Influence of ZnO nanoparticles and stearic acid on physical, mechanical and structural properties of cassava starch-based bionanocomposite edible films

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Abstract

Bionanocomposite consists of natural polymers and the filler of nanoparticles. The aim of this study was to evaluate the effect of zinc oxide (ZnO) nanoparticles (ZnO-NP) and stearic acid on characteristics of cassava starch (CS)-based bionanocomposite edible films. The experiment had 3x2 factorial experiment design (ZnO-NP: 0, 1, 2% and stearic acid: 0, 30% by weight of CS). Glycerol and tween 80 were used as the plasticizer and emulsifier respectively. The results showed the incorporation of ZnO-NP increased the thickness, color difference (ΔE), tensile strength and decrease elongation, water vapor transmission rate (WVTR) and crystalline percentage. While the addition of stearic acid increased the thickness, ΔE and decreased tensile strength, elongation, WVTR, crystalline percentage compared to the cassava starch-based film. ZnO-NP was not observed clearly by using SEM and successfully trapped and coated by starch and stearic acid matrix. XRD showed an increase with the addition of 2% ZnO-NP in the polymers in the both cassava starch and cassava starch + stearic acid films. The C-H and C=O stretching was more intense for film with the addition of stearic acid compared to films without stearic acid by using FTIR. The improvement in mechanical and physical properties were achieved at CS + 2% ZnO-NP and CS + 2% ZnO -NP + 30% stearic acid respectively.

Introduction

Edible films have gained great attentions as an alternative biopackaging because of their advantages over synthetic films petroleum based polymers (Vartiainen *et al.*, 2010). The main advantage of edible films is that they can be consumed with the packaged products. In addition, edible films offer many advantages such as nontoxicity, ecofriendly, biocompatibility, esthetic appearance, water vapor permeability, and low cost (Han, 2000; Abdou and Sorour, 2014). Components used for the preparation of edible films including proteins, lipids, cellulose derivatives, starch, and other components that are generally recognized as safe substances (GRAS). Starch is still one of the most promising biopolymers because it is abundantly available and inexpensive (Ma *et al.*, 2009). It consists of two chain kinds: amylopectin and amylose which is thus a good biopolymers matrix.

Among several kinds of starch, cassava starch has a great potential for edible film production. Indonesia is the second world's largest producer of cassava after Nigeria and above other top producers including Thailand, the Democratic republic of Congo and Angola (Asante-Pok, 2013). Starch has a good barrier for gases but provide a minimal barrier to water vapor due to the hydrophilicity properties of its polymers. One of the most common alternatives to create hydrocolloid films less permeable is to incorporate lipid additives including different fatty acids, waxes and vegetable oils (Yang and Paulson, 2000; Srinivasa *et al*., 2007).

To improve the edible film properties, the incorporation of materials such as lipids has been applied as an alternative. The addition of long-chain fatty acids such as stearic acid can be used in edible film manufacturing because it has low water vapor permeability. The presence of fatty acids promoted an increase in hydrophobicity of samples, characterized by lower moisture uptake, solubility, water vapor permeability (Chana-Thaworn *et al*., 2011; Amini *et al.*, 2015). Previous researchers have studied that the adding of stearic acids at the amount of 20% - 40% (w/w) into fish water soluble proteins and stearic acids at the amount of 30% (w/w) into

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methyl cellulose/corn zein might provide a decrease in water vapor transmission rate value (Park *et al.*, 1994; Tanaka *et al.*, 2001).

Recently, research on edible films has evolved into the development of bionanocomposite. Bionanocomposite is a new generation of nanocomposite which consists of natural polymers and the filler of nanoparticles. The nanoparticles incorporation into biopolymers may provide new opportunities for improving their properties such as barrier capability and mechanical strength (Sorrentino *et al.*, 2007; Shi and Gunasekaran, 2008). Zinc oxide nanoparticles as a polymer filler agent has been interesting material in the food field because ZnO is a safe chemical substance and has been used as a source for zinc supplement and fortification. (Shi and Gunasekaran, 2008; Suyatma *et al.*, 2014). Previous researchers have studied the incorporation of ZnO-NP at the amount of 0.5 - 5.0% (w/w) in fabricating bionanocomposite films from pea starch, pectin, semolina protein respectively and suggested to use ZnO-NPs at the amount of 2% (w/w) for the best improvement in mechanical properties (Ma *et al.*, 2009; Suyatma *et al.*, 2014; Jafarzadeh *et al.*, 2017).

The formulation of bionanocomposite edible films of this study can be applied as free-standing films or food coatings, particularly for postharvest product. It might provide an alternative method in maintaining prolonged of shelf life and quality of postharvest product such as minimally processed fruits and whole fruits. Moreover, bionanocomposites represent a new alternative to improve its antimicrobial potency which is not further discussed in this study. The aim of this study was to evaluate the effect of ZnO-NP and stearic acid on characteristics of cassava starch-based edible films.

Materials and Methods

Materials

Cassava starch was obtained from local starch industry in Ciluar, Bogor (Indonesia), stearic acid was obtained from local market and ZnO-NP with an average particle size of 20 ± 5 nm was purchased from Wako Pure Chemical Industries Ltd (Japan). The emulsifier and plasticizer used were tween 80 and glycerol respectively purchased from Merck (Germany).

Preparation of bionanocomposite edible films

The bionanocomposite edible films were prepared by dispersing ZnO-NP (0, 1 and 2% by weight of CS) in 500 ml distilled water using ultraturrax 15000 rpm for 10 mins at room temperature. The ZnO-NP

solutions were added cassava starch 10g + glycerol 30% by weight of CS slowly into prepared ZnO-NP solutions and blended with constant stirring until they dissolved completely. The tween 80 75% + stearic acid 0 and 30% by weight of CS were added slowly into the solutions and blended with constant stirring until they dissolved completely. Then the mixture was heated to 90°C with continuous stirring for 10 mins before it was cooled to room temperature. The final solutions (30 ml) were poured into casting plates with a 80 mm diameter and placed in an air-circulating oven at 50oC until dry (about 14 - 15 hr). The cast films were cooled to ambient temperature before peeling the films off the plates and kept in a plastic bag. The different formulas of the films were as follows: L0Z0 (CS + 0% stearic acid w/w + 0% ZnO-NP w/w), L0Z1 (CS + 0% stearic acid w/w + 1% ZnO-NP w/w), L0Z2 (CS + 0% stearic acid w/w + 2% ZnO-NP w/w), L1Z0 (CS + 30% stearic acid w/w + 0% ZnO-NP w/w), L1Z1 (CS + 30% stearic acid w/w + 1% ZnO-NP w/w), L1Z2 (CS + 30% stearic acid w/w + 2% ZnO-NP w/w).

Determination of physical properties of edible films

Film thickness was determined with an accuracy of 0.01 ± 0.004 mm using a Micrometer Digital Kincrome at five random positions of the film sample. Three replicates of each sample were measured.

Color difference (ΔE) was measured using a Chroma Meter Minolta CR-300 based on the CIE color system, where color coordinates range from $L^* = 0$ (black) to $L^* = 100$ (white), $-a^*$ (greenness) to $+a^*$ (redness), and $-b^*$ (blueness) to $+b^*$ (yellowness). Before use, the chroma meter was calibrated to a standard white calibration plate ($L^* = 100$, $a^* = -0.23$, $b^* = 0.34$). Film specimens were placed on the surface of a standard white calibration plate. Three replicates of each sample were measured by taking an average of three readings from each film sample. Color difference was calculated by the following equation:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

Where ΔL^*, Δa^* and Δb^* are the color parameter values of the difference between color values of the sample and standard white plate that assumed a clear and transparent film.

Water vapor transmission rate (WVTR) was measured using ASTM D1249-90 method (1993). A film was cut in a circular shape with diameter of 30 mm and placed on the surface of the cups filled with silica gel and coated with paraffin wax around the cups circumference. The water vapor transmission rate of each film was measured at 25 ± 2°C and stored

in glass desiccators containing distilled water to provide 75% RH. The cups were taken out at different time intervals and weighed. Three replicates of each sample were measured. WVTR was calculated by dividing the difference of initial and end weight by the time of transfer for 24 hr multiplied the area exposed to water surface (m^2).

Determination of mechanical properties of edible films

Tensile strength and percent elongation of the films were analyzed according to ASTM D 638 - 99 (1999) using Microcomputer Controlled Universal Testing Machine (model WDW 5E of Time Group Inc, China). The film was cut into 2 cm x 7 cm. Initial grip was set at 17 mm with tensile speed of 20 mm/min. Dividing the maximum load by the specimen area of the film was calculated as tensile strength. The percent elongation was calculated from the maximum elongation during testing. This measurement was performed in three replicates of each sample. The tensile strength was calculated by the following equation:

$$\text{Tensile strength} = F/A$$

where F is the force maximum at rupture of the film in N; A is initial cross-section area of the film in mm^2.

The percent elongation was calculated by the following equation:

$$\% \text{ Elongation} = (L-L_o)/L_o \times 100$$

where L_o is initial gage length; L is the final length.

Determination of structural properties of edible films

Film samples were examined for surface characteristics using a scanning electron microscopy (SEM) model Zeiss EVO MA 10 (USA) operated at 10kV. Film samples were placed on bronze visualization section using double - side tape and the surface of films were coated with gold to enhance surface conductivity. All specimens were viewed in a scanning electron microscope and recorded at a magnification of 1000 x.

The crystalline structure of edible films was observed using X - ray diffractometer (XRD) model Maxima - X, XRD - 7000, Shimadzu (Japan). The spectra were recorded using Cu - Ka radiation operated at 40kV. The scanned range of theta degree (2θ) was from 3 - 60°.

The structural interactions of CS edible films incorporated with stearic acid and ZnO-NP were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR), Bruker Model Equinox 55 (Bruker Co., Ettlingen, Germany). The spectra were obtained at a resolution of $4cm^{-1}$ in the range 400 to $4000cm^{-1}$.

Statistical analysis

The experiment had 3 x 2 randomized factorial design (ZnO-NP: 0, 1, 2% and stearic acid: 0, 30% by weight of CS). The results were statistically evaluated by analysis of variance (ANOVA) using SPSS (Statistical Product and Service Solutions) version 16.0 and followed by Duncan's Multiple Range Test (DMRT) when needed, used to describe results at a significance level of $p < 0.05$.

Results and Discussion

Physical properties of edible films

Values of edible film thickness are ranging from 80.00 to 213.33 μm as shown in Table 1. Those values are still categorized as good films compared to Japanese Industrial Standard (1975) that maximum thickness value is 0.25 mm. The thickness of edible films increased but not significantly from incorporating ZnO-NP, while the addition of stearic acid concentration increased the thickness significantly ($p < 0.05$) and there were no interactions between both factors. In this study, the adding of stearic acid provides more blended solids in solution resulting in thicker films. Increased films thickness due to the base material effect can be related to the compound's unique colloidal features and the interaction between components (Galus and Lenart, 2013). The results are similar with the studies of the addition of palmitic acid in pectin-based edible films and incorporation of ZnO-NP in PVC films and gelatin polymers (Layuk *et al.*, 2002; Li *et al.*, 2010; Shankar *et al.*, 2015).

The consumer's perception of acceptability affected by color of the packaging (Bourtoom and Chinnan, 2008). Considering the important of transparency in edible film application as well as for containers, the parameter color *(L*,a*,b*)* of this study was converted to be total color difference. ΔE Cassava strach films without the incorporation of ZnO-NP appeared clear and transparent. Appearance of the edible film color with the addition of stearic acid affected its higher transparency. The ΔE of edible films are reported in Table 1. The lowest ΔE mean value was cassava starch film without incorporation ZnO-NP and stearic acid (Δ*E*= 3.06). As ZnO-NP and stearic acid concentration increased, ΔE value increased significantly ($p < 0.05$) with the highest ΔE observed at addition of 2% ZnO-NP

Table 1. Physical properties of edible films

Sample	Stearic acid (%)	ZnO-NP (%)	Thickness (μm)	ΔE	WVTR (g/m²·24h)
L0Z0	0	0	80.00 ± 5.77 [Ab]	3.06 ± 1.01 [Cb]	43.28 ± 0.82 [Aa]
L0Z1		1	82.22 ± 7.70 [Ab]	5.36 ± 1.06 [Bb]	41.18 ± 2.53 [Aa]
L0Z2		2	83.33 ± 16.67 [Ab]	7.47 ± 1.88 [Ab]	40.72 ± 2.56 [Aa]
L1Z0	30	0	206.67 ± 32.15 [Aa]	8.24 ± 0.56 [Ca]	36.33 ± 1.46 [Ab]
L1Z1		1	210.00 ± 45.83 [Aa]	10.24 ± 1.37 [Ba]	35.47 ± 1.29 [Ab]
L1Z2		2	213.33 ± 50.33 [Aa]	11.72 ± 0.67 [Aa]	35.23 ± 1.69 [Ab]

Means followed by different letters (small: among different stearic acid concentration; capital: among different ZnO-NP concentration) indicate statistically significant differences (p < 0.05).

and stearic acid 30% (ΔE= 11.72) and there were no interactions between factors. By increasing ZnO-NP concentration, the value of ΔE also increased due to their turbidity. Moreover, it was due to the light-scattering effect of the emulsion that was formed by the stearic acid and starch polymers. Similarly, it has been reported that the transparency of hydrocolloid films decrease as a function of lipid incorporation (Yang and Paulson, 2000; Jimenez *et al.*, 2010; Muscat *et al.*, 2013). The same results reported that total color difference value of high amylose starch-glycerol films and gelatin films increased profoundly after incorporation of ZnO-NP (Shankar *et al.*, 2015). The color changes for composites were considered to be visually perceptible when *ΔE* > 1 and clinically acceptable when ΔE < 3.3 (Ruyter *et al.*, 1987; Seghi *et al.*, 1989).

The WVTR is an important edible film characteristic because of the role of water in deteriorative reactions in foods (Ariaii *et al.*, 2014). Therefore, WVTR should be improved as low as possible. The results of WVTR edible films are shown in Table 1. The WVTR value of cassava starch film without incorporation ZnO-NP and stearic acid was 43.28 g/m²·24 h. Incorporating of ZnO-NP into cassava strach based film formulation at level of 1 and 2% reduced WVTR value but not significantly, different with the addition of stearic acid 30% which is able to reduce WVTR significantly (p < 0.05) and there were no interactions between factors. Cassava starch used as main matrix films are relatively hydrophilic, but stearic acid is more hydrophobic. The hydrophilic based compound is known to enhance the water vapor permeability of hydrocolloid films because of favorable to adsorption and desorption of water molecules (Chana-Thaworn *et al.*, 2011). The incorporation of stearic acid into starch matrix can improve the WVTR by increasing the hydrophobic compound in the edible films. Moreover, the filler of ZnO-NP is able to enhance polymers barrier
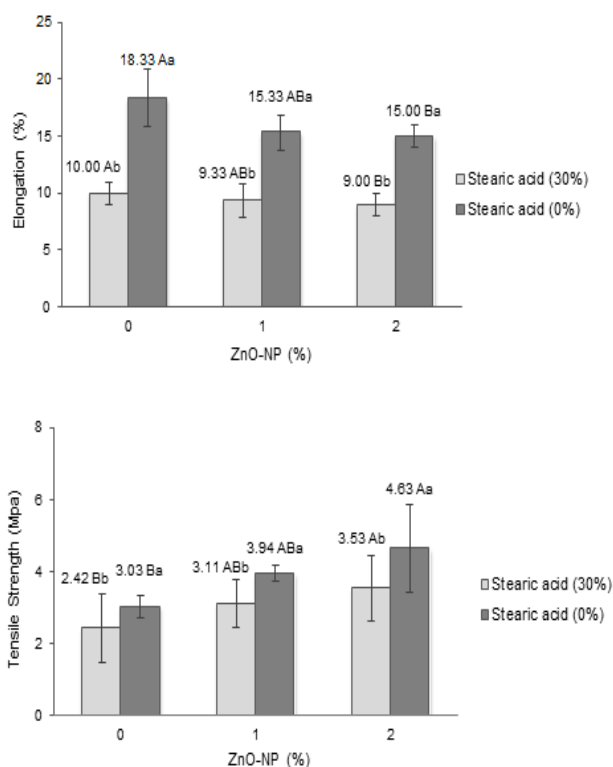

Figure 1. Mechanical properties of edible films. Means followed by different letters (small:among different stearic acid concentration; capital: among different ZnO-NP concentration) indicate statistically significant differences (p < 0.05).

properties by tortuous pathway (Duncan, 2011). However, the WVTR values are not able to meet a good film characteristic. Japanese Industrial Standard (1975) required the maximum WVTR value of good film is 10 g/m²·24h.

Mechanical properties of edible films

Mechanical properties show the potency of edible film to protect the integrity of foods. The ideal film should be resistant to breakage and flexible. Figure 1 shows the mechanical properties of edible films. Value of tensile strength and elongation films are ranging from 2.42 to 4.63 Mpa and 9.00 to 18.33%
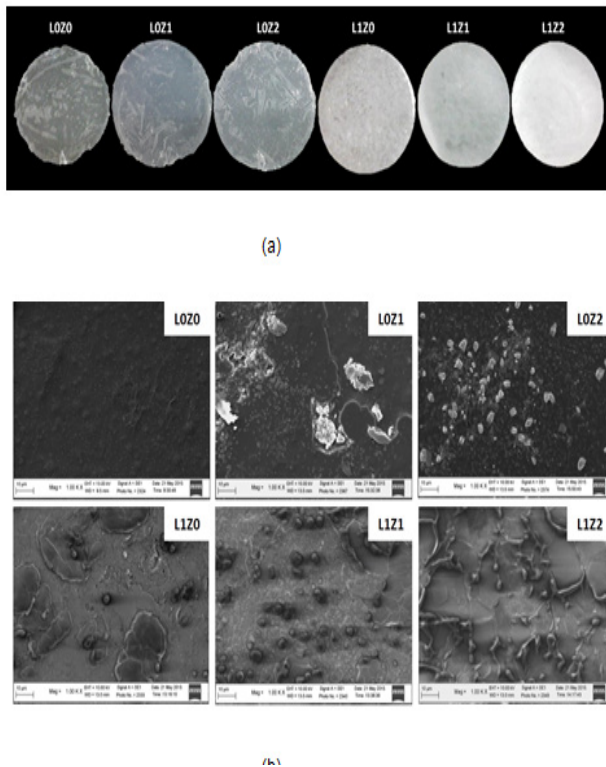
(a)

(b)

Figure 2. (a) Visual characteristic and (b) Scanning electron micrographs of edible films at a magnification 1000x.

respectively. Those mechanical properties are not able to reach Japanese Industrial Standard (1975) for elongation. It stated the minimum of tensile strength and elongation are 3.92 Mpa and 70% respectively. Statistically, incorporation of ZnO-NP 2% into cassava starch-based films increased tensile strength and decreased elongation values significantly (p < 0.05). While the addition of stearic acid decreased tensile strength and elongation values significantly (p < 0.05). There were no interactions between factors both tensile strength and elongation. The same result was found by Colla *et al*. (2006) that the addition of stearic acid into *Amaranthus cruentus* flour-based edible films had negative effects on puncture force and tensile strength. This could be related to interactions between polymer chains and fatty acid which interfere in intermolecular bonds, so that providing in matrix discontinuities (Jimenez *et al.*, 2010; Cerqueira *et al.*, 2012). Moreover, there was a significantly different in both tensile strength and percent elongation of edible films containing ZnO-NP at level 2%. This result is in a good agreement with some studies which found that the improvement of nanofiller materials in mechanical properties were generally achieved at low loads (Ma *et al.*, 2009; Arora and Padua, 2010; Suyatma *et al.*, 2014). The higher tensile strength of the nanocomposite films may also be explained by the increase of contact area between matrix polymer and ZnO-NP, and the ability
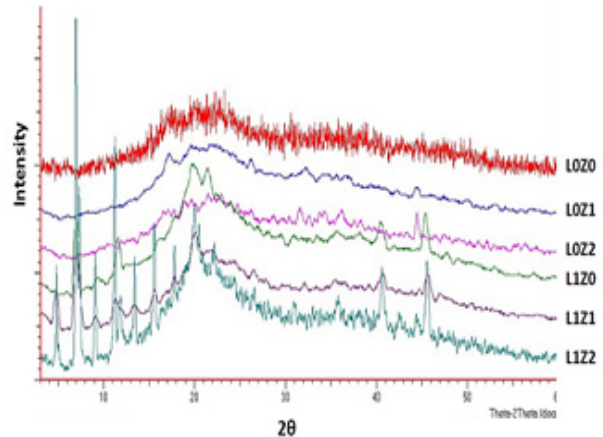

Figure 3. X-ray patterns of edible films

of ZnO-NP to fill the gap beetween polymer chain as well as limiting the matix movements (Li *et al*., 2009; Rhim and Wang, 2013). The best improvement in mechanical properties achieved at cassava starch + 2% ZnO-NP with the highest of tensile strength value and without too much lost in percent elongation.

Structural properties of edible films

Figure 2a and 2b showed the visual cast bionanocomposite edible films and the scanning electron microscopy micrographs respectively. Figure 2a indicated all of dried films had smooth surface, flat and without cracks. Scanning electron microscopy micrographs was used to verify and assure the presence of ZnO-NP in the edible films. Moreover, it was used to observe the microstructure of the film surface. Cassava starch - based film without the incorporation both ZnO-NP and stearic acid (L0Z0) was relatively compact and the film surface has a smooth contour without cracks. L0Z1 and L0Z2 represent cassava starch films containing ZnO-NP 1 and 2%. Microstructure surface of L0Z1 and L0Z2 were relatively rough and cracked. The particles seemed on the surface both L0Z1 nd L0Z2 were suggested as aggregated ZnO-NP. It was supported by Shi and Gunasekaran (2008) that ZnO-NP easily agglomerate in aqueous solution. All films with the addition stearic acid indicated closed structure and irregular surface. Moreover, ZnO-NP were not clearly observed in the microstructure both L1Z1 and L1Z2. It showed that ZnO-NP were successfully trapped and coated by starch and stearic acid matrix.

X-ray patterns help to find out whether a material is crystalline or amorphous. X-ray diffractograms of edible films are shown in Figure 3. The main diffraction peaks of cassava starch (2θ = 12.7, 17.2, 18.23, 22.34 and 22.6°) present in X-ray diffraction pattern. Whereas ZnO-NP peaks were 2θ = 19.65,
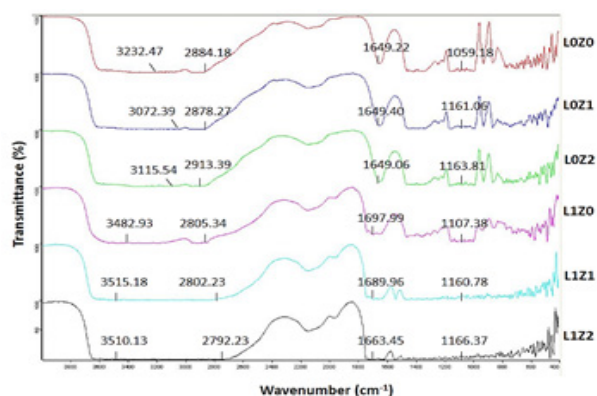
Figure 4. FTIR spectra of edible films

24.04, 31.79, 34.35, 36.19, 47.41, 56.38º and stearic acid peaks were 2θ = 7.05, 20.13, 21.33, 23.98º. However, the ZnO-NP peak intensities were not shown clearly because it was added in very low concentration. The patterns are similar with previous studies that the diffraction peaks of cassava starch were 2θ = 15.3, 17.3, 18.3, 22 and 23.5º (Vercelhaze *et al*., 2012; Matsuda *et al*., 2013). El-kader *et al*. (2013) and Caba *et al*. (2012) found respectively the ZnO-NP peaks were 2θ = 19, 23, 31.88, 34.54, 36.40º and the stearic acid peaks were 2θ= 6.64, 20.2, 21.5 and 24º. As observed, all of films were in amorphous state with crystalline percentage of L0Z0, L0Z1, L0Z2, L1Z0, L1Z1, L1Z2 were 28, 7, 11, 13, 12.91 and 24.3% respectively. The results showed a decrease in the intensity of the crystal facets on both cassava starch and cassava starch + stearic acid films with the addition of ZnO-NP 1% and an increase with the addition of ZnO-NP 2% in the polymers.

The interaction among cassava starch, ZnO-NP and stearic acid were investigated by FTIR. The infrared spectra of edible films are presented in Figure 4. The broad band from 3072.39 - 3515.18cm^{-1} was attributed to hydrogen bond between different O-H groups from OH of starch, OH carboxylic function of stearic acid, OH of tween 80 and OH of glycerol. The band at 2792.23 - 2913.39cm^{-1} was C-H stretching. The band from 1649.22 - 1697.99cm^{-1} was C=O stretching and 1059.18 - 1166.37cm^{-1} was the stretching mode of the C–O bond. This result is similar to previous reports (Zhong and Xia, 2008; Chen and Zhao, 2015; Somboonsub and Thawornchinsombut, 2015). Moreover, the band of ZnO-NP were not clearly observed because it was added in very low concentration. However, some studies reported for ZnO stretching at 482, 527 and 600cm^{-1} (Wang *et al*., 2009; Khan *et al*., 2011; El-kader *et al*., 2013). The chemical interactions among subtances are indicated by changes in the peaks of characteristic spectra. The C-H and C=O stretching was more intense for film with the addition of stearic acid (L1Z0, L1Z1, L1Z2)

compared to films without stearic acid (L0Z0, L0Z1, L0Z2). They showed a shift of absorption band from 2792.23 - 2805.34 and 1663.45 - 1697.99 and It was attributed to the C-H stretching mode of the aliphatic chain of the fatty acid.

Conclusion

The bionanocomposite edible films were successfully prepared by casting the blending solution of cassava starch with or without the addition of ZnO-NP and stearic acid. The results of this study revealed that the addition of ZnO-NP and stearic acid could improve some characteristics of the edible films compared to the cassava starch-based film. The presence of ZnO-NP was not observed clearly by using SEM. The intensity of crystalline structure by using XRD showed an increase in the both cassava starch and cassava starch + stearic acid films with the addition of ZnO-NP 2%. Moreover, FTIR spectra indicated an increase in intensity of C-H and C=O stretching for film with the addition of stearic acid compared to films without stearic acid. The improvement in mechanical properties has been achieved at cassava starch + 2% ZnO-NP which has desirable tensile strength without meaningful reduction elongation. While the best physical properties has been achieved at cassava starch + 2% ZnO-NP + 30% stearic acid with good improvement in water vapor transmission rate. However, those results were still needed further research to meet the requirements of good film properties.

Acknowledgements

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