

WVP

As discussed by Hong and Krochta (2004), the water hindrance and barrier characteristics of several edible films basing on lipids, polysaccharides, and proteins have been the focus of many researches in food science. However, having a relatively high WVP, there has been challenges in using composite films in food industry. Water's diffusivity and solubility within the film matrix controls the permeability of the film. This inferred that the mitigation of water can be prevented in food products using material produced by nanoscience. Different ratios of semolina films and nanocomposite edible films' WVP are shown in Table 1. The semolina films' WVP is shown, by one-way ANOVA, to have been decreased at the presence of ZnO-nr/kaolin. The WVP of 8.61×10^{-7} [$\text{gm}^{-1} \text{h}^{-1} \text{Pa}^{-1}$] was demonstrated for the semolina film without nanocomposite. As it is shown in Table 1, the semolina films' WVP was considerably decreased by the incorporation of ZnO-nr/kaolin which is possibly due to the hydrogen bonding that is formed between the semolina film matrix and the nanofilm on water diffusion. Comparing to the structure of the films without nanoparticles, the films with nanoparticles were shown to have a more compact structure, which resulted in a decrease in water permeability of the semolina films. Comparing to the control film's WVP ($p < 0.05$), there showed to be a 49–56% decrease in the nanocomposite films' WVP depending on the nanocomposite ratio. In our previous work, we observed a 47% reduction in WVP after reinforcing semolina matrix with 5% nanokaolin (Jafarzadeh et al. 2016). In this case, we obtained a 56% reduction in semolina/1% kaolin/4% ZnO-nr using only 1 wt% nanokaolin and combining them with ZnO-nr. An effective barrier effect was produced by the combination of nanokaolin and ZnO-nr. This barrier effect, as demonstrated by the TEM and XRD analysis, was due to the fillers' good dispersion and the high level of crystallinity.

The WVP test showed that the semolina/ZnO/kaolin blend films with 4% ZnO-nr and 1% nanokaolin had lower WVP compared with the other blend films, but the difference with the blend of 3% ZnO-nr and 2% nanokaolin was

not significant. The reduction in WVP of the semolina-based nanocomposite films is mainly due to the water vapor-impermeable aluminosilicate-layered nanokaolin and ZnO-nr that create a tortuous pathway for water vapor diffusion (Sorrentino et al. 2006). In addition, the nanoparticles in the film matrix existed as discontinuous particles and thus prevented the mobility of polymer chains. The reduced mobility of the polymer chains induced by the nanoparticles may have positively affected the WVP of the polymeric films (Su et al. 2010). Our results were consistent with previous results (Kanmani and Rhim 2014).

Mechanical properties

The mechanical properties of the semolina films incorporated with ZnO-nr and nanokaolin are shown in Table 1. The initial tensile strength of the semolina films was 3.41 ± 0.11 MPa, which increased to a maximum value of 5.62 ± 0.49 MPa when the blend of ZnO: nanokaolin (1:4) was added. As shown in Table 1, the tensile strength of the semolina film reinforced with the combination of ZnO-nr and nanokaolin at 1:4 ratio was higher than that of the other films. This result indicates that the tensile strength of the film increased with increasing nanokaolin concentration. This result is due to the increased surface interaction between the polymer matrix and nanokaolin with a high surface area, as well as the hydrogen bond formation between them (Rhim 2011). EB and YM indicate the flexibility and intrinsic stiffness of the films, respectively. EB has a reverse relation to tensile strength in most cases, and YM is directly related to tensile strength. As shown in Table 1, the EB decreased with increasing TS and maximum YM when the combination of ZnO-nr and nanokaolin (1:4) was added. The mechanical properties of the films are closely related to the distribution and density of the intra and intermolecular interactions between the polymer chains in the film matrix. Moreover, the degree of chain elongation and the nature of amino acid sequence might affect the mechanical strength of the protein-based films (Krochta and DeMulder-Johnston 1977). This finding is

Table 1 Mechanical and water vapour permeability (WVP) properties of semolina nanocomposite films

ZnO-nr/nanokaolin (%w/w)	TS (MPa)	EB (%)	YM (MPa)	WVP $\times 10^7$
Control	3.41 ± 0.11^d	59.44 ± 1.79^a	63.12 ± 2.27^d	8.61 ± 0.30^a
3:2	4.11 ± 0.28^c	50.04 ± 3.52^a	72.42 ± 4.51^c	4.006 ± 0.55^c
2:3	4.32 ± 0.12^c	45.04 ± 5.49^b	92.70 ± 7.43^c	4.37 ± 0.26^b
4:1	4.86 ± 0.34^b	37.57 ± 4.00^c	122.45 ± 9.32^b	3.79 ± 0.22^c
1:4	5.62 ± 0.49^a	27.57 ± 3.18^d	188.00 ± 13.78^a	4.46 ± 0.13^b

Values are mean ($n = 5$) $\pm$ SD. Different letters in each column represent significant difference at level of probability among semolina film TS tensile strength, EB elongation-at-break, YM Young's modulus, WVP water vapor permeability

similar to those of Sothornvit et al. (2010) and Rhim et al. (2006).

XRD characterization

In order to attain information about such properties of the examined material as the physical, chemical composition and the crystallographic structure characteristics, the scattered intensity of an X-ray beam on the sample was used by the XRD. (Espitia et al. 2013).

The crystallinity of ZnO-nr and nanokaolin in the semolina/ZnO-nr/nanokaolin composite films at different ratios (i.e. ZnO-nr: nanokaolin 1:4, 2:3, 3:2 and 4:1) was determined through XRD analysis, and the results are shown in Fig. 2. The control films did not show any diffraction peak at the range of test, whereas the semolina/ZnO-nr/nanokaolin films exhibited distinctive diffraction peaks. A steady increase in peak intensity was observed at $2\theta = 31.74^\circ$, $2\theta = 34.37^\circ$, $2\theta = 36.20^\circ$, $2\theta = 47.55^\circ$, and $2\theta = 56.56^\circ$ upon the addition of ZnO-nr content. The peak intensity also increased at

$2\theta = 22.86^\circ$ and $2\theta = 24.86^\circ$ upon the addition of nanokaolin. The increase in the concentration of the matrix's kaolin nanoparticles resulted in the increase in the intensity of the main feature peaks of kaolin. The XRD patterns of the nanocomposite films showed that the addition of the combination of nanokaolin and ZnO-nr affected the crystallinity of the matrix. Hence, the addition of nanoparticles resulted in sharp and strong peaks of the matrix, indicating the high crystallinity of the films.

Scanning electron microscopy and EDX

Figure 3 illustrates the SEM micrographs of the surface of the semolina films in the presence and absence of nanoparticles. Comparing to the homogeneous surface of the control film, the nanokaolin/ZnO-nr incorporated films demonstrated a slightly rough surface which was likely to be the result of the distribution of nanokaolin/ZnO-nr droplets over the matrix of the film. Figure 4 illustrates the EDX spectrum of semolina/ZnO-nr/nano kaolin blend

Fig. 2 XRD control film and semolina film incorporation with nanocomposite

Fig. 3 FESEM micrograph for control semolina film surface and blend of ZnO-nr and nano kaolin incorporated semolina film surface

films. In a case of an increase, signals of the decrease in the content of ZnO-nr or kaolin could be detected. Figure 4 shows the identification of C, Zn, O, Al, Si and Na elements, which is in accordance to the XRD analysis.

Antimicrobial assay

An antimicrobial packaging system can be obtained by directly incorporating antimicrobial agents into packaging films, coating packaging films with these antimicrobial substances and developing packaging materials from polymers. The effectiveness of antimicrobial packaging has been demonstrated over the last decade. Antimicrobial packaging increases the shelf life, safety and quality of many food products due to their great potential to reduce microbial growth in foods (Irkin and Esmer 2015).

Figure 5 shows the antibacterial activity toward the Gram-positive food pathogen *Staphylococcus aureus* of the semolina films and the nanocomposite films containing various ratios of the combination of ZnO-nr and nanokaolin. The increase in the content of the ZnO-nr was shown to significant increase in the nanocomposite films' inhibition zone. The excellent antimicrobial activity of the ZnO nanoparticles and their mechanism of action against microorganisms have already been demonstrated by other researchers (Li et al. 2009). Zhang et al. (2010) elucidated the mechanisms underlying the antibacterial activity of ZnO. In specific, ZnO penetrates through the cell wall of the microorganism, reacts with internal components of the cell, and finally reduces the viability of the organism. In particular, the viability of the organism was reduced through the penetration of ZnO through the wall of the microorganism's cell and accordingly it's reaction with the internal components of the cell.

Fig. 4 EDX spectrum blend of ZnO-nr and nano kaolin incorporated semolina film surface

Fig. 5 Effects of ZnO-nr/nano kaolin contents on the antimicrobial activity of semolina nanocomposite films against *S. aureus*. Inhibition zone = total inhibition area – total film area. The bars represent mean ($n = 5$) $\pm$ SD

Additionally, it is likely that the potential bond between Zn to proteins results in deactivation of them, an interaction with the microbial membrane which in turn leads to changes in the structure and permeability, as well as an interaction with the microbial nucleic acids to avoid replication. Moreover, as maintained by Brayner et al. (2006), considering the microbial membrane, the ZnO nanoparticles' accumulation inside it leads to the disintegration of the membrane as well as the cellular internalization.

Conclusion

This study produced and characterized semolina-based nanobiocomposites of ZnO-nr and nanokaolin for food packaging applications. Due to such characteristics of semolina as its biodegradability, availability in nature, low

cost, as well as having a high content of gluten, it was exploited as a polymetric matrix in this study. The semolina matrix's crystallinity was also shown by the XRD patterns to be affected by the addition of ZnO-nr/nano kaolin. Moreover, it was revealed that the mechanical features of semolina-based films were enhanced and improved by incorporation of nanoparticles as well as by increasing nanokaolin percentage. The WVP permeability of the nanocomposite films significantly decreased with nanokaolin concentration. The optical properties of the nanobiocomposites indicated that UV transmission became almost zero up on the addition of small amounts of ZnO-nr to the biopolymer matrix. Additionally, growth in the Gram-positive food pathogen *S. aureus* was significantly inhibited in the nanocomposite films of semolina-based. The results above indicate that the biopolymer-based nanocomposite films may be used as environment-friendly antimicrobial packaging films to improve the shelf life of food and viable replacement to petroleum-based or synthetic packaging films. Overall, this study suggests that semolina films incorporated with blend of ZnO-nr and nano kaolin show a strong potential and can be applied in the food packaging industry, especially cheeses, because of its good antioxidant and antimicrobial properties.

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