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ORIGINAL RESEARCH PAPER

NANOCOMPOSITE EDIBLE COATING FROM CASSAVA STARCH, STEARIC ACID AND ZnO NANOPARTICLES TO MAINTAIN QUALITY OF FRESH-CUT MANGO CV. ARUMANIS

SRI YULIANI[1], ATA ADITYA WARDANA[2]*, BAYU MEINDRAWAN[2], NUGRAHA EDHI SUYATMA[3], TIEN R. MUCHTADI[3]

[1]*Indonesian Center for Agricultural Postharvest Research and Development, Bogor, 16114, Indonesia*
[2]*Department of Food Technology, Faculty of Engineering, Bina Nusantara University, Jakarta, 15143, Indonesia*
[3]*Department of Food Science and Technology, Bogor Agricultural University, Bogor, 16680, Indonesia*
*Corresponding author: *ataaditya@gmail.com, ata.wardana@binus.edu*

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Fresh-cut mango is one of perishable food products due to its high respiration, transpiration and microbial decay rate. In this study, generation of a new edible coating was chosen as an alternative method for preserving the quality attributes of fresh-cut mango. The objective of this study was to evaluate the effects of nanocomposite edible coating from cassava starch (SC), stearic acid (SA) and/or ZnO nanoparticles (NP-ZnO) on the quality of fresh-cut mango cv. Arumanis, stored for 12 days at 8°C. The formulations of 20 g/L SC, 6 g/L SA, and variable NP-ZnO (0, 1, 2% w/w of SC) were utilized to coat the fresh-cut mango. The result revealed that the treatment of nanocomposite edible coating was able to maintain the quality of fresh-cut mango during the storage periods. The SC, SA, and 2% NP-ZnO formulation was the most effective in reducing weight loss and microbial counts. Our study suggests that the application of nanocomposite edible coating provides a desirable method to maintain storage quality and to improve fresh-cut mango postharvest life.

Keywords: mango, fresh-cut, nanocomposite, ZnO nanoparticles, edible coating

Introduction

Mango *(Mangifera indica L.)* is one of the tropical and climacteric fruits, a rich source of minerals, carotenoids, vitamins A, and B, with a wide demand on the international fruit market (Chiumarelli *et al.*, 2010). The top five mango-producing countries from 2003 to 2005 were India (38.6%), followed by China (12.9%), Thailand (6.2%), Mexico (5.5%) and Indonesia (5.3%) (FAOSTAT, 2007). In Indonesia, mango cv. Arumanis is the most popular mango variety to consume with a weight of about 300–500 g per fruit. The increasing consumer demand for healthy, fresh, and ready-to-eat fruit is a current driving force for the expansion of the fresh-cut mango market. However, fresh-cut mango has a short period of shelf life due to its lack of preparation, which stimulates respiration and transpiration, membrane deterioration, and supports microbial growth (Laurila and Ahvenainen 2002; Rojas *et al.*, 2009). Hence, alternative methods are highly needed to maintain the quality and to prolong the fresh-cut mango storage periods.

Edible coating is one of the recommended methods to inhibit deterioration of fresh-cut products. It has a role as semipermeable barrier, which makes it able to inhibit moisture and solute migration, gas exchange, respiration and oxidative reaction rates, as well as suppress physiological disorders of fresh-cut fruits (Robles-Sánchez *et al.*, 2013). Moreover, edible coatings are also utilized as carrier of food additives including antimicrobial agents (Shi and Gunasekaran, 2008; Suyatma *et al.*, 2014). Among biopolymers matrices, starch is still one of the most promising polymers due to its availability and low cost (Ma *et al.*, 2009). A hydrophilic single coating has a good barrier property to gases but is weak on water vapor resistance. To improve the barrier to water vapor, the incorporation of hydrophobic materials such as long-chain fatty acids were applied as an alternative (Schmidt *et al.*, 2013).

Nowadays, the utilization of nanoparticles (NP) has gained great attention in developing nanocomposites. A nanocomposite is a breakthrough of a microcomposite, which consists of natural polymers as matrix with nanoparticles as filler. The addition of nanoparticles into biopolymers are able to improve their characteristics and functional properties including barrier ability, morphology, and mechanical strength (Sorrentino *et al.*, 2007; Shi and Gunasekaran, 2008; Slavutsky and Bertuzzi, 2014; Shankar *et al.*, 2015). NP-ZnO is one of the nanoparticle substances that has received great attention as nano fillers in the food field. Furthermore, NP-ZnO has been approved as GRAS (Generally Recognized as Safe) substance by the FDA (Sharon *et al.*, 2010). It also was applied as a source for Zn supplementation and fortification (Shi and Gunasekaran, 2008). It also was revealed that NP-ZnO acted as antimicrobial substances. Yu *et al.* (2009) incorporated NP-ZnO into the polymers to reduce the growth of microorganisms on the surface of foodstuffs. Previous studies also found new possibilities of NP-ZnO against *Botrytis cinerea* and *Penicillium expansum* (He *et al.*, 2011), *Escherichia coli* (Zhang *et al.*, 2007), and *Lactobacillus plantarum* (Shi *et al.*, 2012). Thanks to its safety and its beneficial properties, NP-ZnO was selected in this study to develop a nanocomposite edible coating. The aim of this work was to evaluate the effects of a nanocomposite edible coating from cassava starch (SC), stearic acid (SA) and NP-ZnO on the quality of fresh-cut mango *cv.* Arumanis, stored for 12 days at 8°C.

Materials and methods

Materials

The materials used in this study was mango *(Mangifera indica L.)* cv. Arumanis obtained from mango farmers at Astanajapura, Cirebon (Indonesia). The mangoes were harvested approximately 90 days after flowering. Cassava starch was purchased from local starch industry in Ciluar, Bogor (Indonesia). Stearic acid was purchased from local market and NP-ZnO with an average particle size of 20 ± 5 nm was purchased from Wako Pure Chemical Industries Ltd (Japan). In order to obtain good dispersion Tween 80 (Merck, Germany) was used as emulsifier.

Preparation of nanocomposite coating solution and samples

NP-ZnO (0, 1 and 2% $^{w}/_{w}$ of SC) was dispersed in 500 ml distilled water by using an ultraturax (1500 rpm, 10 min) to make the nanocomposite edible coating solutions. An amount of 10 g cassava starch was slowly added and blended under constant stirring until it was dissolved completely. Subsequently, 75% Tween 80 ($^{w}/_{w}$ of SC; or 7.5 g) and 30% SA ($^{w}/_{w}$ of SC; or 3 g) were added into the prepared solutions. The mixture was heated, and stirring was continued until 90^{o}C for 10 min, and then the mixture was left until it reached room temperature (28-30^{o}C) naturally. Thus, three different nanocomposite coating formulations were produced, namely NP-ZnO 0% (SC+ 30% stearic acid + 0% NP-ZnO), NP-ZnO 1% (SC + 30% stearic acid + 1% NP-ZnO), and NP-ZnO 2% (SC + 30% stearic acid + 2% NP-ZnO).

The fresh-cut mango used as samples were prepared aseptically to minimize contamination. Mango fruits were selected for their uniformity in weight (350-400 g) and absence of defective spots, cleaned and washed in 200 ppm chlorine solution. The fruits were peeled manually with a stainless steel knife and sliced from both sides of the seed. Subsequently, flesh of mangoes were cut in pieces (1.5-2 cm^3) and immersed in 1% $CaCl_2$ water for 5 min. Then the mango pieces were dipped for 1 min in the different nanocomposite solutions and drained. After being air-dried, the sliced fruits were placed into polyethylene terephthalate plastic trays (11 x 8 cm). All samples were stored at 8°C for 12 days.

Weight Loss

Weight loss of samples was determined using an analytical balance at the beginning of the experiment after coating and air-drying, and thereafter at 3, 6, 9 and 12 days during the storage period. Measurements were performed with three replications. Weight loss was calculated using equation 1.

$$\text{Weight loss (\%)} = \text{(intial mass - final mass)/initial mass x 100\%} \quad (1)$$

Firmness

Firmness of the samples was measured by using a texture analyzer instrument (CT V1.2 Brookfield, USA) with a probe type TA 39 and 4500 g compression load. Compression was forced in the central zone for each mango cube (1.5-2 cm^3). The firmness of samples was measured as the maximum penetration force (N) recorded during tissue breakage.

Browning Index

The color of mango samples were measured by using a Chromameter 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). The values of measurements were converted to a Browning Index using equation 2 (Ergüneş and Tarhan, 2006).

$$\text{Browning Index} = [100\,(x - 0.31)] / 0.17 \quad (2)$$

where: $x = (a^* + 1.75L^*) / (5.645L^* + a^* - 0.3012b^*)$

Total Microbial Count

Microbial count of samples was determined using the pour plate method and plate count agar obtained from Merck (Germany) as the medium. A portion of 25 g of homogenized fresh-cut mangoes were transferred in 225 mL 0.1% peptone water. Further decimal dilutions were made from this 10^{-1} dilution. Subsequently, each sample was inoculated on to the media and incubated at 37°C for 48 h, following the FDA Bacteriological Analytical Manual (1998). Colony counts were converted into log cfu/g (colony forming units per g of sample).

Statistical analysis

The quality parameters of fresh-cut mango were analyzed statistically using completely randomized design. The results were evaluated by analysis of variance (ANOVA) using SPSS (Statistical Product and Service Solutions) version 16.0 and compared by Duncan's Multiple Range Test (DMRT) when needed, used to represent results at a significance level of $p < 0.05$.

Results and discussion

Weight Loss

Figure 1 shows that the weight loss of fresh-cut mango tended to increase during storage. Lin and Zhao (2007) stated that edible coating application on vegetables and fruits could inhibit gas exchange which ultimately inhibits weight loss. On day 12, fresh-cut mango (control, without coating) has bigger percentage of weight loss (5.7%) than mango with coating treatment (1.5-2.6%). Incorporation of 2% NP-ZnO into nanocomposite (ZnO formulation) resulted in the smallest weight loss. However, there was no statistical difference between the different NP-ZnO concentrations ($p > 0.05$). NP-ZnO is known as a physical barrier for water vapour and gases (Torabi and Nafchi, 2013). The respiration process affects weight loss due to its contribution on water loss through decomposition of complex compounds into CO_2 and H_2O. A similar result was reported by Marpaung *et al.* (2015) with application of 1% starch or 1% pectin and 1% NP-ZnO nanocomposite coating on fresh-cut salak (*Salacca zalacca*) fruit, which showed a weight loss about 3% at the end of storage (day 12). Also here, nanoparticle embedded-coating could surpress the weight loss change compared to the control sample. This phenomenon is caused by inhibition of water evaporation rate, respiration and complex compounds decomposition.

Firmness

The firmness of fresh-cut mango tended to decreased during storage (Figure 2) with 0.16 N to 0.27 N. This result is similar to that observed by Sothornvit and Rodsamran (2008), where the firmness reduction of fresh-cut mango with combination of film wrap and modified atmosphere packaging during 6 days storage was 0.10 – 0.35 N. Figure 2 shows that the different nanocomposite coating treatments did not give any statistical differences ($p < 0.05$). It could however be suggested that coating treatment also does not lead to a negative effect on the firmness of mango. Chatanawarangoon (2000) stated that decreasing firmness of fresh-cut mango is caused by water loss. Decreasing the water content caused decreasing turgor pressure, rigidity level and firmness of fruit. In addition, during the fruit ripening process, insoluble pectin (protopectin) changes into soluble pectin. Microbial activity also causes mango to become soft and watery. Protopectinases secreted by bacteria could speed up protopectin decomposition into pectin, thereby causing the fruit tissue to become soft also.

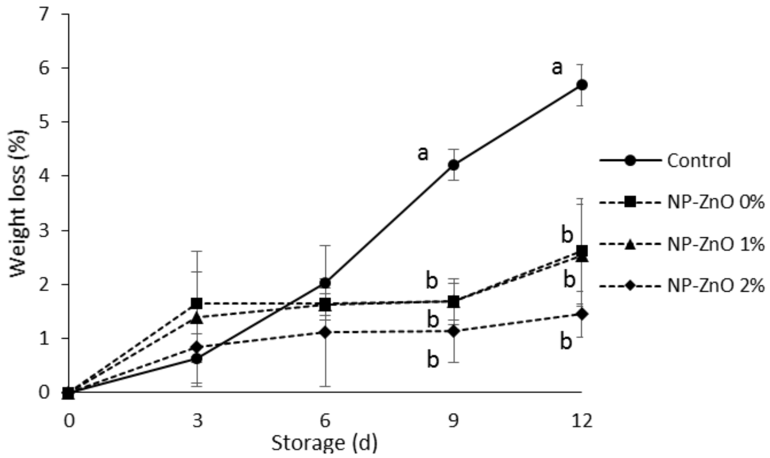

Figure 1. Weight loss of fresh-cut mango during storage. Different letters indicate statistically significant differences ($p < 0.05$).

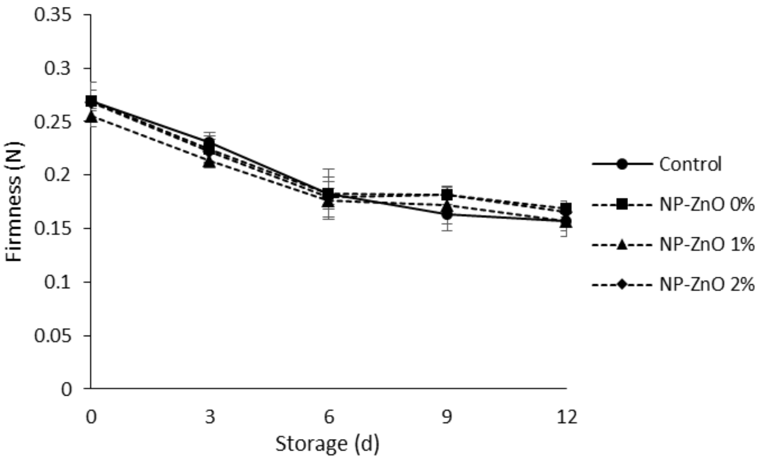

Figure 2. Firmness of fresh-cut mango during storage.

Color Change

The color change of fresh-cut mango was determined using CIE system by calculating L*(brightness), a* (redness) and b* (yellowness) values. Subsequently, they were converted into a browning index. The browning reaction happened to all fresh-cut mango treatments during storage (Figure 3). Enzymatic browning is known to be caused by polyphenol oxidation. This reaction is catalyzed by the polyphenol oxidase enzyme, which form a brown melanine compound. Peeling and cutting could make the contact area between fruit and oxygen become larger, so the activity of phenolase enzyme is increased. Nanocomposite coating could inhibit the enhancement of browning index during storage (Figure 3). Solivia-Fortuny and Martin-Belloso (2003) stated that coating application based on polysaccharides was able to prevent dehydration, lipid oxidation, browning and decrease respiration rate by controlling internal CO_2 and O_2 composition. In this research, nanocomposite coating significantly surpressed the browning index of fresh-cut mango. Application of NP-ZnO formulation resulted on the largest reduction of browning index ($p < 0.05$). Li *et al.* (2011) found similar result on fresh-cut "Fuji" apple when stored with NP-ZnO containing packaging. Li *et al.* (2011) also suggested that the polyphenol oxidase activity was decreased significantly resulting in lower Browning Index than control. Moreover, the change of browning index can also be influenced by microbial activity. Microbes, predominantly molds such as *Aspergillus niger*, contribute to the browning reaction. This is indicated by large-sized spots that make the fruit color become brown or dark.

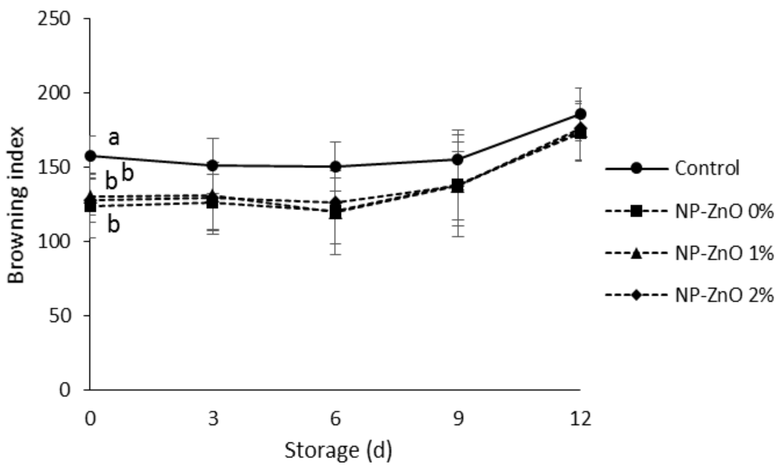

Figure 3. Browning index of fresh-cut mango during storage. Different letters indicate statistically significant differences ($p < 0.05$).

Microbiological analysis

Total microbes in all treatments increased during storage as shown in Figure 4 by which the initial and the end microbial counts of fresh-cut mango reached 3.03 and 8.38 log cfu/g respectively. Indonesia National Agency of Drug and Food Control (BPOM) (2009) regulates that the maximum of microbial contamination on fruit is 5.00 log cfu/g. On day 6, nanocomposite coating treatments significantly suppressed microbial growth below the safe threshold for consumption compared to control (5.38 ± 0.04 log cfu/g) and NP-ZnO 0% coated mango (5.36 ± 0.05 log cfu/g). This is due to the nanocomposite NP-ZnO filler which has antimicrobial ability. Several mechanisms of NP-ZnO as antimicrobial have been reported, such as i) intracellular NP-ZnO accumulation, ii) destruction of bacterial cell membranes, iii) H_2O_2 generation and iv) by releasing Zn^{2+} ions. *E.g.*, NP-ZnO penetrate into the cells of bacteria through a hole or protrusion causing membrane disruptions, so that the cell experienced lysis (Yousef and Danial 2012). Others suggested that the antimicrobial mechanism could be seen from the interaction of NP-ZnO with phosphorus groups in DNA causing replicating inactivation and inhibition of enzyme function of bacteria (Arabi *et al.*, 2012).

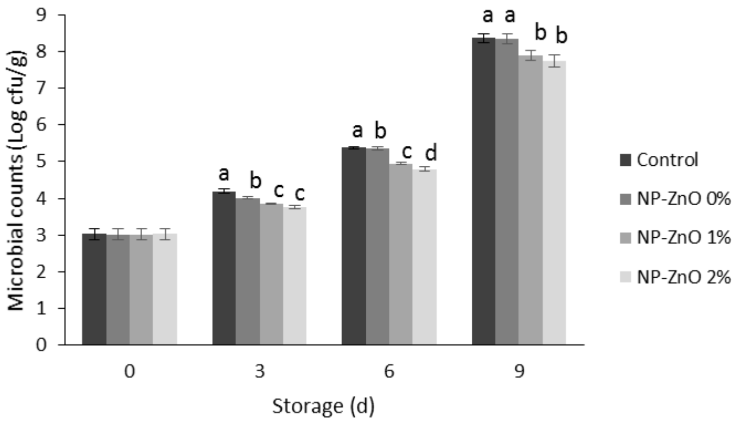

Figure 4. Microbial counts of fresh-cut mango during storage. Different letters indicate statistically significant differences ($p < 0.05$).

To provide better illustration of the antimicrobial effect of the nanocomposite NP-ZnO, Figure 5 demonstrates a comparison of all fresh-cut mangoes at the initial day (day 0) and the end storage (day 12). At the end of storage some microbial colonies were clearly visible on the surface of the control and NP-ZnO 0% marked by several dark spots. These are reduced or absent on the NP-ZnO 1% and 2% formulations.

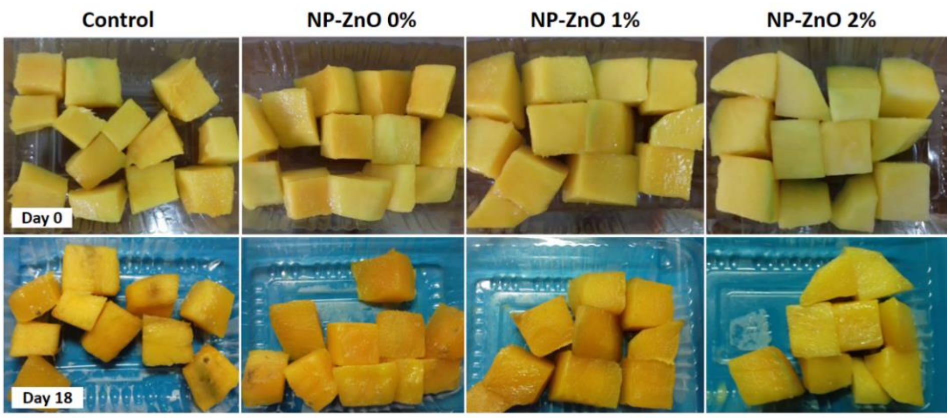

Figure 5. Comparison of fresh-cut mango during storage (day 0 and day 12).

Conclusions

We have developed novel nanocomposite coatings containing cassava starch, stearic acid and various amounts of NP-ZnO. Application of these nanocomposite coatings on fresh-cut mango was capable of suppressing the weight loss without negatively affecting the firmness of the fresh-cut mango during storage at 8^{o}C, for 12 days. Furthermore, at day 6 of storage nanocomposite coating treatments of NP-ZnO 1% and 2% suppressed microbial activity below the safe threshold for consumption (5.00 log cfu/g) to 4.95 ± 0.03 and 4.80 ± 0.07 log cfu/g, respectively. At the same time the mango control (5.38 ± 0.04 log cfu/g) and ZnO 0% coated mango (5.36 ± 0.05 log cfu/g) were not feasible to be consumed with respect to safety. The edible coating with 2% ZnO (of SC) performed superior in all aspects of the analyses. By considering our results, the novel nanocomposite coatings represent a possible alternative to maintain quality of fresh-cut mango with the objective to preserve the weight loss during storage and to delay the microbial growth.

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