

## Characterization of Semolina Protein Film with Incorporated Zinc Oxide Nano Rod Intended for Food Packaging

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This study intended to provide biopolymer films used as food packaging, which will result in reducing environmental pollution produced by the activities of synthetic food packaging. We used zinc oxide nanorods (ZnO-nr) and we prepared nanocomposite films by means of solvent casting. FTIR and SEM were employed to characterize the final films. SEM images revealed that ZnO-nr particles were homogeneously distributed throughout the film surface. The thermal, optical, and heat sealability properties of the films were also examined. Adding ZnO-nr significantly reduced oxygen permeability and heat sealability. The semolina films' UV absorbance was highly impacted by the degree of ZnO-nr addition. The nanocomposite films absorbed above 90% of the near infrared spectra. In addition, the zeta potential revealed the surface charge of ZnO-nr had a negative charge of about -33.9 mV.

### 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]. Not only do these edible films protect physically foods, they also prevent the mass transfer of aromas, oxygen, carbon dioxide, moisture, lipids, and flavors, into and from food products [Marcuzzo *et al.*, 2010]. Considering nutritive merits and superior features, protein-based biopolymers have received considerable attention regarding the development of edible films [Genadios, 2004]. These polymers are remarkable oxygen hurdles and they have certain mechanical properties to the films [Sothornvit *et al.*, 2009].

Different types of proteins are used as components of biodegradable packaging [Khwalidia *et al.*, 2010]. Of these proteins, the wheat protein is a potential constituent of packaging materials due to its expense effectiveness, renewability, biodegradability, and favorable film-forming and cohesive/adhesive features [Türe *et al.*, 2013]. Semolina is considered as a type of wheat with flour rich in high gluten content [Quaglia, 1998;

Jafarzadeh *et al.*, 2016]. The gluten strengthens the nutrient value of edible films. Semolina grain is highly hard, light colored, translucent, and displays antioxidant activities. Further, semolina extracts prevent radical-prompted liposome lipid peroxidation. They also show radical cation-scavenging performance [Onyeneho & Hettiarachchy, 1992; Dufresne, 2006; Jafarzadeh *et al.*, 2016].

Nevertheless, the poor water and mechanical sensitivity of biopolymers restrict their application in the activities of food packaging. Nanomaterials, which reinforce biopolymers through the formation of nanocomposites, have been recently employed to overcome these limitations [Pettersson & Oksman, 2006]. The nanoparticles used in the biopolymer matrix remarkably strengthen the physicochemical, thermal, optical properties of nanocomposites in comparison with pure biopolymer [Kovacevic *et al.*, 2008].

With respect to their enormous particular surface area and high energy of surface, nano-fillers display good interfacial relationship with polymer branches and as a result significantly promote polymer properties [Kumar & Singh, 2008]. Zinc oxide (ZnO) has been broadly used as a functional filler in UV absorbers in cosmetics, pharmaceuticals, pigments and coating materials [Li *et al.*, 2009; Li *et al.*, 2010; Rajendra *et al.*, 2010]. ZnO nanoparticle is able to potentially obstruct infectious diseases *via* the antimicrobial impacts of ZnO

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[Yu *et al.*, 2004; Rajendra *et al.*, 2010; Zhang *et al.*, 2008]. The morphology, size, composition, crystallinity and shape of ZnO nanoparticles have an effect on their intrinsic properties [Lin *et al.*, 2009; Shahrom & Abdullah, 2007]. Lin *et al.* [2009] stated that ZnO nanorods (ZnO-nr) display maximum UV-absorption performance.

Semolina has good properties for edible film production and ZnO-nr are powerful materials in enhancing the physicochemical, thermal, and hurdles properties of semolina. In addition to these drawbacks, ZnO-nr-reinforced semolina has not been widely understood. In the current study, we proposed that by adding ZnO-nr with low-concentration into semolina films we can improve the thermal and barrier properties of films and that the final biopolymeric films display UV-blocking properties. With their desirable antioxidant activities, the suggested films could be utilized as food packaging particularly for cheese. The current study took advantage of ZnO-nr as fillers to make semolina film bionanocomposites ready and described the physicochemical, morphology, thermal and barrier properties of the prepared films.

## MATERIALS AND METHODS

### 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 & Abdullah [2007].

### Preparation of bionanocomposite films

Semolina flour (4 g) was dispersed by magnetic stirring in 80 mL of distilled water at room temperature, and the pH of the dispersion was adjusted to 8 with 1 mol NaOH. Similarly, various concentrations of ZnO powder (1%, 2%, 3%, 4%, and 5%; w/w of total solid) and 2 g of a sorbitol and glycerol (3:1) mixture were 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). Subsequently, the dispersions of semolina flour and ZnO-nr plasticizer were mixed and stirred at 90°C for 1 h. For the preparation of nanocomposite films, the homogenous mixtures were poured into plates and the solvents were allowed to evaporate at room temperature for 24 h.

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.

### Oxygen permeability (OP)

OP was determined using Mocon Oxtran 2/21 System (Minneapolis, MN, USA) at 25°C and 55±1% RH in accordance with the ASTM Standard Method D3985–05 [ASTM,

2005]. The films were placed on an aluminum foil mask that allowed an exposure area of 5 cm<sup>2</sup>. Three replicates of each film were evaluated.

### Heat seal strength measurement

In order to seal the two parts of film samples together, an Impulse Auto Sealer was utilized (Mercier Corporation, ME-455A1, Taipei, Taiwan). The machine was also exploited in the manipulation of Pressure and Heat. The highest factor of heat seal was previously measured. This was done to enable us to generate the maximum seal strength in the used samples. With this regard, the specified heat seal temperature, dwell time, and pressure were kept at 110±5°C, 0.85 s, and 1.8×10<sup>3</sup> Pa, respectively. In an attempt to inspect the needed tensile force in keeping the seal apart by the crosshead speed of 1 mm/s and the preliminary distance of 25 mm, we made use of TA XT Plus Texture Analyzer (Stable Micro System). Keeping at the angle of 180°, the peeled samples were attached at non-heat seal section. In order to gauge the strength of the seal (utmost seal/load length), the optimal load obtained was taken into consideration. The valuation of the peel seal was executed after 48 h of the heat sealing operation. The average value of the number of twelve samples, keeping in similar conditions, was determined. The calculation of the seal strength was obtained using the following method:

$$\text{Seal strength} = \text{peak force} / \text{film width} \quad (1)$$

Newton/meter (N/m) was stated for the seal strength to demonstrate the expected maximum force needed to trigger the seal to split.

### Fourier transform infrared spectroscopy (FT-IR)

To determine the Fourier Transform Infrared Spectroscopy (FTIR) range of the designated films, FTIR spectrometer (Thermo Scientific, Madison, USA) was exploited by means of an attenuated total reflection (ATR) at the temperature of 25°C. After placing the films onto the crystal cells, they were fixed into the FTIR spectrometer's mount. 32 scans at 4 cm<sup>-1</sup> resolution were exploited in the process of collecting the 650–4000 cm<sup>-1</sup> ranged spectra with automatic signal gain. They were also ratioed at the temperature of 25°C adjacent to a background spectrum which was recorded from the empty clean cell. The OPUS 3.0 (Bruker, Ettlingen, Germany) was employed as the data gathering programme for the purpose of analyzing the spectral data. The baseline correction and normalization of the spectra was carried out prior to the analysis of data.

### Optical properties

We studied the 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.

### Decomposition temperature

The samples (~15 mg) were scanned in a thermogravimetric analyzer (TGA-1, Perkin Elmer, Massachusetts, USA)

from 40°C to 800°C at a rate of 10°C/min in a nitrogen environment [Nuthong *et al.*, 2009].

### 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. In addition, energy-dispersive X-ray spectroscopy (EDX) was conducted under 15 kV incident electron energy.

### Zeta potential

The zeta potential of ZnO-nr was determined using Zeta sizer Nano-ZS90 (Malvern Instruments). The analysis was performed at a scattering angle of 90° at a temperature of 25°C using samples diluted to different intensity concentration with deionized distilled water.

### Statistical analysis

Experiments were performed in triplicate (n=3) with three different lots of film samples and a completely randomized design (CRD) was used. ANOVA and Tukey's post-hoc tests were used to evaluate the mean values of the physical, barrier and thermal properties of the prepared semolina films at the 5% significance level. Statistical analysis was conducted using SPSS version 22.0.

## RESULTS AND DISCUSSION

### Oxygen permeability

OP has been the most widely investigated transport property of edible polymer films. As a matter of fact, diverse factors influence the transport property of gases through polymer films. These properties include, according to Sanchez-Garcia *et al.* [2008], such properties as their path's tortuosity through the structure of the polymer; the extent to which they are exfoliated or dispersed; the properties of the filler in terms of the type, content, orientation and aspect ratio; the crystallinity of the induced filler; immobilization of polymer chain; and the propensity and retention of solvent in the induced filler. Various studies, for example Padua & Wang [2002], Tharanathan [2003], and Hong & Krochta [2003], have shown that due to the existence of polar interactions, an excellent OP properties can be observed in films which are produced from plant-based protein polymers.

The highest content of gluten can be found in semolina flour among the numerous types of protein-rich flours available. The formation of film is facilitated through the impartation of integrity due to the flexible and cohesive properties of gluten. Moreover, the main components of gluten are gliadins and glutenins which contain low-molecular-weight and high-molecular-weight proteins respectively. Accordingly, as maintained by Wittaya [2012], films are strengthened by high-purity gluten which in turn are useful barriers to oxygen.

As can be seen in Table 1, the increase in the content of ZnO-nr significantly decreases the OP. The OP and bar-

TABLE 1. Permeability to oxygen of semolina nanocomposite films.

ZnO-nr (% w/w)	OP cc mil/(m <sup>2</sup> ·day·atm)
Control	2.04±0.04 <sup>a</sup>
1%	1.13±0.02 <sup>b</sup>
2%	1.01±0.03 <sup>c</sup>
3%	0.90±0.02 <sup>d</sup>
4%	0.82±0.02 <sup>c</sup>
5%	0.71±0.10 <sup>f</sup>

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

rier property are largely reduced and improved respectively, in the semolina film with ZnO-nr (5%). A ca. 65% reduction can be noticed in films containing 5% ZnO-nr. It is expected that for the diffusion of the oxygen molecules, a tortuous pathway is created by the nanoparticles fused into the matrix. It can also be argued that the reduction seen in the permeability coefficients can be interpreted as the passage of diffusing gases through this long path [Bourtoom & Chinnan, 2008]. This is conversely in line with the finding of studies such as Bae *et al.* [2009] and Türe *et al.* [2013].

### Heat seal strength

Heat sealability is a critical property of films used in packaging. Figure 1 shows the seal strengths of the nanocomposite films. The control films exhibited the strongest seal strength among all the films prepared. However, the seal strength weakened with increasing ZnO-nr content. During sealing, two pieces of biofilms were inserted between two heated plates. We hypothesized that the nanoparticles in the protein polymer matrix possibly block the interaction between the two melted surfaces of the films during heat sealing. Our study revealed that the interactions occurring between the active groups of semolina were reduced by the nanoparticles inside the polymer matrix, which consequently weakened the seal strength of the bionanocomposite films; in addition, the reduced seal strength may be attributed to the reduction

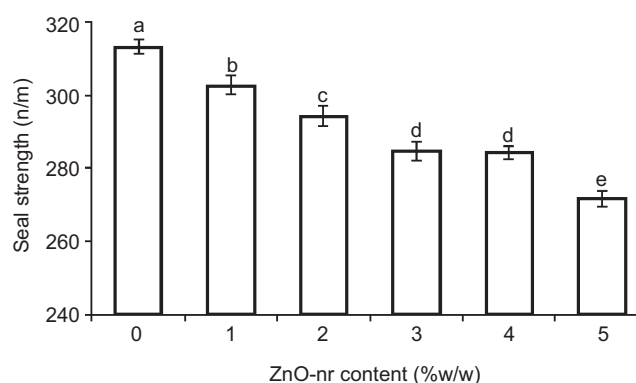


FIGURE 1. Effects of ZnO-nr contents on the heat sealability of semolina nanocomposite films. The bars indicate mean (n = 5) ± SD. Different letters on the bars represent significant difference among the films at the 5% level of probability.

TABLE 2. Light transmittance values of semolina films as affected by ZnO-nr incorporation.

ZnO-nr (%w/w)	Light transmittance (%) level							
	200	280	350	400	500	600	700	800
Control	0	1.01	14.75	18.67	24.84	27.28	29.24	31.12
1%	0	0.33	3.479	3.955	10.413	16.602	22.29	27.368
2%	0	0.098	0.928	1.294	4.883	9.595	14.856	20.325
3%	0	0	0.061	0.366	1.367	2.905	5.139	7.959
4%	0	0	0.061	0.293	0.793	1.501	2.71	4.48
5%	0	0	0	0.146	0.439	0.671	1.038	1.66

in the moisture content and flexibility of the films with increasing ZnO-nr content [Abdorreza *et al.*, 2011]. Heat seal strength is usually used to evaluate the opening properties of the sealed package. High seal strength is desirable to realize tightly sealed food packaging, whereas low seal strength is suitable to obtain easy-open packaging.

### Optical properties

In order to maintain the quality of food, the optical properties of biopolymer films are of highly significance in packaging food. This is due to the fact that light protection is of high priority when regarding the food quality.

According to 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 accordingly the nutrients shortfall. There are three zones identified for UV region: UVC (180–280 nm), UVB (280–320 nm), and UVA (320–400 nm). By means of a UV-vis spectrophotometer, the absorbance of biopolymer film properties and their nanocomposite were measured, the result of which can be seen in Figure 2 and Table 2. Not possessing nanoparticles, the semolina films as the control element exhibited an acceptable quality against 180–280 nm range UV. As discussed by Arfat *et al.* [2014], the existence of aromatic amino acids in high levels has resulted the protein based films to be commonly considered as great barriers against UV.

A clear peak of absorption was observed by nanocomposite films. An increase in the content of ZnO-nr resulted in an

increase in the peak of absorption. Semolina/ZnO-nr composite's absorption was at its peak at 380 nm. The blue-shift phenomenon was clearly seen at these bionanocomposites' peak of absorption. Due to the effect of quantum confinement, the ZnO-nr would increase, the result of which is the emission of ZnO-nr biocomposites and accordingly the blue shift phenomenon [Subramani *et al.*, 2007]. CMC/ZnO nanocomposite films revealed the similar results as well [Yu *et al.*, 2009].

### FTIR analysis

The vibration properties of synthesized materials can be noticeably examined through the usage of FTIR spectroscopy. The properties that influence the absorption peak and band positions are the structure, the chemical composition as well as morphology of thin films. There are four regions viewed for FTIR spectroscopy which extends between: 1) ranges from 4,000 to 2,500, 2) ranges from 2,500 to 2,000, 3) ranges from 2,000 to 1,500 and 4) ranges from 1,500 to 400. In condition of a peak of 4,000 to 2,500 for the spectrum, a consistency of peak with absorption can be noticed stimulated by C-H, O-H and N-H single bonds.

Alternatively, a peak of spectrum ranging from 2,500 to 2,000, the consistency can be observed for the peak with triple-bond induced absorption. This agreement would be observed with double bond absorption, including C=N, C=O and C=C, when the spectrum peak ranges from 2,000 to 1,500. The semolina-based FT-IR spectra and the semolina nanocomposite films are presented in Figure 3. Ranging from

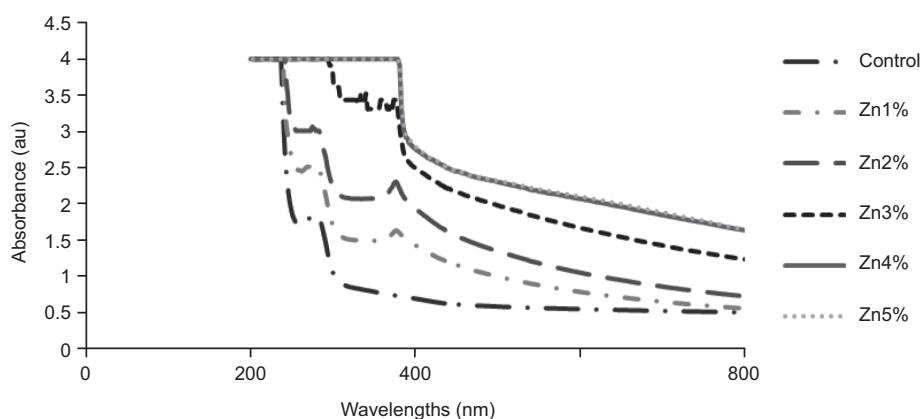


FIGURE 2. UV-vis absorbance of semolina nanocomposite films at 25°C.



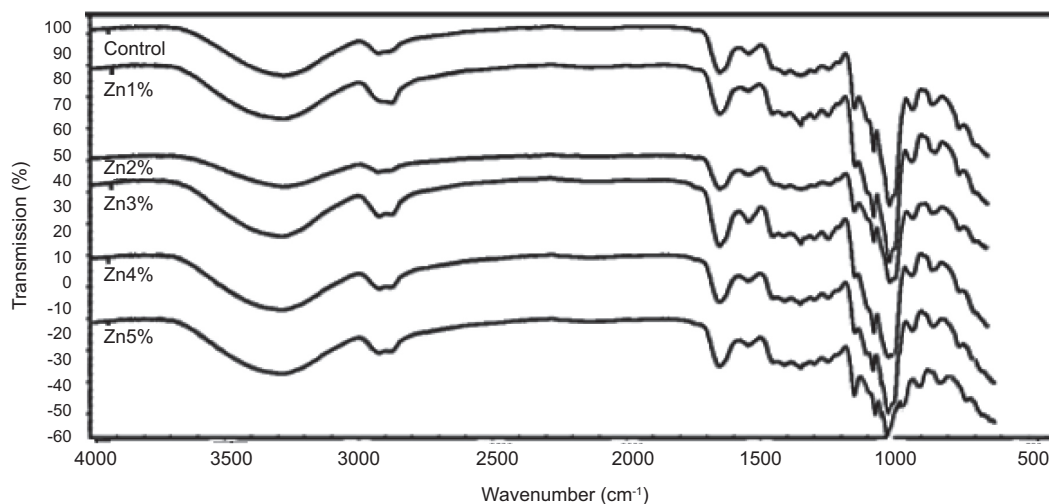


FIGURE 3. FT-IR transmittance spectra of semolina nanocomposite films at 25°C.

3287  $\text{cm}^{-1}$  to 664  $\text{cm}^{-1}$ , different properties of the peaks were shown for the spectrum of nano-composite film. The peaks of absorption ranging from 400 to 700  $\text{cm}^{-1}$  could be ascribed to stretching modes of all ZnO samples [Djaja *et al.*, 2013]. The vibration of ZnO at 664  $\text{cm}^{-1}$  was the determinant factor for the peak of absorption in the present research. There was found no new functional group after the fusion of nano-composite, which could be perceived as a physical contact between nanocomposite and film matrix.

**Scanning electron microscopy (SEM), EDX and TEM**

SEM is the most widely applied technique to characterize the shape, size, morphology, and porosity of matrices. Figure 4 shows the SEM images and EDX spectra of the semolina films and ZnO-nr-reinforced films. TEM also revealed that the nanorods were cylindrical with hexagonal cross section (Figure 4). The control film exhibited a smooth and compact surface morphology, whereas the nanocomposite films showed a slightly rough surface. SEM images revealed that

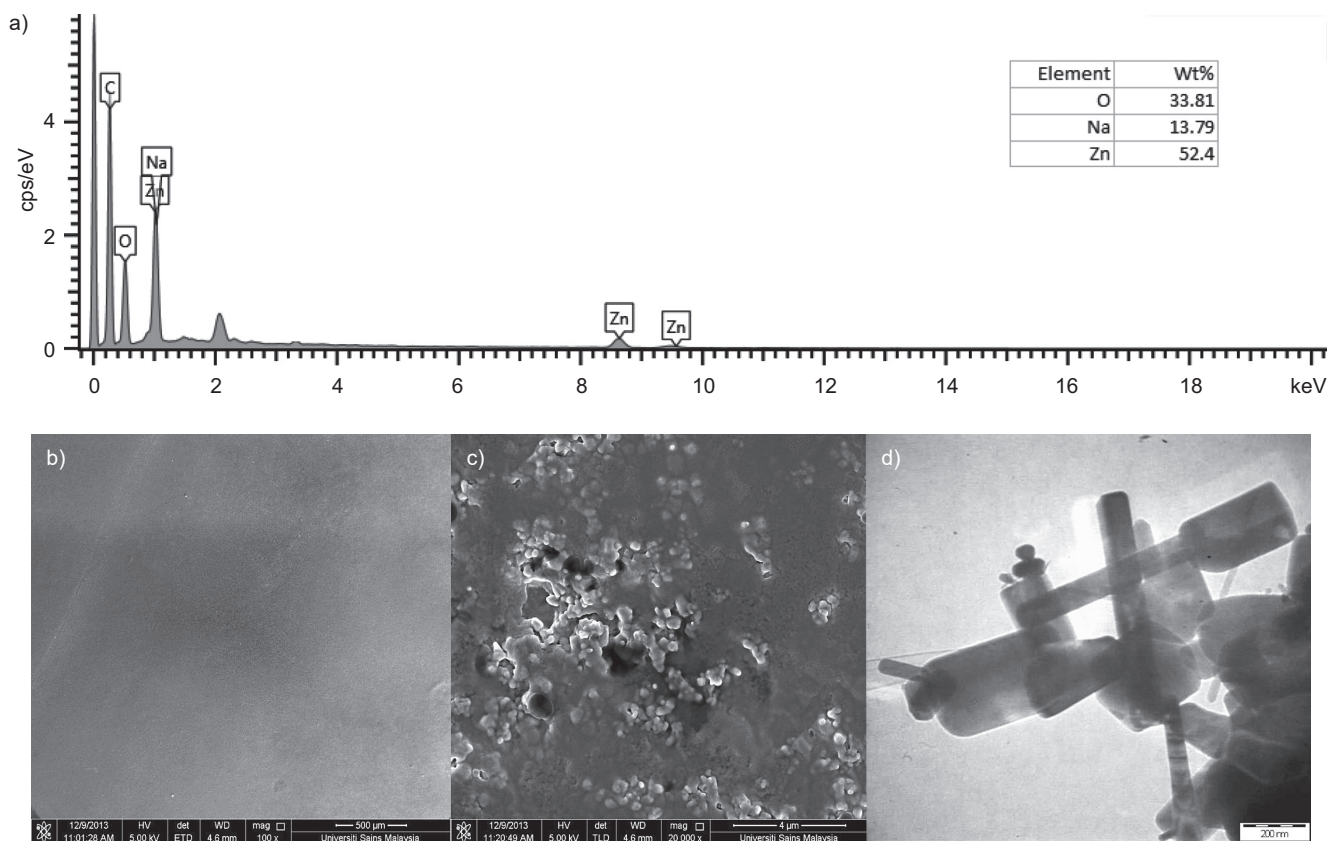


FIGURE 4. (a) EDX spectrum, (b)FESEM micrograph of pure semolina film surface, and (c) ZnO-nr-reinforced semolina film surface, (d) TEM micrograph of ZnO-nr.

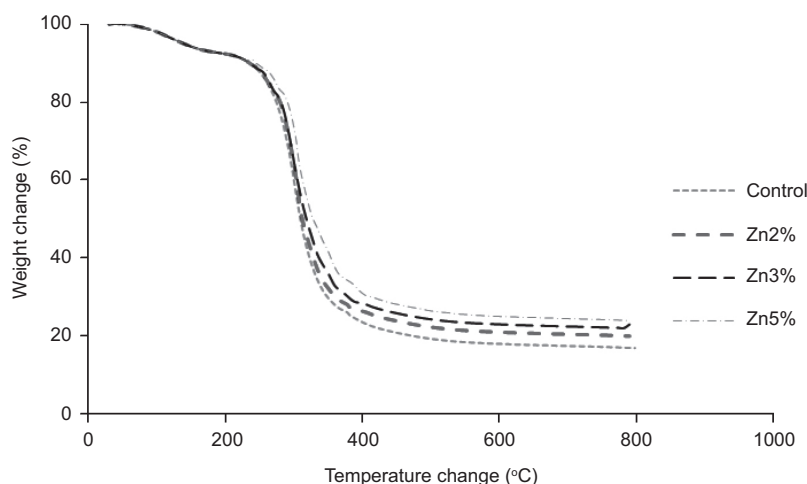


FIGURE 5. Decomposition curves of semolina films compared with ZnO-nr-reinforced films.

ZnO-nr particles were homogeneously 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. Figure 4 illustrates the EDX spectrum of semolina/ ZnO-nr films. If ZnO-nr content was increased, their signals could be detected. As shown in Figure 4, C, Zn, O and Na elements were identified.

#### TGA

The control biopolymer's thermal stability and the associated nanocomposite films are displayed in Figure 5. Considering semolina and ZnO-nr-reinforced films, a slight variation in the temperature of decomposition was discovered by using TGA thermogram. As can be seen in Figure 5, there is approximately 18%, 22% and 5% of residue for the control and the ZnO-nr-reinforced film. Nevertheless, the divergence in the temperature of films decomposition was insignificant, which could be the result of an insignificant volume of the added nanoparticles. However, contrary to this finding, the study by Zou & Yoshida [2010] indicates an increase in the temperature of polymeric films decomposition and difference in the volume of nitrogen residue by adding nanoparticle.

#### Zeta potential-surface charge

The stability of particle in suspension has a great influence on the surface charge or Zeta potential which is done through the electrostatic repulsion among particles. In other words, the higher repulsion between particles would lead to a higher Zeta potential. A surface charge is possessed by nanoparticles through which a thin layer of opposite charge ions is attracted to the surface of the nanoparticle. As the solution causes this double layer of ions to diffuse with the nanoparticle to diffuse, it moves with the nanoparticle. The particles' Zeta potential is the electric potential placed at the edge of the double layer. This electric potential normally has the volume between +100 mV to -100 mV. As can be observed in Figure 6, a negative charge of approximately -33.9 mV can be valued for ZnO-nr surface. Higher measures of stability can also be detected for nanoparticles with Zeta Potential of the values higher than +25 mV or smaller than -25 mV.

#### 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

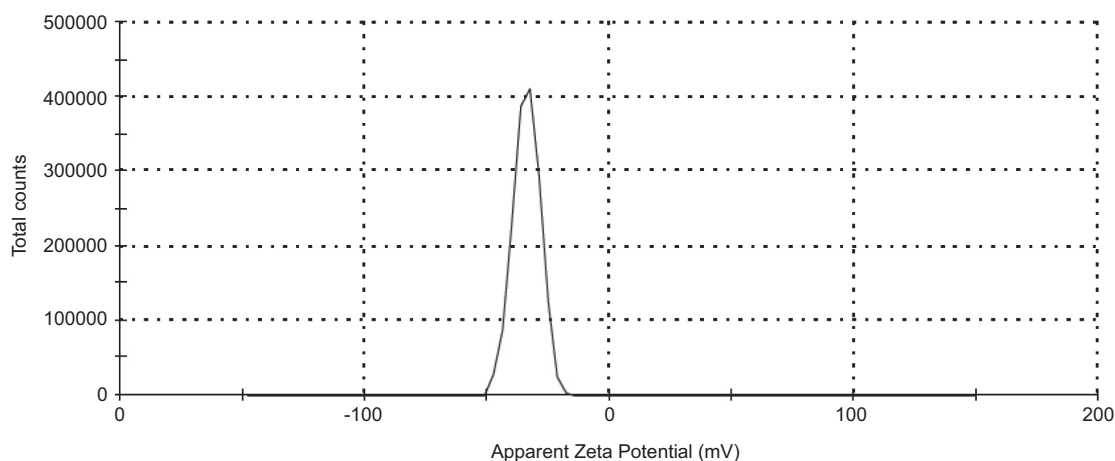


FIGURE 6. Zeta potential of ZnO-nr.

a polymeric matrix including its great accessibility in nature, biodegradability, low expenditure, and great gluten content, which enhance the biopolymer films' nutritional properties.

ZnO-nr played a crucial role in improving the physical properties of semolina-based biocomposites. Having incorporated low degree of ZnO-nr fillers, important differences were witnessed in the film properties, especially in barrier and UV support activities. The optical property of bionanocomposites showed that the nanocomposite films had absorbed above 90% of the near infrared spectra *via* adding small degree of ZnO-nr to the biopolymer matrix. The Zeta potential test showed that the surface charge of ZnO-nr was -33.9 mV, and that the higher the surface charge was the higher was the repulsion and dispersion between particles. The FTIR spectra displayed the physical relationship between ZnO-nr and the semolina. The crystal facets also maximized the UV absorption. The present findings stressed that the biopolymer-based nanocomposite films are environment friendly in films 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.

#### RESEARCH FUNDING

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#### CONFLICT OF INTEREST

Author declare no conflict of interest.

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