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Application of chitosan as biomaterial for active packaging of ethylene absorber

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Abstract. Chitosan was used for active packaging of ethylene absorber that can change the head space of food packaging to extend the shelf life. The purpose of this study was to develop active packaging from chitosan and KMnO4 and apply the active filmto package tomatoes. Active film was prepared by mixing chitosan 6 g, 140 mL of acetic acid 1%, 60mL of aquadest, 2mL sorbitol, and $KMnO_4$ with concentration of 3 g, 5 g, and 7 g. After 5 days of storage, the film used to wrap the tomatoes was sweated. The best formulation to absorb the ethylene was made from 7 g of KMnO4 since it could inhibit tomatoes from shortly ripening compared to other formulations. The fruits were packed at room temperature had a high hardness as much as 17,79 mm/50mg/5s compared to the control of 3,47 mm/50mg/5s, while at the refrigerator, the tomato had lower hardness value of the 2,72 mm/50mg/5s compared to the control of 4,29 mm/50mg/5s. Addition of KMnO4 on the film could maintain the value °Hue either for all treated sample and control in the range of the yellow to red.

Key words : Biomaterial; chitosan; ethylene absorber; tomatoes

1. Introduction

Packaging has important role in food processing, mainly to protect and distribute of the product. Packaging should protect the food from unpleasant environment such as light, gas, moisture, microbe, mechanical stress and dirt [1]. So far, modern packaging have been developed to be more effectively integrated with the needs of the distribution supply chain [1] include modified atmospheric packaging (MAP), active packaging and smart packaging. This packaging technology was aimed to maximally improve the safety and the quality of the food product. Regarding to the active packaging, Warsiki *et al*. [12] has been researched the development of chitosan-based active anti-oxidant package with the addition of anti-microbial agents such as garlic and betel leaves extract. Terry *et al.* [10] developed a new material to absorb ethylene by using Palladium (Pd)-promote powder. Warsiki *et al*[12] has also examined the evaluation of physical-mechanical properties and the permeability of chitosan films.

Chitosan has been commonly selected as the base for filmmakers because it can be formed into films easily in low temperature with a good permeability [6]. Chitosan film has strong properties i.e. elastic, flexible and difficult to be torn [4]. In addition, this chitosan film has a high permeability, sealableand easy to be added some additives [12] thus it is possible to use this chitosan film as a matrix to carry such potassium permanganate as active packaging of ethylene absorber. According to Day [5] potassium permanganate ($KMnO_4$) is one of the additional ingredients that serve as an ethylene absorbent material. This compound has been applied commercially to prolong the shelf life of climacteric fruits. Widayani *et al.*[13] and Syamsu *et al.* [9] has demonstrated that potassium permanganate could effectivelyprolong the shelf life of banana as 27 days. Commonly, ethylene absorber was formed in the sachet, however in this study, the absorbent compounds of potassium permanganate and chitosan are mixed to be made into an ethylene absorbent wrap. The film was used to package fruits to slow the ripening process and keep its freshness longer.

2. Materials and Methods

2.1 Materials and apparatus

The materials are used to make the film of active packing were chitosan, glacial acetic acid 1%, distilled water, and $KMnO_4$. While the apparatus were magnetic stirer, thermometer, analytical balance, aluminum and glass plates as well as oven.

2.2 Ethylene Absorbent Film

Chitosan of 6 g was dissolved in 1% acetic acid as much as 140 mL and stirred it until homogenous using magnetic stirrer for 1 hour at 40°C. Then as much as 60 mL of aquadest was introduced into chitosan solution and added with sorbitol of 2 mL. After it was homogen, the film solution was well mixed with KMnO4 powder with a concentrations of 3 g, 5 g, and 7 g. The solution was continue stirred until homogen, then it was cooled at room temperature (32°C). The film was casted on a glass plate with size of 20 cm × 30 cm, then stored in a 50°C oven for 24 hours. The film was characterized visually. Table 1 showed the formula code based on the treatments.

Table1.Code of sample

Sample Code	Formula			Drying temperature (°C)
	Chitosan (g)	$KMnO_4$ (g)	Sorbitol (mL)	
F1	6	3	2	50 °C
F2	6	5	2	50 °C
F3	6	7	2	50 °C

2.3 Application of ethylene absorbent packaging

Active film was used to wrap tomatoes. Every single tomato was packagedinto ethylene absorber film and then store into room (32°C) and refrigerator temperature (9°C) for 7 days. The stored tomatoes and then analyzed its quality including the hardnessand the degree of color.

2.4 Data Analysis

The experimental was designed in a complete factorial randomized design with two factors and two replications. The factor used was the concentration of $KMnO_4$ added to film solution storage temperature. In this experiment it would see the effect of these factors on the performance of the ethylene adsorbent packaging. The measured variable data was then analyzed using the SPSS version 16.0 statistical program

3. Results and Discussions

3.1 Visually film characteristics

The three formulas were prepared with different concentrations of KMnO4 i.e. F1 (3 g), F2 (5 g), and F3 (7 g). KMnO4 is an aggressive organic material thus when it was added into film solution, a clumping and rising temperature has occurred. This is due to the reactive nature of this compound (Anonymous 2013). Based on the visual characterization of the film, the results obtained that Formula 1 (F1), Formula 2 (F2), and Formula 3 (F3) have different characteristics. The thickness and fragility of the resulting ethylene adsorbent film was affected by the difference in the amount of KMnO4 added to each of the formulas. Table 2 shows that F3 has characteristics of less thickness and breakable. The more $KMnO_4$ added, the film has an increasingly fragile. It seems that $KMnO_4$powder was not really compatible with the chitosan powder thus the bond between $KMnO_4$and chitosan was not strong enough. The characterization results in Table 2 also show that the three formulas have elastic properties. This elastic was caused naturally by sorbitol which was used as plasticizer material.

Plasticizer can reduce the intermolecular forces along the polymer chains thus it accentuates the increasing of film flexibility [3].

Table 2.The characteristic of ethylene absorber film

Code	Results
F1	Thick, elastic
F2	Thick, fragile, elastic
F3	Thin, fragile, elastic

3.2 Application of ethylene absorber film

Application of ethylene absorbent packaging was performed to see the performance the film in absorbing ethylene gas produced from fruit. The experiment was carried out by wrap tomatoes using an ethylene absorbent film. The packaged was sealed then stored at room temperature (32^{o}C) and refrigerator temperature (9^{o}C) for 5 days. The tomatoes then analyzed for their physical and chemical quality changes. Based on visual observations, the film used to pack the tomatoes becomes sweaty. Sweat was a water vapor produced from tomatoes due to respiration process. Both of these storage treatments show a difference results.

At room temperature, fruits tended to has faster maturation when compared with tomatoes stored at refrigerator storage temperature (9^{o}C). The tomato stored at room temperature was shown in Figure 1 (a1), while the tomatoes stored at the refrigerator temperature are shown in Figure1 (a2). Additionally, the plastic film storage at 32^{o}C has more moisture than the film kept at refrigerator temperature (9^{o}C). This occurs because of the difference in respiration rate of the fruit at each of the temperature treatments. According to Pantastico *et al.*[7] the temperature was one of the external factors that affect the rate of respiration. Turiska [11] stated that the higher the storage temperature, the faster the rate of respiration and discoloration of the fruit. A high rate of respiration would result on faster ripening of the fruits which it was indicated by changing color of the fruit skin.

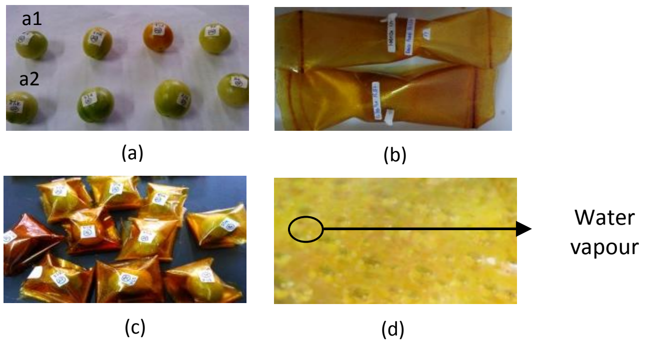


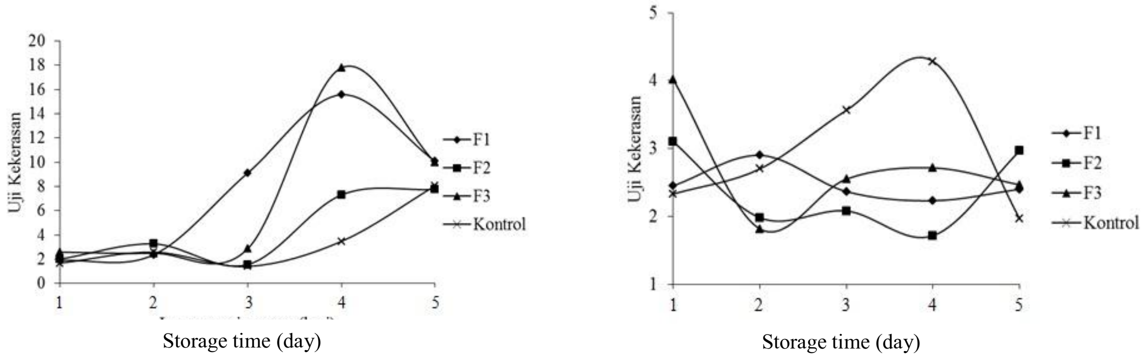
Figure1. (a) Tomatoesstore at : (a1) room temperature (32°C); (a2) refrigerator (9°C); (b) plastic film of ethylene absorber; (c) tomatoes wrapped into film; (d) visually changing of ethylene absorber film

3.3 Changing fruits quality during storage

3.3.1 Hardness

The hardness of fruits is affected by turgor from living cells that are constantly changing in the process of maturation. This is due to the changing cell wall components, these changes will affect the fruit hardness that is often physically observed by fruit firmed [14].

Hardness is one of the criteria used by consumers to determine the fruit maturity level which is observed by the depth of needle into the fruit thus the greater the value of fruit hardness the lower the quality of fruit [8]. The higher the hardness means the more soft fruit that indicates that the fruit is already mature. Hardness test at room temperature for 4day of storage showed that the control sample had lower hardness value than other sample, that was equal to 3,47mm/50mg/5s, while formula F1, F2, and F3 on the same day respectively had higher value of 15.57; 7.30 and 17.79mm/50mg/5s. The relationship between hardness value and storage time (day) at room (32°C) and refrigerator (9°C) can be seen in Figure 2.



(a) (b)

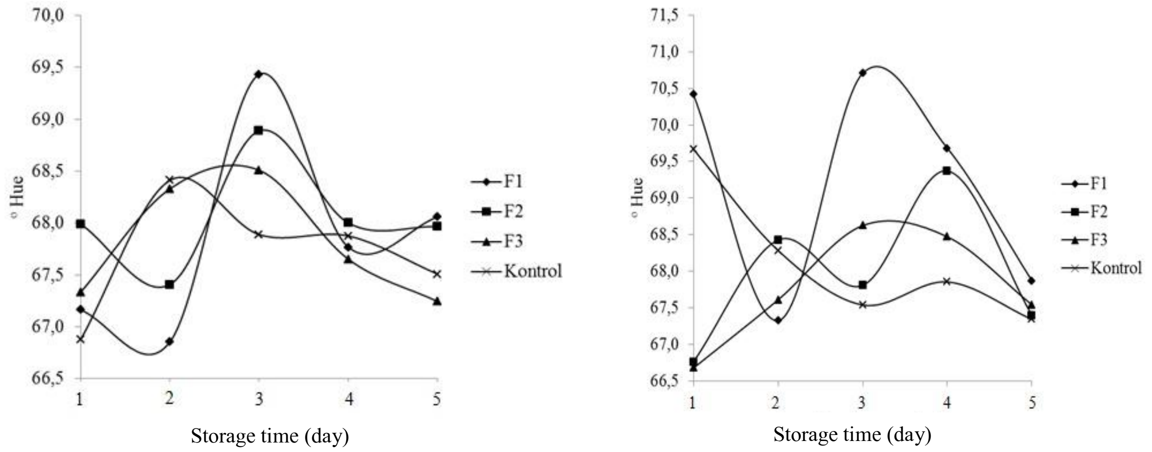
Figure 2. Hardness value (mm/50mg/5s) along the storage at 32°C (a) and 9°C (b)

The fruit will be softer with increasing storage time. The softening of this fruit was indicate the beginning of the maturation process. Pantastico [7] suggested that fruit hardness was reduced due to the destruction of insoluble protopectin to a soluble acid and pectin. The observation of the 4th day of the control sample has a higher hardness value of 4.29mm/50mg/5s when compared to the formula F1, F2, and F3 with the value of 2.23, 1.72, and 2.72mm/50mg/5s respectively. The more KMnO4 concentration would resulted on decreasingthe hardness of the fruit. This showed that the ethylene absorber film in F1, F2, and F3 may inhibit the rate of tomato respiration. Based on statistical analysis on the confident level of 0.05 indicated that the temperature storage influences the hardness of the tomato fruit, but no significant effect for the addition of KMnO4 or the interaction between KMnO4 concentration and storage temperature.

3.3.2 Value of °Hue

The relation between °hue and storage time (days) at refrigerator was shown in Figure 3. Based on this observation, the control has °hue lower (67.86) compared to sample of F1 (69,68), F2 (69,37), and F3 (68,47). However, the difference between these values between F1, F2, F3 and control was not significant difference. It mean that the adding of $KMnO_4$ was inadequately inhibited the fruit ripening. It looks that KMnO4 used in the formulation was too small thus it was not enough to slow the maturing process of the fruit.

The observations showed that treated sample and control has °hue values in the range of 54°-90°, which mean the tomato skin color changedfrom yellow to red. The more mature the tomato, then the value of °hue will be bigger and closer to the value of 90° or the skin fruit visually change ro red. Based on this observations, the control tomatoes store in room temperature has a °hue of 67.87°, while the sample of F1 and F3 have value of 67.77° and 67.65°. This indicated that the control sample was facing faster maturation. With the presence of ethylene absorbent packaging for wraping the tomato, it can be conclude that the film could slightly inhibit fruit ripening. The relationship between °hue value during storage ws shown in Figure 3.



(a) (b)

Figure 3. Value °hue during storage at 32°C (a) and 9°C (b)

4. Conclusions

Chitosan and KMnO4 can be used as a base material for the preparation of ethylene absorber film. After storage for 5 days it was obtained that the film was sweated. The ethylene absorber packaging has less thickness and elastic. The best formulation was the addition KMnO4 of 7 g. The packed fruit at room storage temperature has a higher hardness value than the control sample, whereas at the storage temperature, the packed sample has a hardness value lower than the control. Both sample and control has a °hue values were in yellow-red color range. Further study is required in order to produce better ethylene absorber film. It is recommended to conduct further research on KMnO4 concentrations greater than 7 g and observation time longer than 2 weeks.

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