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Browning inhibition of fresh-cut apple by coating carrageenan/ascorbic acid/ ZnO nanoparticles

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Abstract

In this study, a nanocomposite coating method was applied to inhibit the browning kinetics of apple "Malang", an Indonesian local commodity that is extensively produced in the Batu city area. Fresh-cut apple was coated with carrageenan in combination with ascorbic acid (1% by weight of carrageenan) and zinc oxide (ZnO) nanoparticles (0, 1% by weight of carrageenan) as filler. The results revealed that all composite materials were completely blended and confirmed by Fourier-transform infrared (FTIR). Scanning electron microscopy (SEM) exhibited that ZnO was successfully trapped by the carrageenan matrix. Notably, no differences in overall liking between uncoated and coated fruit were observed. The lower browning index (BI) rate in the nanocomposite coated fruit confirms its effectiveness in maintaining the visual appearance of fresh-cut apples.

1. Introduction

The minimally processed fruit products are increasing rapidly as a result of consumer demands for fresh, nutritious and convenient foods (Bitencourt *et al.,* 2014). Moreover, fresh-cut produce also provides other benefits in terms of waste management, shipping and in-store labour cost reduction (He and Luo, 2007). Apple "Malang" is one of the Indonesian local commodities which is mostly produced in Batu - East Java and offers a valuable source of minimally processed fruit.

Enzymatic browning is a widespread phenomenon occurring in fresh-cut fruit due to the breaking of the cell membrane allowing the interaction of oxygen, phenolic compounds and polyphenol oxidase (Ioannou and Ghoul, 2013; Javdani *et al.,* 2013). Although enzymatic browning offers advantages to improve colour and flavour in some foods, it might be detrimental to the fresh-cut fruit and vegetable Industry. Fruit and vegetable commodities including apple, pear, banana, peach, lettuce and potato, are susceptible to a browning reaction during production and display on the shelf (He and Luo, 2007). Edible coatings have emerged as a potential alternative as active packaging in inhibiting browning reactions.

Carrageenan, a hydrocolloid produced from red algae, is broadly used as a food coating agent due to its functional properties. It has three major fractions (kappa, iota, and lambda) depending on the number and position of the sulphate contents. Previous works showed the beneficial properties of carrageenan as an edible coating material for fruits (Plotto *et al.,* 2010; Meindrawan *et al.,* 2018).

Nanocomposite based coating has gained great attention to improve the performance of the conventional composite. Generally recognized as safe substance (GRAS) nanoparticle filler into biopolymers, such as ZnO, is considered to improve their barrier properties (Sharon *et al.,* 2010). Many reports documented the beneficial properties of ZnO nanoparticles in the terms of antimicrobial, mechanical, and barrier properties (Meindrawan *et al.,* 2018; Wardana *et al.,* 2018; Yuliani *et al.,* 2018; Lavinia *et al.,* 2020). In addition, ascorbic acid (Asc) has been widely known as an antioxidant which is able to inhibit the enzymatic browning reaction by reducing enzymatic oxidation of monophenols into o-diphenols and o-diphenols into quinones (Özǒlu and Bayndrl, 2002; He and Luo, 2007). In this work, the application of edible coatings, to inhibit its browning kinetics of apple, comprised of carrageenan/ascorbic acid/ZnO nanoparticles was investigated.

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2. Materials and methods

2.1 Materials

Apple var. Rome Beauty was obtained from a local store (Hypermart) in Tangerang, Indonesia. Kappa-carrageenan, glycerol (Sigma Aldrich, Germany), ascorbic acid, as well as ZnO with an average particle size of 20 nm (Wako, Japan) were utilized to make a composite solution.

2.2 Preparation of coating solution and application for fresh-cut apple

The method of coating preparation was prepared following the method by Kanmani and Rhim (2014). ZnO 1% (by weight of carrageenan) in distilled water was homogenized using ultraturrax at 15000 rpm for 10 minutes. Subsequently, each distilled water and ZnO solution (500 ml) was added 4 g of carrageenan and 2.5 ml of glycerol by constant stirring using a magnetic stirrer at 60°C for 40 minutes. After cooled at 28°C, each solution was mixed with ascorbic acid 1% (by weight of carrageenan) to fabricate carrageenan/asc and carrageenan/asc/ZnO sample respectively.

Apple with diameter 7±1 cm, weight 70-100 g, the similarity of colour and maturity level without any physical damage was washed and cut into a circle shape with diameter 4±1 cm. The whole surfaces of fruits were immersed in a coating solution for 30 s, taken out, and dried. The effect of coating treatment was evaluated by comparing (a) control (uncoated fruit), (b) Carrageenan/asc, and (c) Carrageenan/asc/ZnO.

2.3 Coating characteristic

FTIR spectroscopy analysis was done to observe the functional groups of each composite material using FTIR (Thermo Fisher Scientific, iN10). The transmittance of thin coating films was measured by ATR method at wavenumber ranges of 4000-500 cm^{-1}. The surface and cross-section of the fresh-cut apple were observed using Antscope 3IN1 Digital Microscope.

2.4 Evaluation of composite coating to inhibit browning kinetics of fresh-cut apple

Determination of reaction order of apple browning, zero-order (Equation 1) and first-order kinetic models (Equation 2), was done according to BI parameter (Equation 3). BI value was converted from color measurement using NH310 colorimeter 3nh technology referring to CIE *L**, *a**, *b** system.

$$C = C_o \pm kt \quad (1)$$

$$C = C_o \exp(\pm kt) \quad (2)$$

$$BI = \frac{(100\,(x - 0.31))}{0{,}17} \text{ , while } x = \frac{(a* + 1.75\,L*)}{(5.645\,L* + a* - 3.012b*)} \quad (3)$$

Where *C* and *C*o were the *BI* at end of storage time and the early *BI* respectively, *t* for the time of storage and *k* for the reaction constant.

2.5 Total phenolic content

The total phenolic content of the sample was evaluated by the spectrophotometric method according to Blainski *et al.* (2013). Measurement was performed by Folin-Ciocalteu reaction from the sample stored at 25°C for 0 and 120 minutes.

2.6 Sensory evaluation

A sensory evaluation test was done involving thirty untrained panellists for several hedonic aspects such as appearance, smell, texture, taste and overall liking based on a 7 degree of preference scale.

2.7 Statistical analysis

The data were evaluated by using analysis of variance (ANOVA) for sensory evaluation and total phenolic compound, followed by Duncan's Multiple Range Test (DMRT) at a significance level of $p<0.05$ using SPSS (Statistical Product and Service Solutions) version 16.0.

3. Results and discussion

3.1 Coating characteristic

The FTIR spectrogram of carrageenan, ascorbic acid, ZnO, and coatings are shown in Figure 1a. Some characteristic peaks of carrageenan demonstrated the presence of sulphate ester (1227 cm^{-1}), glycosidic linkage (1076 cm^{-1}), 3,6-anhydro-d-galactose (891 cm^{-1}), and D-galactose-4-sulphate (848 cm^{-1}) which were similar to other studies (Van de Velde *et al.,* 2002; Webber *et al.,* 2012). Those absorption peaks represent κ-type carrageenan. The typical peaks of ascorbic acid were obtained at 1025, 1112, 1313, 1656, 3001, 3406 and 3524 cm^{-1}. Those attributes were similar to the previous study which found peaks at 1141, 1321 and 1673 cm^{-1} indicating C=O and OH groups in ascorbic acid molecules (Desai and Park, 2005). As for ZnO, metal oxides were commonly indicated by fingerprint region below 1000 cm^{-1} due to inter-atomic vibrations (Kumar and Rani, 2013). A similar result of ZnO peak attributes was found by Mitra *et al.* (2012). The bands arising at 1036, 1349, 1682 and 1039, 1349, 1681 cm^{-1} in the spectrum of carrageenan/asc and carrageenan/asc/ZnO composite respectively were attributed to the shifting vibrations of C=O and OH groups of ascorbic acid. The absorption peaks at 1213, 1036, 924, 849 and 1211, 1036, 923, 849 cm^{-1} in both composites were associated with the property of the carrageenan spectrum. The ZnO peaks appeared slightly at below

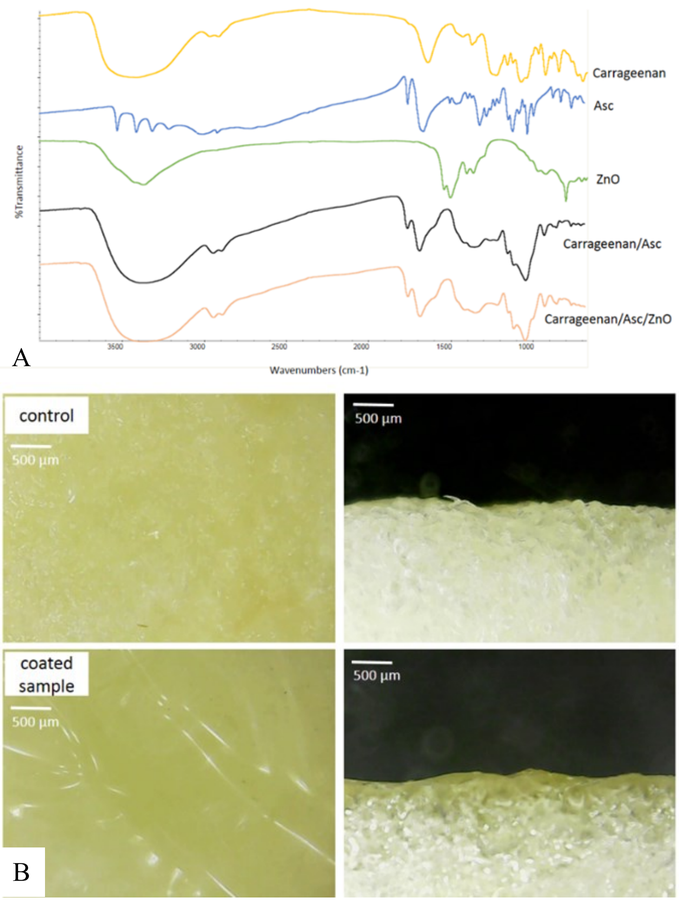

Figure 1. Characteristics of prepared coating solution (a) FTIR spectra, (b) The microstructure of the surface and cross section of uncoated and representative coated fresh-cut apple (carrageenan/asc/ZnO film).

1000 cm^{-1} region indicating the molecular biocompatibility of carrageenan, ascorbic acid, and ZnO of carrageenan/asc/ZnO film

The representative microstructure of the surface and cross-section of fresh-cut apple was successfully captured to observe the surface characteristics of the coating film. Figure 1b shows that the carrageenan/asc/ZnO coating film completely cover the whole of fruit flesh. The rough surface of the coated sample was observed that the film-forming caused a corresponding increase in coating thickness as a consequence of solution viscosity (Parreidt *et al.,* 2018). The coating film displays a smooth and homogeneous surface with thinness around tens µm. Previous work documented a similar finding that the blending of the composite was highly miscible and homogeneous on the surface of fruit (Yusof *et al.,* 2017).

3.2 Evaluation of nanocomposite coating to inhibit browning kinetics of fresh-cut apple

Enzymatic browning reaction occurring in fruit is the most important parameter affecting the commercial value of fresh-cut fruits. In this study, the browning kinetic of fresh-cut apples were determined in terms of BI by following zero-order and first-order kinetics models which are depicted in Figure 3 with their loss rates and R^2 correlations in Table 1. BI in all samples was in general increased during storage at various levels of rates depending on the storage temperature. The quality deterioration of samples in terms of BI fit best following first-order kinetic.

BI shows the purity of brown colour occurring in the process as a result of an enzymatic and nonenzymatic browning reaction (Maskan, 2001). Table 1 and Figure 2 demonstrate that coating treatment on fresh-cut apples could suppress BI. The BI was greatly decreased by nanocomposite coating, indicating that the application of carrageenan/asc/ZnO could keep the BI of fresh-cut apple. The reduction in the browning reaction was associated with physiological effect including lower respiration rates and a delay of the rise in ethylene (Solomos, 1997). The coatings could act as a barrier oxygen access, consequently, low-O_2 and high-CO_2 conditions were created (Li *et al.,* 2011). It was confirmed by the previous investigation that coating could retard the quality of minimally processed fruit including colour deterioration (appearance) (Amiri *et al.,* 2018; Yuliani *et al.,* 2018). The filler of nano-ZnO was also contributed to improving barrier properties of nanocomposite coating. The formation of a tortuous pathway through the matrix of the coating film by the

Table 1. The estimated kinetic parameters of zero- and first-order models for fresh-cut apple BI at different temperatures.

Sample	Temperature (°C)	Zero-order		First-order	
		k (min^{-1})	R^2	k (min^{-1})	R^2
Control	10	28.490	0.952	0.367	0.946
	25	25.680	0.883	0.299	0.927
	37	36.562	0.971	0.305	0.967
Carrageenan/Asc	10	3.128	0.891	0.097	0.882
	25	3.980	0.963	0.111	0.967
	37	6.060	0.972	0.612	0.979
Carrageenan/Asc/ZnO	10	1.206	0.976	0.033	0.976
	25	3.012	0.987	0.080	0.994
	37	2.126	0.989	0.050	0.990

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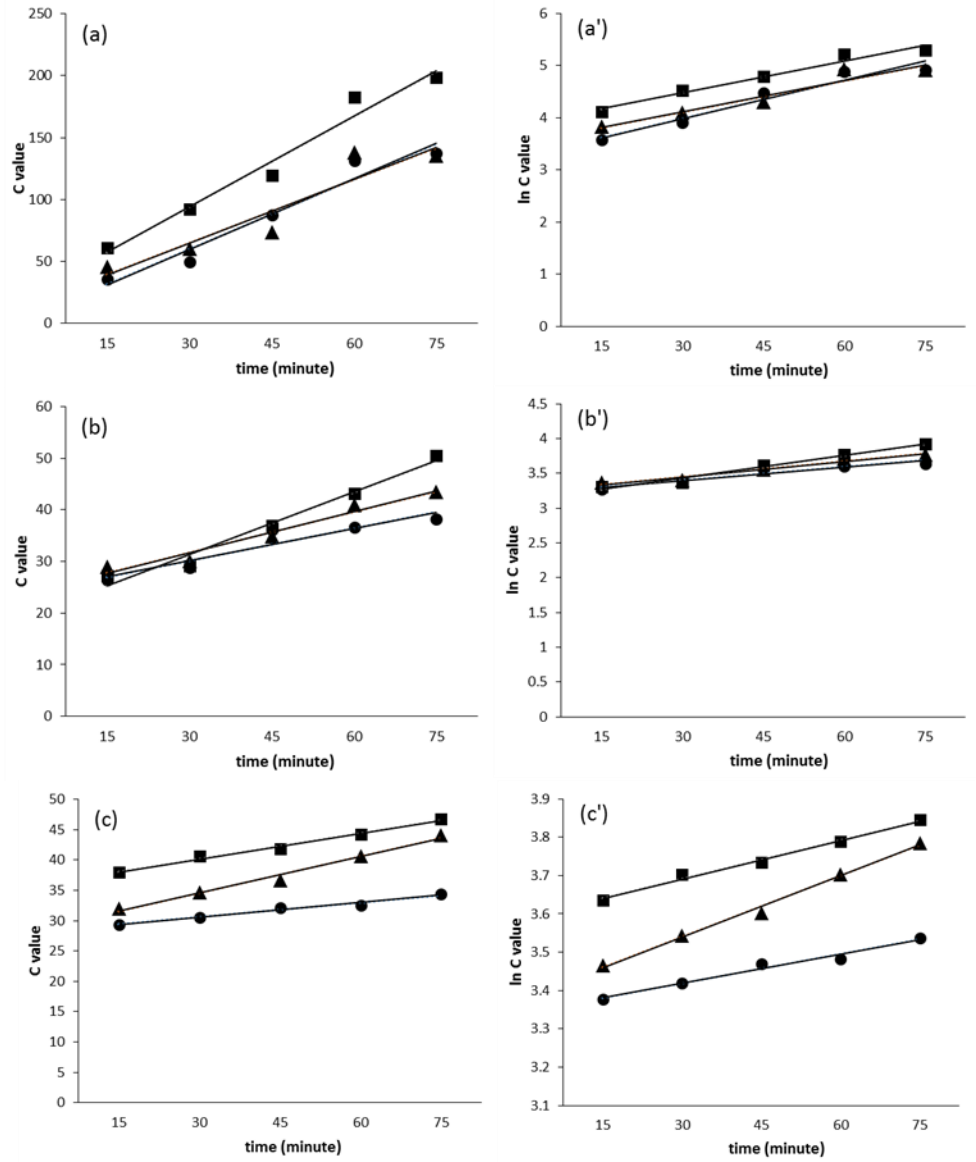

Figure 2 .The fitted zero- and first-order kinetic models of fresh-cut apple BI during storage at 10°C (l), 25°C (5), and 37°C (n), treated by (a) control (b) Carrageenan/Asc, and (c) Carrageenan/Asc/ZnO.

incorporation of ZnO might be responsible for this phenomenon.

3.3 Total phenolic content

The total phenolic content of fresh-cut apples during storage are shown in Figure 3. The total phenolic content of all samples decreases significantly during storage without any significant difference among samples. The highest phenolic content was found in carrageenan/asc/ZnO (9.78 mg GAE/100 g) followed by carrageenan/asc (9.59 mg GAE/100 g) and the lowest was found in Control sample (9.47 mg GAE/100 g) at storage time of 120 min. Although no signs of total phenolic content were demonstrated by the coated sample in comparison with the uncoated sample, both coating treatments were probably still contributed to the inhibition of total phenolic loss.

3.4 Sensory evaluation

Sensory evaluation data for fresh-cut apples are presented in Figure 4. The smell and taste of coated apples were significantly less preferable in comparison with the uncoated sample (control). This might be attributed to that unnatural odour and sour taste were present as a consequence of the addition of ascorbic acid. However, those were distinct from the appearance parameter, which represents the colour of apple surface, shows that coated apples were more preferable

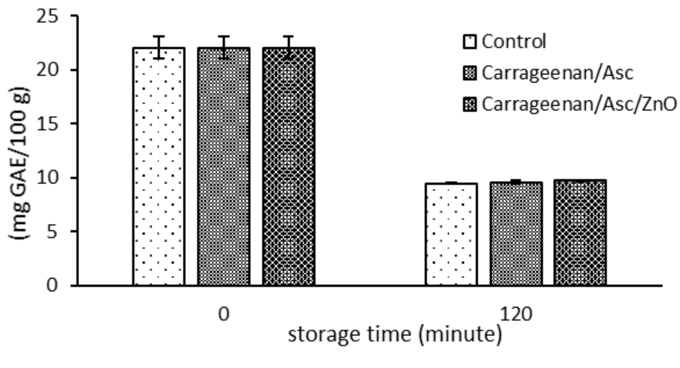

Figure 3. Total phenolic compounds of fresh-cut apple

significantly compared to control. The application of edible coatings considerably maintain the visual changes in fruits due to the modified atmosphere formed with high levels of CO_2 and low levels of O_2, hence retarding the maturation processes (Bosquez-Molina, 2005). Furthermore, there was also no significant difference in overall liking and texture scores among the samples. The results were in accordance with a previous study that reported that carrageenan coating could retard quality deterioration and extend the shelf life of several kinds of fruit (Ribeiro *et al.,* 2007; Meindrawan *et al.,* 2018; Yuliani *et al.,* 2018). Hence, carrageenan containing asc/ZnO could serve as an alternative coating to maintain the quality of fresh-cut apple, but some improvement was necessary for odour and taste acceptance.

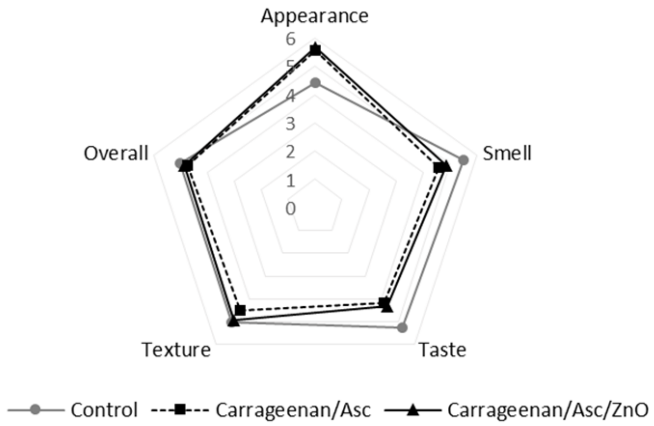

Figure 4. The spider web of the average scores of consumers' preference

4. Conclusion

The composite coating made from carrageenan combined with asc or asc+ZnO was successfully applied to the preservation in the browning kinetic rates of fresh-cut apple “Malang”. The results showed that the carrageenan/ascorbic acid/ZnO coating was more beneficial in inhibiting browning reaction than the uncoated and carrageenan/ascorbic acid-coated apples. All of the components were successfully blended into nanocomposite confirmed by FTIR spectra and observed by SEM for its microstructure surface. The coating film has a quite smooth and homogeneous surface indicating completely to cover the whole of the fruit surface. Sensory evaluation data indicated no significant difference in overall liking which mean that nanocomposite treatment was still acceptable. However, the smell and taste scores of the coated samples were negatively affected by asc. Thus, application carrageenan/ascorbic acid/ZnO could be an alternative coating, however, further improvements were still needed.

Conflict of interest

The authors declare no conflict of interest.

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