One-step preparation of banana powder/silver nanoparticles composite films

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Abstract Silver nanoparticles (Ag-NPs) were synthesized using banana powder as a reducing and stabilizing agent, and banana/Ag-NPs composite films with different concentration of Ag-NPs were prepared simultaneously. The composite films were yellowish brown and exhibited characteristic plasmon resonance peak of Ag-NPs at 430 nm. The optical, mechanical, water vapor barrier, thermal stability, and antimicrobial properties of the composite films were greatly influenced by the concentration of Ag-NPs. The composite film with a silver concentration of 1.0 mM demonstrated the highest tensile strength, thermal stability, transparency, and water contact angle with the lowest water vapor permeability ($1.36 \pm 0.10 \times 10^{-9}$ g m/m² Pa s). Also, the composite films incorporated with 1.0 mM of Ag-NPs exhibited a strong antibacterial activity against both Gram-positive (*Listeria*

monocytogenes) and Gram-negative (*Escherichia coli*) food-borne pathogenic bacteria.

Keywords Banana powder · Silver nanoparticles · One-step preparation · Composite films · Antimicrobial activity

Introduction

Biopolymers have been developed to replace the conventional non-biodegradable petroleum-based plastics, especially in the food packaging industries, due to their safety, functionality, renewability, sustainability, and environmental friendly nature (Rhim et al. 2013; Shankar and Rhim 2015). However, biopolymer-based packaging materials have not been widely used in the packaging industry, because of their poor mechanical and processing properties as well as high production cost (Tunc and Duman 2011). To overcome such limitations of biopolymer-based films, the development of bio-nanocomposite films attracted renewed interests recently. A homogeneous blending of biopolymers with various types of nano-sized filler materials has been attempted to improve the physical, mechanical, ultra-violet (UV) light screening, gas barrier, and antimicrobial properties of the films. Incorporation of inorganic nanoparticles into the polymeric matrix to enhance the properties of polymeric materials has been widely tested (Díez-Pascual and Díez-Vicente 2014; Rhim et al. 2014; Shankar and Rhim 2015). Recently, the utilization of metallic nanoparticles, such as silver, TiO₂, CuO, and ZnO as reinforcing fillers has emerged due to their high thermal stability, large surface area, and high specificity such as a strong antimicrobial activity (Othman et al. 2014; Rhim et al. 2014; Shankar et al. 2014a, b, 2015).

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Owing to the unique properties of silver, silver nanoparticles (Ag-NPs) have been one of the most widely used nanofillers for the development of nanocomposite for food packaging or biomedical applications (Cheviron et al. 2014; Rhim et al. 2013; Shukla et al. 2012). Recently, green method for the synthesis of Ag-NPs using natural biopolymers such as agar, chitosan, and starch has paid intense attention because of their availability, renewability, and biocompatibility (Cheviron et al. 2014; Huang and Yang 2004; Shukla et al. 2012). Banana is one of the interesting materials for the green synthesis of Ag-NPs since it is abundant tropical fruits containing a high amount of starch, protein, fat, fibers, and phenolic compounds (Pelissari et al. 2013; Pereira and Maraschin 2015; Sothornvit and Pitak 2007; Waliszewski et al. 2003). Also, the banana powder has good film forming properties with heat sealability and excellent O₂ barrier properties (Pelissari et al. 2013; Sothornvit and Pitak 2007). The Ag-NPs production function and film forming properties of banana powder can be properly utilized to form banana/Ag-NPs composite films in a single step.

The main objective of the present study was to prepare banana/Ag-NPs composite films in a single step and to test the effect of the concentration of Ag-NPs on the optical, mechanical, water vapor barrier, thermal stability, and antimicrobial properties of the composite films.

Materials and methods

Materials

Unripe banana (*Musa sapientum* Linn “Klui Namwa”) in the green stage (112–116 days after petal fall) was obtained from an orchard at Kasetsart University, Nakhonpathom, Thailand. Silver nitrate (AgNO₃) was purchased from Duksan Pure Chemicals Co., Ltd. (Gyeonggi-do, Korea). *Escherichia coli* O157: H7 ATCC 43895 and *Listeria monocytogenes* ATCC 15313 were obtained from Korean Collection for Type Cultures (KCTC, Seoul, Korea). The bacterial strains were cultured on tryptic soy (TS) agar and brain heart infusion (BHI) agar media and subsequently stored at 4 °C for further analysis. All chemicals were of analytical grade and used without any further purification.

Preparation of banana powder

Banana powder was prepared following the method of Sothornvit and Pitak (2007). The chemical composition per 100 g of the banana powder was as follows: moisture 8.17 ± 0.04 g, starch 75.09 ± 0.43 g, protein 10.79 ± 0.14 g, fat 0.36 ± 0.07 g, and ash, 5.59 ± 0.31 g.

Phytochemical tests

The existence of phytochemicals in the banana powder was tested using the method of Patil et al. (2012) with a slight modification. The banana powder (1 g) was suspended in 100 mL of distilled water and boiled for 30 min to obtain the homogeneous suspension of banana powder. The suspensions were cooled, and qualitative tests have been performed to test the existence of each phytochemical as follows:

Saponins: The banana powder suspension (5 mL) was diluted to 20 mL with distilled water. The suspension was shaken in a graduated cylinder for 15 min and checked for the formation of foams.

Phenolic compounds: A few drops of neutral ferric chloride (5 g/100 mL) solution was added to 5 mL of banana powder solution and color change was monitored.

Tannins: Few drops of ferric chloride (0.1 g/100 mL) were added to 5 mL of banana powder solution and monitored color change.

Total flavonoids: Five milliliters of dilute ammonia solution were added to 5 mL of banana powder solution followed by the addition of a drop of concentrated sulfuric acid.

Terpenoids: Five milliliters of banana powder solution were mixed with 2 mL of chloroform and 3 mL of concentrated sulfuric acid to form an interface layer.

Simultaneous synthesis of Ag-NPs and banana/Ag-NPs composite films

Banana/Ag-NPs composite films were prepared using a solution casting method (Rhim et al. 2011). Four grams of banana powder were added slowly into 150 mL of distilled water with stirring and heated at 90 °C for 20 min to dissolve completely, and 1.2 g of glycerol was added as a plasticizer. Then, the aqueous solution of AgNO₃ was added dropwise into the above solution to make a final concentration of 0.5, 1, and 2 mM of silver and heated at 90 °C continuously with stirring for 4 h. The film forming solution was cast on a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 cm × 30 cm) and allowed to dry at room temperature (23 ± 2 °C) for 2 days. The completely dried film was peeled off from the plate and preconditioned in a constant humidity and temperature (25 °C, 50% RH) chamber (model FX 1077, Jeio Tech Co. Ltd., Ansan, Korea) for at least 48 h for conditioning the films before further analysis. The composite films with 0.5, 1.0, and 2.0 mM of AgNO₃ were designated as banana/Ag-NPs0.5, banana/Ag-NPs1.0, and banana/Ag-NPs2.0, respectively.

Characterization of banana/Ag-NPs nanocomposite films

Morphology and optical properties

The microstructure of the film samples was observed using a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) with an accelerating voltage of 5.0 kV.

The surface color of the films was measured using a Chroma meter (Konica Minolta, CR-400, Tokyo, Japan) by the method of Shankar and Rhim (2015).

The absorbance of the films was taken in the wavelength of 200–700 nm using UV–Vis spectrophotometer (Mecasys Optizen POP Series UV/Vis, Seoul, Korea). Transparency and UV light screening capacity of the films were evaluated as the percentage of transmittance at 660 nm (T_{660}) and 280 nm (T_{280}), respectively.

Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectra of the films were obtained in the wave number range of 4000–600 cm^{-1} using an attenuated total reflectance-Fourier transform infrared (ATR-FT-IR) spectrophotometer (TENSOR 37 spectrophotometer with OPUS 6.0 software, Billerica, MA, USA).

Mechanical properties

Mechanical properties such as tensile strength (TS), elongation at break (EAB), and elastic modulus (EM) of each film sample were evaluated using an Instron Universal Testing Machine (Model 5565, Instron Engineering Corporation, Canton, MA, USA) in accordance with the ASTM Method D 882-88 (Shankar and Rhim 2015).

Water vapor permeability

The water vapor permeability (WVP) of films was determined gravimetrically following the standard method of ASTM E96-95 (Reddy and Rhim 2014). Films were cut into a rectangular shape (7.5 cm $\times$ 7.5 cm) and directly placed on the top of cups containing 18 mL of water and sealed tightly. The assembled cup was weighed and subsequently placed in a humidity chamber controlled at 25 °C and 50% RH. Weight change of the cup was determined at every 1 h for 8 h. The slopes of the steady-state (linear) portion of weight loss versus time curves were used to calculate the water vapor transmission rate (WVTR; $\text{g/m}^2 \text{ s}$) of the film. Then, the WVP ($\text{g m/m}^2 \text{ s Pa}$) of the film was calculated as follows:

$$\text{WVP} = \frac{\text{WVTR} \times L}{\Delta P}$$

where L was the mean thickness of the film (m) and ΔP was partial water vapor pressure difference (Pa) across the film.

Water contact angle, moisture content, and water solubility

Surface hydrophilicity or hydrophobicity of the film was determined by measuring the water contact angle (WCA) of the film using a WCA analyzer (model Phoenix 150, Surface Electro Optics Co., Ltd., Kunpo, Korea) (Shankar and Rhim 2015). Moisture content (MC) of the films was determined using a drying oven method (Rhim and Wang 2013). The water solubility (WS) of the film samples was determined as the percentage of dissolved dry matter after immersion in water. Three randomly selected specimens of each type of film (3 cm $\times$ 3 cm) were first dried at 60 °C for 24 h to determine the initial dry matter (W_1). Each film was immersed in 30 mL of distilled water in a 50 mL beaker with gentle stirring for 24 h. The film samples were removed and dried in a drying oven at 105 °C for 24 h to determine the undissolved final dry weight (W_2). The WS of the sample was calculated as follows:

$$\text{WS} = \frac{W_1 - W_2}{W_1} \times 100$$

Thermal stability

Thermal stability of banana powder and composite films was determined using a thermogravimetric analyzer (Hi-Res TGA 2950, TA Instrument, New Castle, DE, USA). Approximately 5 mg of sample was taken in a standard aluminum pan and heated from 30 to 600 °C at the heating rate of 10 °C/min under a nitrogen flow of 50 cm^3/min . A derivative form of TGA (DTG) was obtained using differentials of TGA values, calculated using a central finite difference method as follows (Shankar and Rhim 2015):

$$\text{DTG} = \frac{W_{t+\Delta t} - W_{t-\Delta t}}{2\Delta t}$$

where $w_{t+\Delta t}$ and $w_{t-\Delta t}$ are the residual weight of the sample at time $t + \Delta t$ and $t - \Delta t$, respectively, and Δt is the time interval for reading residual sample weight. The maximum decomposition temperature (T_{max}) of the banana powder and composite films was obtained from DTG curve, and the char content, as well as weight loss (%), were measured using the TGA curve (Reddy and Rhim 2014).

Antimicrobial activity

The antimicrobial activities of the neat banana and composite films were examined by the method of Shankar et al. (2015). *L. monocytogenes* and *E. coli* were aseptically inoculated in 20 mL of BHI and TS broth, respectively, and subsequently incubated at 37 °C for 16 h. A 20 mL of bacterial suspension (10^6 – 10^7 CFU/mL) was taken in 100 mL of the conical flask containing 100 mg of film samples and subsequently incubated at 37 °C for 16 h under mild shaking. The same bacterial suspension without film sample was used as a control. The cell viability of each pathogen was calculated by counting bacterial colonies on the plates at 0, 3, 6, 9, and 11 h. Antimicrobial tests were performed in triplicate with individually prepared films.

Statistical analysis

A completely randomized experimental design was used to test the effect of the concentration of silver on the properties composite films. Three replicates of individually prepared films were used, and the results were provided with mean values and standard deviations (SD). One-way analysis of variance (ANOVA) was performed, and the significance of each mean property value was determined ($p < 0.05$) by Duncan's multiple range test using the SPSS statistical analysis computer program for Windows (SPSS Inc., Chicago, IL, USA).

Results and discussion

Phytochemical analysis

Qualitative test results on the existence of phytochemicals indicated the presence of various types of phenolic compounds in the banana powder. The formation of 2 cm layer of foam after shaking of the banana powder suspension indicated the existence of saponins. The development of dark green color after the addition of a few drops of neutral 5% ferric chloride solution showed the presence of phenolic compounds. The development of brownish green color by the addition of a few drops of 0.1% ferric chloride in banana powder solution revealed the presence of tannins. The appearance of yellow color after addition of ammonia solution in the banana powder solution indicated the presence of flavonoids. A reddish brown color development at the interface showed the presence of terpenoids (Patil et al. 2012).

Synthesis of silver nanoparticles

Synthesis of Ag-NPs and preparation of composite films were performed in a single step. As the silver salt has been

reduced by banana powder, the color of the solution changed from yellow to dark brown indicating the formation of Ag-NPs. In the synthesis of Ag-NPs, banana powder functions as reducing and stabilizing agents. In addition to the general components such as starch, protein, fat, and ash, various phytochemicals in the banana powder played an important role in this process. The amino group of protein, terpenoids, and the phenolic –OH groups of tannins acted as reducing agent for reduction of Ag⁺ ions to Ag-NPs, while the starch acted as a stabilizing agent for the Ag-NPs (Patil et al. 2012; Vigneshwaran et al. 2006). Similar observations in green synthesis of Ag-NPs using plant extracts have been reported by many researchers (Donda et al. 2013; Kokila et al. 2015; Prakash et al. 2013; Shankar et al. 2014a; Shinde et al. 2014).

Morphology and optical properties of banana/Ag-NPs composite films

The surface morphology of neat banana and composite films was observed using FE-SEM micrograph as shown in Fig. 1. The neat banana film exhibited a smooth and compact surface, while composite films showed rough surface structures with evenly distributed Ag-NPs. The size of the Ag-NPs increased with the increase in AgNO₃ concentration. When 0.5 mM of AgNO₃ were added, the Ag-NPs were predominantly spherical in shape with approximately 100 nm in diameter. However, the diameter increased up to 200–300 nm and the shape become cubic when AgNO₃ concentration increased to 2 mM.

The formation of Ag-NPs is characterized by the appearance of surface plasmon resonance (SPR) bands around 400–450 nm (Cheviron et al. 2014; Shankar and Rhim 2015). Figure 2 illustrates the UV–visible spectra of the neat banana and composite films. The composite films showed an SPR band with the maximum peak intensity at 430 nm of metallic Ag-NPs, along with a broad shoulder peak around 280 nm that might be due to the protein and phenolic compounds present in the banana powder. The absorption peaks of banana/Ag-NPs0.5 and banana/Ag-NPs1.0 were sharp; however, the peak of banana/Ag-NPs2.0 was broad. This widening of the peak with shifting to higher wavelengths indicates the presence of uneven silver nanoparticles and nanoparticle clusters (Shinde et al. 2014).

Apparently, the neat banana film was transparent with a yellowish tint, but the films incorporated with Ag-NPs were brownish yellow in color as shown in the insert of Fig. 2a. The surface color and transmittance values of the films are shown in Table 1. Banana films showed high Hunter L-value (lightness) of 80.8, however, after blending with Ag-NPs, L-value decreased significantly ($p < 0.05$) with an increase in the concentration of silver. Hunter

Fig. 1 FE-SEM micrographs of banana and banana/Ag-NPs composite films

a-value (redness) of the composite films increased significantly ($p < 0.05$) up to 1 mM of Ag-NPs, then it decreased with further increase in the concentration of silver. Compared to the neat banana film, Hunter b-value (yellowness) of the composite films with 0.5 mM of Ag-NPs increased. However, it decreased with a higher concentration of silver. This result indicates that the color of composite films depends on the concentration of silver used. As a consequence, the total color difference (ΔE) of composite films increased remarkably compared to the neat banana film. These results were in good agreement with the visual observation (inserts in Fig. 2a).

The transmittance of light at 280 nm (T_{280}) and 660 nm (T_{660}) of the neat banana and composite films are also shown in Table 1. UV-light transmittance (T_{280}) of the neat banana film was 7.5%, and it decreased significantly ($p < 0.05$) after the formation of composite films with Ag-NPs. The low transmittance of light at 280 nm of the neat banana film was mainly due to the UV-light absorption capacity of phenolic compounds and protein in the banana powder (Kanmani and Rhim 2014; Shankar and Rhim 2015). Visible light transmittance (T_{660}), a measure of the transparency of the film, of the neat banana film was 54.5%, which indicates that the banana film is rather

translucent. The T_{660} also decreased significantly ($p < 0.05$) after the formation of composite films with Ag-NPs. Also, the transparency of the composite film decreased linearly with an increase in the concentration of silver. This is mainly due to the light blocking effect of Ag-NPs. Such a reduction in both UV and visible light transmittance by the Ag-NPs has frequently been observed with other types of nanocomposite films (Shankar and Rhim 2015). UV light screening capacity of composite films can be applied as food packaging to prevent light-induced changes in the packaged foods and to increase the shelf-life of UV-sensitive food.

FT-IR analysis

FT-IR spectra were recorded in the range of 4000–600 cm^{-1} for the neat banana and composite films, to compare the types of interactions taking place in the film structures (Fig. 2b). The bands observed in the region of 3200–3498 cm^{-1} in the spectra of the films can be assigned to the stretching of the –OH groups, caused by the formation of hydrogen bonds of starch (Kanmani and Rhim 2014). The peak at 2926 cm^{-1} was due to the existence of the CH_2 group. The band at 1613 cm^{-1} corresponds to the

Fig. 2 **a** UV–Vis spectra and **b** FT-IR spectra of banana and banana/Ag-NPs composite films. *Inserts* in the figure show the color of nanocomposite films

Table 1 Surface color and optical properties of banana and banana/Ag-NPs composite films

Films	L	a	b	ΔE	T ₂₈₀ (%)	T ₆₆₀ (%)
Banana	80.8 ± 1.3 ^d	3.3 ± 0.4 ^a	14.0 ± 0.9 ^b	18.1 ± 1.6 ^a	7.5 ± 1.9 ^c	54.5 ± 4.0 ^c
Banana/Ag-NPs0.5	46.7 ± 2.7 ^c	16.7 ± 1.4 ^c	21.7 ± 1.5 ^d	54.3 ± 1.7 ^b	3.2 ± 0.8 ^b	40.5 ± 3.6 ^b
Banana/Ag-NPs1.0	38.1 ± 2.6 ^b	21.3 ± 2.0 ^d	16.2 ± 2.6 ^c	62.1 ± 1.4 ^c	0.9 ± 0.4 ^a	37.4 ± 3.8 ^b
Banana/Ag-NPs2.0	29.0 ± 3.8 ^a	9.9 ± 6.4 ^b	7.2 ± 3.9 ^a	63.5 ± 14.9 ^c	0.2 ± 0.1 ^a	18.3 ± 7.9 ^a

Values with the same superscript letter in the same column indicate that they are not statistically different ($p < 0.05$). The values were presented as mean ± SD

amide I group of proteins. The band at 1337 cm⁻¹ corresponds to the amide III group of protein (Pelissari et al. 2013; Shinde et al. 2014). The bands at 1412 and 1413 cm⁻¹ are associated with the symmetric stretching of the carboxyl group (–COOH) (Kizil et al. 2002). The band located at 993 cm⁻¹ in the films is related to the amount of amorphous structure of the films (Van Soest et al. 1995).

The bands at 926 and 927 cm⁻¹ observed are attributed to the glycosidic bonds of starch. The absorptions between 703 and 762 cm⁻¹ indicate the presence of aromatic structures, which could be associated with the presence of phenolic compounds in the banana powder (Arcan and Yemencioğlu 2011). There were no changes in the position of peaks after the formation of Ag-NPs, however, the

Table 2 Thickness, mechanical properties, moisture content (MC), water solubility (WS), water contact angle (WCA), and water vapor permeability (WVP) of banana and banana/Ag-NPs composite films

Films	Thickness (μm)	TS (MPa)	EAB (%)	EM (GPa)	MC (%)	WS (%)	WVP ($\times 10^{-9}$ g m/m ² Pa s)	WCA ($^{\circ}$)
Banana	73.1 $\pm$ 2.5 ^b	16.0 $\pm$ 2.9 ^a	6.1 $\pm$ 3.6 ^b	0.87 $\pm$ 0.17 ^a	9.4 $\pm$ 0.2 ^b	14.0 $\pm$ 1.5 ^b	2.32 $\pm$ 0.42 ^b	39.4 $\pm$ 5.0 ^a
Banana/Ag-NPs0.5	72.2 $\pm$ 4.9 ^{ab}	16.3 $\pm$ 2.9 ^a	4.3 $\pm$ 1.9 ^a	0.99 $\pm$ 0.18 ^b	8.6 $\pm$ 1.3 ^{ab}	14.1 $\pm$ 0.7 ^b	1.61 $\pm$ 0.25 ^a	41.5 $\pm$ 3.6 ^{ab}
Banana/Ag-NPs1.0	70.1 $\pm$ 2.9 ^a	18.9 $\pm$ 2.3 ^b	2.7 $\pm$ 1.0 ^a	1.18 $\pm$ 0.07 ^c	8.6 $\pm$ 0.2 ^{ab}	12.9 $\pm$ 0.3 ^{ab}	1.36 $\pm$ 0.10 ^a	44.7 $\pm$ 3.7 ^c
Banana/Ag-NPs2.0	73.1 $\pm$ 3.3 ^b	17.2 $\pm$ 2.9 ^{ab}	3.5 $\pm$ 1.4 ^a	1.05 $\pm$ 0.14 ^b	7.2 $\pm$ 1.9 ^a	12.2 $\pm$ 0.3 ^a	1.50 $\pm$ 0.12 ^a	42.2 $\pm$ 5.2 ^{ab}

Values with the same superscript letter in the same column indicate that they are not statistically different ($p < 0.05$). The values were presented as mean $\pm$ SD

intensity of some peaks increased, which indicates the role of banana powder in the reduction of silver ions to metallic silver nanoparticles.

Mechanical properties

The mechanical properties of neat banana and composite films are presented in Table 2. The thickness of the composite films was not significantly ($p > 0.05$) different from that of the neat banana film. The TS, EAB, and EM of the neat banana film were 16.0 MPa, 6.1%, and 0.87 GPa, respectively, which indicates that the strength, flexibility, and stiffness of the banana film are rather low. However, the mechanical properties of the banana film were influenced significantly after the formation of a composite with Ag-NPs. When the film was incorporated with 1 mM of Ag-NPs, the TS and EM of the banana film increased from 16.0 $\pm$ 2.9 to 18.9 $\pm$ 2.3 MPa and 0.87 $\pm$ 0.17 to 1.18 $\pm$ 0.07 GPa, respectively. On the contrary, the EAB decreased significantly ($p < 0.05$) after the formation of nanocomposite with Ag-NPs. The mechanical properties such as TS and EM of the composite films increased with increase in the content of Ag-NPs up to 1.0 mM, then decreased afterward. It might be due to the formation of large particles or agglomeration of Ag-NPs in the film matrix when a higher concentration of silver was added, which induced the lower interaction between Ag-NPs and the film matrix (Yoksan and Chirachanchai 2010). Shankar and Rhim (2015) reported the decrease in mechanical properties of agar films when blended with Ag-NPs. The mechanical properties of the films are closely related to the distribution and density of intra- and intermolecular interactions between polymer chains in the film matrix (Chambi and Grosso 2006).

Moisture content, water solubility, water vapor permeability, and water contact angle

The result of the moisture content (MC), water solubility (WS), water vapor permeability (WVP), and water contact angle (WCA) of the neat banana and

composite films are shown in Table 2. The MC and WS of banana/Ag-NPs composite films decreased significantly compared with the neat banana film. This is probably due to the addition of the hydrophobic metallic Ag-NPs, which reduced the hydrophilicity of polymer. The WVP of the neat banana film decreased significantly ($p < 0.05$) when the film was blended with Ag-NPs. The decrease in the WVP of composite films was attributed to the distribution of Ag-NPs as a discontinuous phase in the film matrix, which prevented the diffusion of water vapor resulting in an increase in the tortuous path (Wang and Rhim 2015; Su et al. 2010). Surface hydrophobicity of the neat banana and composite films was determined by measuring the water contact angle (WCA) of films. The WCA of all films was less than 65 $^{\circ}$ (Table 2), which indicated that the surface of the banana and composite film was considered as hydrophilic (Vogler 1998). Similar results were observed with other biopolymer films such as gelatin/Ag-NPs and agar/Ag-NPs composite films (Rhim et al. 2014; Shankar et al. 2015). The addition of Ag-NPs to the banana films slightly increased the surface hydrophobicity of the films, probably due to the addition of hydrophobic metallic silver to the films (Kammani and Rhim 2014). However, the WCA of banana/Ag-NPs2.0 composite film was lower than banana/Ag-NPs1.0 composite film, which was probably due to the aggregation of Ag-NPs or formation of a large cluster of Ag-NPs in the banana/Ag-NPs2.0 composite films as shown in the SEM micrograph (Fig. 1).

Thermal stability

The thermal stability of the neat banana and composite films was tested using TGA and the resulting TGA and DTG curves are presented in Fig. 3. The TGA curves of the films showed the weight loss pattern with increasing temperature and the DTG curves clearly exhibited the decomposition temperature at each stage of thermal decomposition. All the films exhibited multiple steps of thermal degradation. The initial weight loss of all films was

Fig. 3 Thermal stability of banana and banana/Ag-NPs composite films shown as **a** TGA and **b** DTG curves

observed around 60–100 °C with about 7–12% of weight decrease, which was mainly due to the removal of moisture from the films (Martelli et al. 2013). The subsequent steps of degradation were varied depending on the type of films. The second decomposition step of the banana and banana/Ag-NPs composite films was observed approximately 220–320 °C, which was ascribed to the volatilization of glycerol added as a plasticizer and the thermal degradation of the banana based film matrix (Rhim et al. 2013; Reddy and Rhim 2014). The main stage of weight loss or the maximum thermal decomposition (T_{max}) exhibited around 290, 290, 295, and 310 °C for the neat banana, banana/Ag-NPs0.5, banana/Ag-NPs1.0, and banana/Ag-NPs2.0 composite films, respectively. These results indicate that the thermal stability of the banana film increased after formation of nanocomposite with Ag-NPs, and it increased with an increase in the concentration of silver, which was mainly due to the heat stable metallic Ag-NPs (Rhim et al. 2014; Shankar and Rhim 2015). This result also suggests that the processing temperature of the banana films should be lower than 290 °C to avoid thermal decomposition of

the polymer (Martelli et al. 2013). After the final thermal decomposition, the residues left at 600 °C were 19.9, 21.3, 25.4, and 21.7% for the neat banana film, banana/Ag-NPs0.5, banana/Ag-NPs1.0, and banana/Ag-NPs2.0 composite films, respectively.

Antimicrobial activity

The antimicrobial activity of the banana film and composite films was tested against Gram-positive (*L. monocytogenes*) and Gram-negative (*E. coli*) food-borne pathogenic bacteria using viable colony count methods (Shankar and Rhim 2015), and the results are shown in Fig. 4. As expected, the neat banana film did not show any antimicrobial activity against both *L. monocytogenes* and *E. coli*. However, the composite films exhibited distinctive bactericidal activity against *E. coli*, while they showed only bacteriostatic activity against *L. monocytogenes*. These

Fig. 4 Antimicrobial activity of banana and banana/Ag-NPs composite films against **a** *L. monocytogenes* and **b** *E. coli*

results were consistent with the previously reported results that Ag-NPs have stronger antimicrobial activity against Gram-negative bacteria than Gram-positive bacteria (Shankar and Rhim 2015). The antimicrobial activity of composite films depended on the contact surface area (Shankar and Rhim 2015), and it was found that the activity was increased with increasing concentration of silver used. The banana/Ag-NPs2.0 composite film showed the bactericidal effect against *E. coli* after 3 h and killed the bacteria completely in 9 h. However, the antibacterial effect was delayed in the composite film with a lower concentration of silver. The difference in the antimicrobial activity of Ag-NPs between Gram-positive and Gram-negative bacteria could be due to the charge on the cell membrane and the difference in the structure and thickness of their cell wall (Shankar and Rhim 2015). Since the concentration of silver used to develop composite films was very low, the developed composite films have a high potential for the application in food packaging materials to extend the shelf-life of packaged food (Rhim et al. 2013).

Conclusion

Banana/Ag-NPs composite films were prepared in a single step using a solvent casting method, in which banana powder was used as a reducing and stabilizing agent as well as the polymer matrix. The amino group of protein, terpenoids, and the phenolic –OH groups of tannins of banana powder were responsible for the reduction of silver ions into metallic Ag-NPs. The composite films showed the characteristic absorption peak at 430 nm confirming the formation of silver nanoparticles in the composite films. The concentration of silver played an important role in maintaining film properties such as surface color, optical, mechanical, water solubility, water vapor barrier, thermal stability, and antimicrobial properties. However, the glycerol used as a plasticizer maintained the flexibility of the film. The composite films showed functional properties such as UV light barrier and antimicrobial properties. The results suggested that the composite films can be used as an active food packaging or edible coating materials to extend the shelf-life of packaged foods.

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