CHARACTERIZATION OF SEMOLINA BIOPOLYMER FILMS ENRICHED WITH ZINC OXIDE NANO RODS

SHIMA JAFARZADEH*[a], FAZILAH ARIFFIN[b], SHAHROM MAHMUD[c], ABD KARIM ALIAS[d], ALI NAJAFI[e] and MEHRAJ AHMAD[f]

[a]PhD candidate, Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, University Sains Malaysia, 11800 Minden, Penang, Malaysia

[b]Associate Professor, Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, School of Industrial Technology, University Sains Malaysia, 11800 Minden, Penang, Malaysia

[c]Associate Professor, Nano Optoelectronic Research (NOR) Lab, School of Physics, University Sains Malaysia, 11800 Minden, Penang, Malaysia

[d]Professor, Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, University Sains Malaysia, 11800 Minden, Penang, Malaysia

[e]Senior lecturer, Food Biopolymer Research Group, Food Science and Technology Department, Damghan Branch, Islamic Azad University, Damghan, Semnan, Iran

[f]Senior lecturer, Institute of Nutrition (INMU), Mahidol University, 999 Phutthamonthon 4 Rd, Salaya, Nakhon Pathom 73170, Thailand

*Corresponding author. shimajafar@yahoo.com

ABSTRACT

This research aimed to develop biopolymer-based antimicrobial films as food packaging that will consequently reduce environmental pollution caused by the accumulation of petroleum origin food packaging. Zinc oxide nanorods (ZnO-nr) were incorporated as the antimicrobial component in nanocomposite films based on semolina, which were prepared by solvent casting. SEM and XRD were used to characterize the resulting films. The mechanical, barrier, optical, physical and antimicrobial properties of the films were also analyzed. The addition of ZnO-nr reduced the solubility, WVP, and elongation at break while increased the tensile strength and modulus of elasticity of the nanocomposite films compared with the control film. The apparent surface color and UV transmittance of the semolina films was greatly influenced by the amount of ZnO-nr. The nanocomposite films exhibited 0% UVA in transmittance the near infrared spectra. Furthermore, the ZnO-nr semolina films exhibited strong antimicrobial activity against *Staphylococcus aureus*.

1. INTRODUCTION

A large number of biodegradable polymers have been studied to develop edible films and finally lower the amount of waste produced through non-degradable petroleum-based food packaging activities (THARANATHAN, 2003; JAFARZADEH *et al.*, 2016). These edible films not only provide physical protection to foods but also prevent the mass transfer of moisture, oxygen, carbon dioxide, lipids, flavors, and aromas into and from food products (MARCUZZO *et al.*, 2010). Given their nutritive value and superior properties, protein-based biopolymers have attracted considerable interest for the development of edible films (GENNADIOS and YADA, 2004). These polymers are excellent oxygen barriers and they render certain mechanical properties to the films (SOTHORNVIT *et al.*, 2009).

Different types of proteins are used as components of biodegradable packaging (KHWALDIA *et al.*, 2010). Among these proteins, the protein from wheat is a potential component of packaging materials because of its cost effectiveness, biodegradability, renewability, and favorable film-forming and adhesive/cohesive properties (TÜRE *et al.*, 2013). Semolina is a type of wheat whose flour contains high gluten content (QUAGLIA, 1988). The gluten increases the nutrient value of edible films. Semolina grain is extra hard, translucent, light colored, and exhibits antioxidant activities (ONYENEHO and HETTIARACHCHY, 1992; JAFARZADEH *et al.*, 2017b). In addition, semolina extracts suppress radical-induced liposome lipid peroxidation and show radical cation-scavenging activity (ONYENEHO and HETTIARACHCHY, 1992).

However, the poor mechanical and water sensitivity of biopolymers limit their application in food packaging. Nanoparticles, which reinforce biopolymers through the formation of nanocomposites, have been recently employed to overcome these limitations (DUFRESNE, 2006). One of the most successful applications of nanotechnology in the field of packaging concerns the development of "nanocomposites"(UNALAN *et al.*, 2014). The nanoparticles dispersed in the biopolymer matrix considerably reinforce the mechanical, thermal, optical, and physicochemical properties of nanocomposites compared with pristine biopolymer (PETERSSON and OKSMAN, 2006). Given their large specific surface area and high surface energy, nanofillers exhibit excellent interfacial interactions with polymer branches and consequently enhance polymer properties significantly (KOVACEVIC *et al.*, 2008). Zinc oxide (ZnO) has been widely applied as a functional filler in UV absorbers in pharmaceuticals, cosmetics, coating materials, and pigments (KUMAR and SINGH, 2008; Li *et al.*, 2009; Yu *et al.*, 2004). ZnO nanoparticles can potentially prevent infectious diseases through the antimicrobial effects of ZnO (LI *et al.*, 2009; Li *et al.*, 2010; RAJENDRA *et al.*, 2010; ZHANG *et al.*, 2008). The size, morphology, crystallinity, composition, and shape of ZnO nanoparticles affect their intrinsic properties (SHAHROM and ABDULLAH, 2006; JAFARZADEH *et al.*, 2017a). LIN *et al.* (2009) reported that ZnO nanorods (ZnO-nr) exhibit optimal UV-absorption activity. Semolina displays excellent properties for edible film production, and ZnO-nr are potent materials in reinforcing the mechanical, physicochemical, and barrier properties of semolina. Despite these advantages, ZnO-nr-reinforced semolina remains poorly understood. Studies published on semolina thus far are limited. To the best of our knowledge, there is no information regarding of the preparation blend films from semolina, Zno-nr as filler and glycerol and sorbitol as plasticizer. In the present study, we hypothesized that low-concentration ZnO-nr addition into semolina films improves the hydrophobicity of the films and that the resulting biopolymeric films exhibit UV-blocking, low WVP and antimicrobial properties. Given their favorable antimicrobial activities, the proposed films can be used as food packaging especially for cheese. In this study was used ZnO-nr as fillers to prepare semolina film

bionanocomposites and characterized the morphology, physicochemical, mechanical, and barrier properties of the prepared films.

2. MATERIALS AND METHODS

2.1. Materials

Semolina flour (14.2% protein, 18.5% gluten) was purchased from the local market in Tehran, Iran and then stored in a dry and cool place until the tests. Food-grade glycerol was obtained from SIM Company Sdn. Bhd. (Penang, Malaysia), whereas food-grade liquid sorbitol was purchased from LiangtracoSdn. Bhd. (Penang, Malaysia). The magnesium nitrate used to control humidity was purchased from Sigma Aldrich (Kuala Lumpur, Malaysia), and ZnO-nr was synthesized through the catalyst-free combust-oxidized mesh process as described by SHAHROM and ABDULLAH (2007).

2.2. Preparation of bionanocomposite films

Semolina flour (4g) was dispersed by magnetic stirring in 80 mL of distilled water (based on water or water/ethanol) at room temperature, and the pH of the dispersion was adjusted to 8 with 1M NaOH. Similarly, various concentrations of ZnO powder (1%, 2%, 3%, 4%, and 5%; w/w of total solid) and 2g of a sorbitol and glycerol (3:1) mixture were dispersed in 20 mL of distilled water for 30min followed by sonication in an ultrasonic bath (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil) (JAFARZADEH *et al.*, 2017c). Subsequently, the dispersions of semolina flour and ZnO-nr plasticizer were mixed and stirred for 1 h at 90 °C. For the preparation of nanocomposite films, the homogenous mixtures were poured into plates and the solvents were allowed to evaporate at room temperature for 24h.
The films were dried under controlled conditions in a humidity chamber (25 °C and 58% relative humidity (RH). A control film was prepared in a similar manner except for the addition of nanoparticles. The dried films were peeled and stored at 23 ± 2 °C and 58% RH until use.

2.3. Characterization studies

2.3.1 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 made at five random points. Measurements were obtained using a micrometer (Model No. 2046-08; Mitutoyo Tokyo, Japan).

2.3.2 Water solubility

The solubility of the semolina/ZnO-nr films in deionized water was calculated as the ratio of the solubilized material in water to the initial dry weight of the film (RHIM *et al.*, 1999). The initial dry weight of films 2.5cm × 2.5cm in dimension was obtained after dehydration for 3 days at 25 °C in a desiccator with phosphorus pentoxide (0% RH). The samples were placed in a beaker with 80 mL of deionized water (18 MX) and then gently shaken at 40 rpm for 1 h at room temperature. The remaining pieces of the films were separated using a filter paper (Whatman No. 1) and then dried to a constant weight in an oven at 60 °C for

24h. Finally, the weight of the dried insoluble material was determined. The weight of the water-soluble material was calculated by subtracting the weight of the insoluble dry matter from that of the initial dry matter. The film samples were weighed to the nearest 0.0001g before and after drying. The solubility of the films was determined in triplicate.

2.3.3 Moisture content

To measure the moisture content of the bionanocomposite films, approximately 50mg of the films were conditioned at 58% RH and 25 °C for 2 days. Subsequently, the films were dried at 105 °C for 1 day (until equilibrium weight was attained). The moisture content was obtained using the following equation:

$$Moisture\ content = \frac{Mi-Mf}{Mt} \times 100$$

Where Mi and Mf are the initial and final weights (mg) of the dried samples, respectively. The weight of each sample was measured three times.

2.3.4 Water vapor permeability (WVP)

WVP tests for the semolina films were performed gravimetrically following the ASTM Standard Method E96-05 (ASTM, 2005).

2.3.5 Mechanical properties

A minimum of seven 100mm × 25mm films were conditioned at 25Ċ and 58% RH for at least 48 h in an environmental test chamber (Sang Woo Co., Korea). A texture analyzer (TA-XT2, Stable Micro Systems, Surrey, UK) was used to measure the tensile strength [TS (MPa)], Young's modulus [YM (MPa)], and elongation at break [EB (%)] of the films in accordance with the ASTM Standard Method D882-10 (ASTM, 2010). The initial grip separation was set at 50mm, and the crosshead speed was set at 0.5 mm/s.

2.3.6 Optical properties (color and Light transmission)

We studied the transmittance 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 (60mm × 4mm) and directly placed in a spectrophotometer test cell. An empty glass plate served the reference.
The color of the biofilms was determined by using a colorimeter (Hunter Lab system, model Miniscan XE, USA). The CIELab scale was applied to measure the following parameters: L* (luminosity), a* (red to green), b*(yellow to blue), Chroma (C*), and hue (h*). Measurements were obtained in five different points in each nanocomposite film (RHIM et al., 1999).

2.3.7 Film morphology

The conditioned bionanocomposite samples were vacuum coated with gold for field-emission scanning electron microscopy. The surface microstructure of the nanocomposite films was visualized using a Leo Supra 50 VP field-emission scanning electron microscope (Carl-Ziess. SMT, Oberkochen, Germany) equipped with an Oxford INCA 400 energy dispersive.

We used a Phillips CM12 transmission electron microscope and Siemens D5000 X-ray diffractometer to investigate the crystallinity of the semolina nanocomposite films. In addition, energy-dispersive X-ray spectroscopy (EDX) was conducted under 15 kV incident electron energy.

2.3.8 Antimicrobial assay

The antimicrobial activity of the ZnO-nr-reinforced 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 foodborne pathogens and spoilage bacteria, such as the Gram-positive *Staphylococcusaureus*. Circular samples (5mm) were sterilized under UV radiation for 2h to eliminate surface contamination and were subsequently placed on nutrient agar plates that had been previously smeared with 100 µL of inoculum containing approximately 10^6–10^7 CFU/mL *S. aureus*. The plates containing the films were stored at 37°C for 24h. Thereafter, we measured the zone of inhibition produced with the nanocomposite films.

2.3.9 Statistical analysis

ANOVA and Tukey's post-hoc tests were used to evaluate the mean values of the physical, optical, mechanical, barrier, and antimicrobial properties of the prepared semolina films at the 5% significance level. Statistical analysis was conducted using SPSS version 22.0.

3. RESULTS AND DISCUSSION

3.1. Thickness

Table 1 shows the thickness of the control semolina film and those reinforced with various concentrations of ZnO-nr. The thickness of the films significantly increased with increasing ZnO-nr concentration ($p < 0.05$). This result can be attributed to the increased solid content of the films (AHMAD *et al.*, 2012).

Table 1. Mechanical, water vapor permeability, thickness of semolina nanocomposite films.

ZnO-nr (%w/w)	TS (MPa)	EB (%)	YM (MPa)	Thickness(mm)	WVP × 10⁻⁷ [g m⁻¹ h⁻¹ Pa⁻¹]
Control	3.40± 0.105[e]	59.43±1.79[a]	63.12±2.27[f]	0.143±0.005[e]	8.61±0.304[a]
1%	3.53±0.098[e]	52.09±2.79[b]	73.49±3.30[e]	0.149±0.001[cd]	6.71±0.26[b]
2%	3.85±0.113[d]	46.87±2.96[c]	85.64±3.13[d]	0.152±0.005[cd]	5.84±0.24[c]
3%	4.21±0.211[c]	40.90±3.12[d]	100.03±4.99[c]	0.158±0.005[bc]	5.03±0.23[d]
4%	4.64±.0262[b]	33.53±2.52[e]	117.40±3.07[b]	0.163±0.001[ab]	5.03±0.23[d]
5%	5.13±0.151[a]	27.61±2.10[f]	143.51±4.37[a]	0.166±0.005[a]	4.40±0.19[e]

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

3.2. Moisture content and water solubility

Most biopolymers are sensitive to water. However, incorporating lipids and nanoparticles, as well as the enhanced crosslinking in the biofilm, may reduce the sensitivity of the biopolymers to water (PAVLATH and ORTS, 2009).

Figure 1 illustrates the solubility and the moisture content of the control and nanocomposite films. Compared with the control, the nanocomposite films showed lower moisture content. In addition, the solubility of the films decreased with increasing ZnO-nr content. This finding may be attributed to the interaction among the plasticizer, biopolymer matrix, and ZnO-nr, which consequently reduced the amount of hydroxyl groups that react with water, thereby creating a less hygroscopic matrix. Our results were consistent with those of TUNC and DUMAN (2010) and MÜLLER *et al*. (2011).
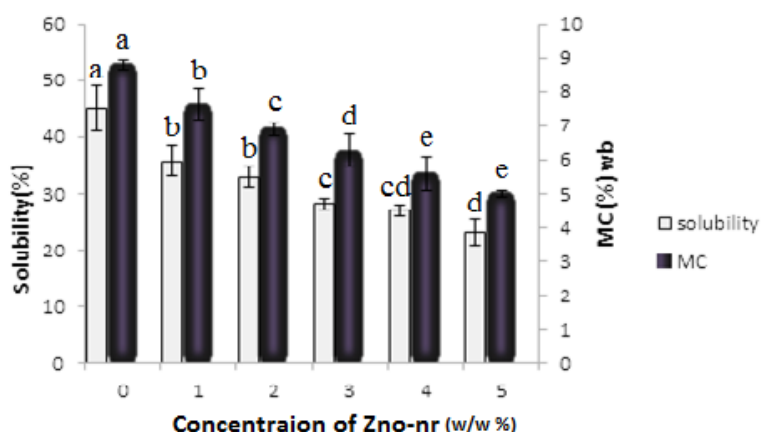

Figure 1. Effects of ZnO-nr on water solubility (empty bars) and moisture content (filled bars) of the semolina films. The bars represent mean (n = 5) $\pm$ SD. Different letters on the bars represent significant difference at the 5% level of probability.

3.3. WVP

WVP is a serious problem in the food industry; food packaging must prevent a contact between the food and the environment, and protect food products from any harmful agents. The problem with composite films in the food industry is the relatively high WVP of edible films. Film permeability is controlled by the diffusivity and solubility of water within the film matrix. Thus, nanoscience can be used to develop a material that prevents the migration of water in food products. Table 1 shows the WVP of semolina films as a function of ZnO-nr content.

The WVP of the control semolina film was 8.61×10^{-7}, which was significantly higher than that of the nanocomposite films. The lowest WVP was found in the semolina film incorporated with 5% of Zn0-nr, which is significant when compared to the control or other percentage.

The enhanced water vapor barrier property of the nanocomposite films can be attributed to the impermeability of the ZnO-nr in the polymer matrix to water vapor and the formation of a tortuous pathway for the diffusing water molecules (YU *et al*., 2009). The WVP of the films reinforced with 5% ZnO-nr was significantly reduced by 4.40×10^{-7} compared with that of the control film (p < 0.05). These results showed that the water

vapor barrier property of the bionanocomposite films was stronger than that of the biopolymer films. Similar results have been reported for nanocomposite protein films (JAFARZADEH et al., 2015).

3.4. Mechanical properties

ZnO-nr significantly affected the mechanical properties of the bionanocomposite films. Table 1 shows the TS, EB, and YM of the bionanocomposite films. The maximum stress that the film can withstand while being stretched or pulled before failing or breaking is known as TS. EB and YM indicate the flexibility and intrinsic stiffness of the films, respectively. Compared with those of the control films, the TS (5.13 MPa) and YM (143.51 MPa) of the bionanocomposite films significantly increased as the amount of ZnO-nr was increased from 1% to 5%. This result indicates that the bionanocomposite films had greater rigidity than the control film.

This result is due to the increased surface interaction between the protein matrix and Zno-nr with a high surface area, as well as the hydrogen bond formation between them (RHIM, 2011).

EAB 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 5% ZnO-nr 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 (SHELLHAMMER and KROCHTA et al., 1977).This finding is similar to those of SOTHORNVIT et al (2009).

3.5. Color

The surface color of the bionanocomposite is a critical parameter because it affects the general appearance and appeal of the food packaging to consumers (BOURTOOM and CHINNAN, 2008).

Table 2 presents the color properties of the semolina films and their nanocomposite counterparts.

Table 2. Colorimetric parameters for the transparency of semolina films.

ZnO-nr (%w/w)	L^*	a^*	b^*	C^*
Control	94.84±0.016[a]	−0.794±0.017[b]	4.06±0.12[e]	4.11±0.12[e]
1%	84.06±0.116[b]	−0.74±0.090[ba]	12.86±0.10[d]	12.86±0.10[d]
2%	82.20±0.009[c]	−0.684±0.033[ba]	13.34±0.012[c]	13.35±0.012[c]
3%	78.11±0.08[d]	−0.674±0.024[ba]	13.345±0.20[c]	13.36±0.20[c]
4%	74.86±0.70[e]	−0.44±0.064[ba]	15.24±0.004[b]	15.26±0.004[b]
5%	71.68±0.014[f]	−0.35±0.061[a]	15.82±0.020[a]	15.84±0.019[a]

Values represent mean (n = 5) ± SD. Different letters in each column represent significant difference among semolina films at the 5% level of probability.

Incorporation of Zno-nr had a significant effect on the L*-value, b*-value, and C*-value of the resulting film ($p<0.05$). Evidently, the control film was colorless and transparent,

whereas the semolina/ZnO-nr composite films became less transparent with increasing ZnO-nr content from 1% to 5%. This finding indicates that ZnO-nr addition influenced the coloring properties of the biopolymer films. As the content of ZnO-nr was increased, the b* (indicating blueness/yellowness) and C* values of the composite films significantly increased, whereas a* values (indicating greenness/redness) of the bionanocomposite films only slightly increased. By contrast, the L* values (indicating lightness) significantly decreased from 94.84 to 71.68 upon the addition of ZnO-nr into the semolina films.

These results are consistent with those of NAFCHI *et al.* (2013), who found that adding ZnO-nr in sago starch significantly reduces the L* value and increases a* and b* values compared with the control.

3.6. Light transmission

The optical properties of biopolymer films are highly important in food packaging because protection against light is a basic requirement to preserve the food quality.

Fig. 2 shows the UV transmission in the control and nanocomposite films. The control films exhibited a relatively high transmittance within the UV range of 290-400 nm. The addition of ZnO-nr completely prevented UV transmission. NAFCHI *et al.* (2013) reported that adding 5% ZnO-nr into starch film reduces UV transmission to almost 0%. We obtained a similar result but with 3% instead of 5% ZnO-nr. By contrast, YU *et al.* (2009) have recently reported that adding 4% ZnO-nr into starch film allows 3.4% UV light transmission. Moreover, the transmission of visible to IR (> 400 nm) spectra decreased by > 50% after adding ZnO-nr. The different behavior of ZnO in the present study can be attributed to the nanorod morphology of the particles (LIN *et al.*, 2009). These findings suggest the applicability of ZnO-nr-reinforced biopolymer films as UV-blocking films in the packaging industry.
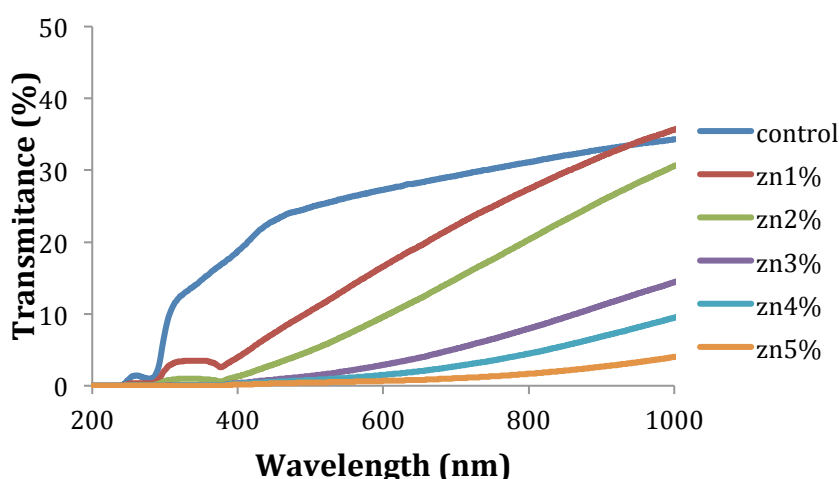

Figure 2. UV-vis transmittance of semolina nanocomposite films at 25 °C.

3.7. XRD analysis

XRD analyzes the scattered intensity of an X-ray beam on a material to reveal its crystallographic structure, chemical composition, and physical properties. This technique is widely used to characterize various materials because it is nondestructive and does not require elaborate sample preparation (ESPITIA *et al.*, 2013). Thus, we analyzed the control

film and their nanocomposite counterparts through XRD [Figs. 3(a) and 3(b)]. This work presents the results obtained at the maximum amounts of ZnO nanoparticles, where the main characteristic peaks of the ZnO nanoparticles with hexagonal cross section were observed at $2\theta = 31.64°, 34.32°, 36.14°, 47.44°, 56.53°, 62.82°, 67.92°$. Moreover, the intensity of the major peaks of ZnO-nr increased as the ZnO-nr concentration in the matrix was increased.

Furthermore, the XRD patterns of the nanocomposite films revealed that ZnO-nr affected the crystallinity of the matrix. The addition of ZnO nanoparticles in the matrix produced sharp and strong peaks, indicating greater crystallinity of the nanocomposite films than the control film.

3.8. Transmission electron microscopy (TEM)

Fig. 3(c) shows the TEM images of ZnO-nr. The ZnO-nr crystallites exhibit a rather hexagonal morphology with a diameter of 40-100 nm and a length of 200nm.

3.9. Scanning electron microscopy (SEM) and EDX

SEM is the most widely applied technique to determine the shape, size, morphology, and porosity of matrices. Fig. 3 shows the SEM images of the semolina films and ZnO-nr-reinforced films; the prepared ZnO-nr are evidently a nanostructure. TEM also revealed that the nanorods are cylindrical with hexagonal cross section. The control film exhibited a smooth and compact surface morphology, whereas the nanocomposite films showed a slightly rough surface. SEM images revealed that ZnO-nr particles were homogenously distributed throughout the film surface, which possibly rendered the surface of the nanocomposite films rough. This finding is possibly associated with the protruded film structures resulting from the increased thickness of the films (Table 1). ZnO-nr particles were uniformly dispersed in the nanocomposite films, which triggered an effective force transfer from the protein matrix to the ZnO-nr reinforcing phase. This finding may be attributed to the higher TS of the semolina nanocomposite films with 5% ZnO-nr compared with the other films (Table 1). Fig 3(d) illustrates the EDX spectrum of semolina/ ZnO-nr blend films. If Zno-nr content was increased, their signals could be detected. As shown in Fig. 3 (d), that C, Zn, O and Na elements were identified. This result agreed well with XRD analysis.

3.10. Antimicrobial assay

Fig. 4 shows the antibacterial activity toward the Gram-positive food pathogen *S. aureus* of the semolina films and the nanocomposite films containing various contents of ZnO-nr. The inhibition zone of the control and nanocomposite films significantly increased with increasing ZnO-nr content. The excellent antimicrobial activity of ZnO nanoparticles and the mechanism of action against microorganisms have already been demonstrated by other researchers (LI *et al.*, 2009; YU *et al.*, 2004). ZHANG *et al.* (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. Moreover, Zn ions may bind to proteins and deactivate them, may interact with the microbial membrane to cause changes in the structure and permeability, and may interact with the microbial nucleic acids to prevent replication. Furthermore, accumulation of ZnO nanoparticles in the microbial membrane causes membrane disintegration and cellular internalization (BRAYNER *et al.*, 2006).

ZHANG *et al.* (34) also reported that nano-sized ZnO is more effective than micro-sized ones because the former easily penetrates through the cell wall of microorganisms. Nano rods can act as needles for easy penetration through the cell wall (NAFCHI, 2013).
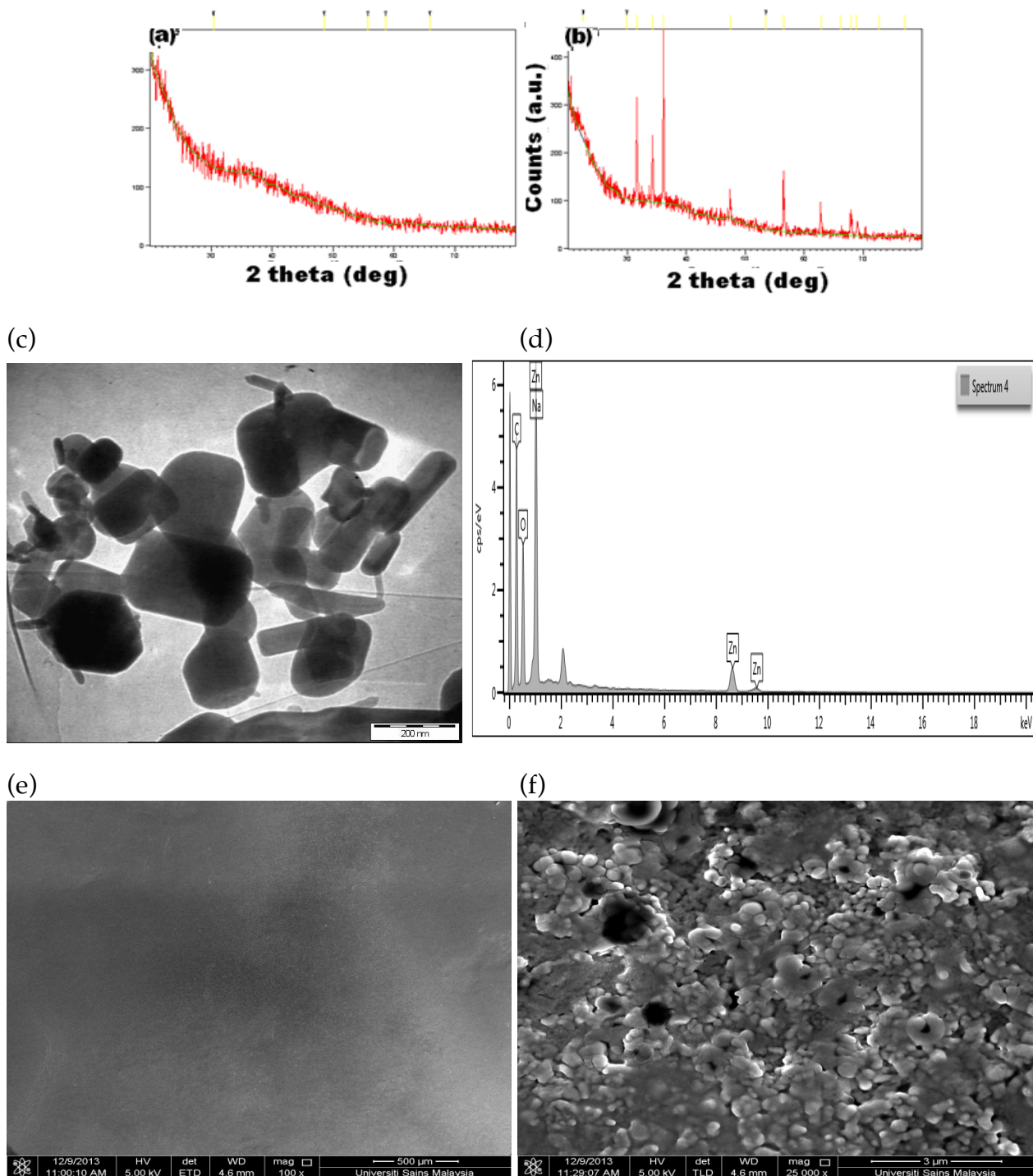

Figure 3. (a) XRD pattern of pure film, (b) 5% ZnO-nr-reinforced semolina, (c) TEM micrograph of ZnO-nr, (d) EDX spectrum (e) FESEM micrograph of pure semolina film surface, and (f) ZnO-nr-reinforced semolina film surface.
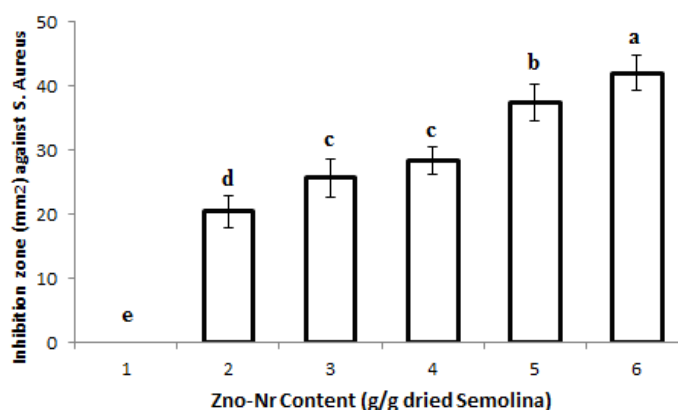
Figure 4. (a) Effects of ZnO-nr contents on the antimicrobial activity of semolina nanocomposite films against *S. aureus*. Inhibition zone = total inhibition area − total film area. The bars represent mean (n = 5) ± SD. Different letters on the bars represent significant difference at the 5% level of probability.
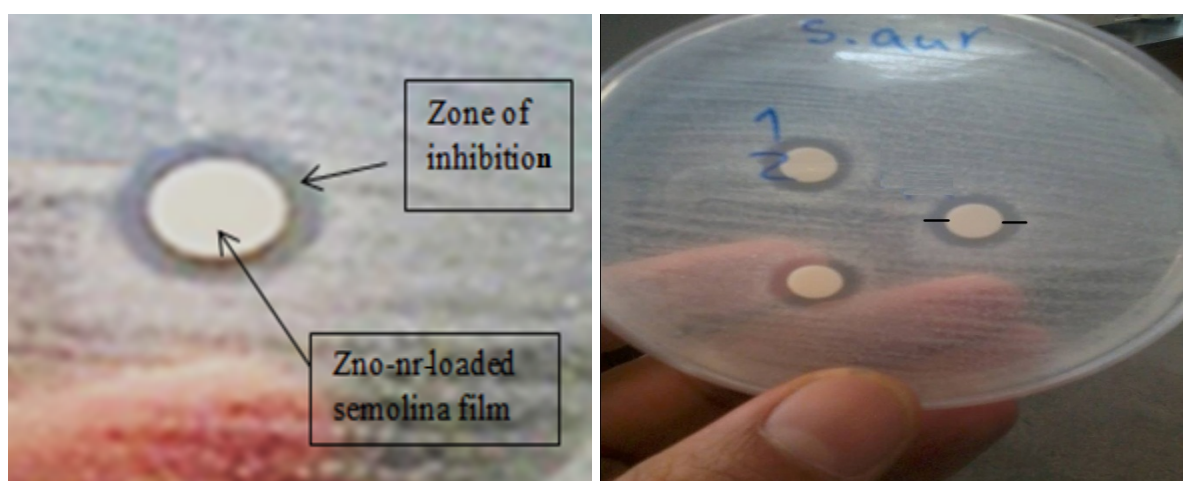

Figure 4. (b) Antimicrobial assay of ZnO-nr supported semolina films.

4. CONCLUSIONS

The present research characterized and created semolina-based nanobiocomposites of ZnO-nr for food packaging purposes. There are some reasons why semolina was employed as a polymeric matrix including its great accessibility in nature, biodegradability, low expenditure, and great gluten content, which enhance the edible films'nutritional properties.

ZnO-nr played an important role in enhancing the physical properties of semolina-based biocomposites. After the incorporation of low levels of ZnO-nr fillers, significant differences were observed in the film properties, particularly in mechanical, barrier, microbial and UV protection activities. The optical properties of bionanocomposites indicated that the UV transmission becomes almost zero with the addition of small

amounts of ZnO-nr to the biopolymer matrix. XRD diffraction shows that the intensity of the crystal facets of (100), (101) and (002) increased with increasing ZnO-nr concentrations in the biocomposite matrix. Moreover, the semolina-based nanocomposite films inhibited the growth of the Gram-positive food pathogen *S. aureus.* The present findings stressed that the biopolymer-based nanocomposite films are environment friendly in films antimicrobial packaging to make an improvement in the shelf life of food as well as viable replacement to petroleum-based or synthetic packaging films. Overall, this study suggests that semolina films incorporated with Zno-nr show a strong potential to be used as active films.

REFERENCES

Ahmad M., Benjakul S., Prodpran T. and Agustini T.W. 2012. Physico-mechanical and antimicrobial properties of gelatin film from the skin of unicorn leatherjacket incorporated with essential oils. Food Hydrocolloid. 28:189-199.

ASTM. 2005. Annual Book of ASTM Standards. ASTM, Philadelphia, PA.

ASTM. 2010. Standard test method for tensile properties of thin plastic sheeting D882-10. In: Annual book of ASTM standards. American Society for Testing and Materials, PA, Philadelphia.

Bourtoom T. and Chinnan M.S. 2008. Preparation and properties of rice starch–chitosan blend biodegradable film. Lwt-Food Sci. Technol. 41:1633-1641.

Brayner R., Ferrari-Iliou R., Brivois N., Djediat S., Benedetti M.F. and Fiévet F. 2006. Toxicological impact studies based on Escherichia coli bacteria in ultrafine ZnO nanoparticles colloidal medium. Nano Lett. 6:866-870.

Dufresne A. 2006. Comparing the mechanical properties of high performances polymer nanocomposites from biological sources. J. Nanosci. Nanotechno. 6:322-330.

Espitia P.J.P, Soares N.D.F.F, Teófilo R.F., dos Reis Coimbra J.S., Vitor D.M, Batista R.A. and Medeiros E.A.A. 2013. Physical-mechanical and antimicrobial properties of nanocomposite films with pediocin and ZnO nanoparticles. Carbohyd Polym. 94:199-208.

Gennadios A. and Yada R.Y. 2004. Edible films and coatings from proteins. Proteins in food processing. Woodhead Publishing, Cambridge. pp. 442-467.

Gontard N., Guilbert S. and CUQ, J.L. 1992. Edible wheat gluten films: influence of the main process variables on film properties using response surface methodology. Journal of Food Science 57(1):190-195.

Jafarzadeh S., Alias A.K., Ariffin F., Mahmud S. and Najafi A. 2015. Preparation and characterization of bionanocomposite films reinforced with nano kaolin. Journal of Food Science and Technology pp.1-9.

Jafarzadeh S., Alias A.K., Ariffin F., Mahmud S., Najafi A. and Ahmad M. 2016. Fabrication and characterization of novel semolina-based antimicrobial films derived from the combination of ZnO nanorods and nanokaolin. Journal of Food Science and Technology, 1-9.

Jafarzadeh S., Ariffin F., Mahmud S., Alias A.K., Hosseini S.F and Ahmad M. 2017a. Improved the physical and protective functions of semolina film by embedding blend nanocomposite (ZnO-nr and nano-kaolin). Food Packaging and Shelf life.

Jafarzadeh S., Alias A.K., Ariffin F., Mahmud S., Najafi A. and Sheibani S. 2017b. Characterisation of new biodegradable edible film based on semolina loaded with nano-kaolin.

Jafarzadeh, S., Alias A., Ariffin F. and Mahmud S. 2017c. Characterization of Semolina Protein Film with Incorporated Zinc Oxide Nano Rod Intended for Food Packaging. Polish Journal of Food and Nutrition Sciences.

Khwaldia K., Arab-Tehrany E. and Desobry S. 2010. Biopolymer coatings on paper packaging materials. Compr Rev Food Sci. F. 9:82-91.

Kovacevic E., Stefanovic I., Berndt J., Godde C., Winter J. and Boufendi L. 2008. The nanoparticle formation in hydrocarbon plasmas. Publ. Astron. Obs Belgrade. 84:151-152.

Kumar A.P. and Singh R.P. 2008. Biocomposites of cellulose reinforced starch: improvement of properties by photo-induced crosslinking. Bioresource Technol. 99:8803-8809.

Li J.H, Hong R.Y, Li M.Y, Li H.Z, Zheng Y. and Ding J. 2009. Effects of ZnO nanoparticles on the mechanical and antibacterial properties of polyurethane coatings. Prog. Org. Coat. 64:504-509.

Li X.H, Xing Y.G, Li W.L, Jiang Y.H. and Ding Y.L. 2010. Antibacterial and physical properties of poly(vinyl chloride)-based film coated with ZnO nanoparticles. Food Sci. Technol Int. 16:225-232.

Lin O.H, Akil H.M. and Mahmud S. 2009. Effect of particle morphology on the properties of nanoZnO/polypropylene composites. Adv Compos Lett. 8:77-83.

Maizura M., Fazilah A., Norziah M.H. and Karim A.A. 2007. Antibacterial activity and mechanical properties of partially hydrolyzed sago starchealginate edible film containing lemongrass oil. J. Food Sci. 72:C324-C330.

Marcuzzo E., Sensidoni A., Debeaufort F. and Voilley A. 2010. Encapsulation of aroma compounds in biopolymeric emulsion based edible films to control flavour release. Carbohyd. Polym. 80:984-988.

Muller C.M.O, Laurindo J.B. and Yamashita F. 2011. Effect of nanoclay incorporation method on mechanical and water vapor barrier properties of starch-based films. Ind. Crop. Prod. 33:605-610.

Nafchi A.M, Nassiri R, Sheibani S, Ariffin F. and Karim A.A. 2013. Preparation and characterization of bionanocomposite films filled with nanorod-rich zinc oxide. Carbohyd Polym. 96:233-239.

Onyeneho S.N. and Hettiarachch N.S. 1992. Antioxidant activity of durum wheat bran. J Agr Food Chem. 40:1496-1500.

Pavlath A.E. and Orts W. 2009. Edible films and coatings: why, what and how? pp. 1-23. In: Edible films and coatings for food applications. Embuscado ME, Huber KC. (Eds.), Springer, New York.

Petersson L. and Oksman K. 2006. Biopolymer based nanocomposites: comparing layered silicates and microcrystalline cellulose as nanoreinforcement. Compos. Sci. Technol. 66:2187-2196.

Quaglia G.B. 1988. Other durum wheat products. In: Durum chemistry and technology, AACC International, St. Paul, MN, pp. 263-282.

Rajendra R, Balakumar C, Ahammed H, Jayakumar S, Vaideki K. and Rajesh E. 2010. Use of zinc oxide nano particles for production of antimicrobial textiles. Int. J. Eng. Sci. Tech. 2: 202-208.

Rhim J.W, Wu Y, Weller C.L. and Schnepf M. 1999. Physical characteristics of a composite film of soy protein isolate and propyleneglycol alginate. J. Food Sci. 64: 149-152.

Shahrom M. and Abdullah M.J. 2006. Nanotripods of Zinc Oxide pp. 442-446. In: IEEE Conference on Emerging Technologies - Nanoelectronics, 10-13 January, Singapore.

Shahrom M. and Abdullah M.J. 2007. Tapered head of ZnOnanorods. J. Solid State Sci. Tech. 15:108-115.

Shellhammer T.H. and Krochta J.M. 1997. Whey protein emulsion film performance as affected by lipid type and amount. Journal of Food Science, 62(2), pp.390-394.

Sothornvit R., Rhim J.W. and Hong S.I. 2009. Effect of nano-clay type on the physical and antimicrobial properties of whey protein isolate/clay composite films. J. Food Eng. 91:468-473.

Tharanathan R.N. 2003 Biodegradable films and composite coatings: past, present and future. Trends Food Sci Tech. 14:71-78.

Tunc S. and Duman O. 2010. Preparation and characterization of biodegradable methyl cellulose/montmorillonitenanocomposite films. Appl. Clay. Sci. 48:414-424.

Türe H., Gällstedt M., Johansson E. and Hedenqvist M.S. 2013. Wheat gluten/montmorillonite clay multilayer-coated paperboards with high barrier properties. Ind. Crop Prod. 51:1-6.

Yu D., Cai R. and Liu Z. 2004. Studies on the photodegradation of rhodamine dyes on nanometer-sized zinc oxide. Spectrochim Acta A. 60:1617-1624.

Yu J., Yang J., Liu B. and Ma X. 2009. Preparation and characterization of glycerol plasticized-pea starch/ZnO-carboxymethylcellulose sodium nanocomposites. Bioresource Technol. 100:2832-2841.

Zhang L., Ding Y., Povey M. and York D. 2008. ZnOnanofluids – a potential antibacterial agent. Prog. Nat. Sci. 18:939-944.

Zhang L., Jiang Y., Ding Y., Daskalakis N., Jeuken L., Povey M., O'Neill A. and York D. 2010. Mechanistic investigation into antibacterial behaviour of suspensions of ZnO nanoparticles against *E. coli.* J. Nanopart. Res. 12:1625-1636.

Unalan I.U, Cerri G., Marcuzzo E., Cozzolino C.A. and Farris S. 2014. Nanocomposite films and coatings using inorganic nanobuilding blocks (NBB): current applications and future opportunities in the food packaging sector. RSC advances 4(56):29393-29428.