Visual Ph-Sensing Films Based Nata De Coco Containing Curcumin as Package Indicator Labels for Detecting Fish Freshness

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Abstract: Currently, chemical indicators have been used for fresh meat and aquatic products to monitor their freshness. Among these, the colorimetric indicators like pH-sensitive dyes provide visual information of packaged foods to consumers. In recent years, several studies have been carried out using colorimetric indicators to evaluate fish freshness by utilizing changes in pH in fish. Natural dye pigments can be used as an alternative to colorimetric indicators which are considered safer, non-toxic, easy to prepare, and economical when compared to chemosynthetic dyes. Recently, more researches have focused on curcumin (CR), which is extracted from the curcumin. Curcumin based edible freshness sensor with membrane nata de coco bacterial cellulose can be applied on the packaging of mackerel fillet as an indicator freshness. The edible freshness sensor is light yellow when the mackerel fillet is fresh and brown when the mackerel is rotten. The pH value was observed to increase as the freshness level of the fish decreased.

1 INTRODUCTION

Fishery products are one of the food ingredients favored by the community. Mackerel fish (*Rastelliger spp*) is the result of processing fishery products that are often found in the market. Fish are susceptible to damage and have a short shelf life (Pacquit et al., 2008). The deterioration of fish quality is caused by enzymatic action and bacterial action, which are able to decompose the components that make up fish body tissues so as to produce physical changes such as soft fish meat and chemical changes that produce volatile compounds and have a foul smell (D. A et al., 2017). Currently, the assessment of fish quality degradation is still using sensory methods, such as seeing the appearance and color of the fish, smelling the fish's aroma, feeling the texture of the fish. Fish that are damaged by microorganisms will produce volatile nitrogenous base compounds or also called total volatile bases nitrogen (TVB-N). Traditional methods of quality evaluation can provide precise quantitative results (S. T et al., 2006), but they are time-consuming and have complicated procedures (Z. L et al., 2011). For example, Kjeldahl method for total volatile basic nitrogen (TVB-N) content, an important indicator of fish spoilage (R. J & E. L, 1991).

Hence, the development of convenient, rapid and low-cost methods to evaluate fish freshness is in great demand. One concept is that of an intelligent or smart food packaging which gives an indication of the freshness of fish samples end-to-end (B. L et al., 2002). This novel packaging can be made available for consumers or users to evaluate the real-time freshness. Currently, chemical indicators have been used for fresh meat and aquatic products to monitor their freshness. Among these, the colorimetric indicators like pH-sensitive dyes provide visual information of packaged foods to consumers. The mechanism is that the release of volatile amines results in pH increase of the packaging headspace, and then a color change of the pH-sensitive dye physically trapped in the polymer film will be observed when volatile amines are in high enough concentrations in headspace (P. A et al., 2007).

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In recent years, several studies have been carried out using colorimetric indicators to evaluate fish freshness by utilizing changes in pH in fish. Huang, et al. (Huang et al., 2011) who evaluated the freshness of fish using bromcresol purple, green and cresol red. Likewise Kuswandi, et al. (Kuswandi et al., 2012), who evaluated polyaniline-based colorimetric indicators for detecting spoilage in fish. However, the use of these chemical compounds is starting to be avoided because they have potential harmful effects on humans that are carcinogenic or mutagenic (Srivastava et al., 2004; Zhang et al., 2014). Natural dye pigments can be used as an alternative to colorimetric indicators which are considered safer, non-toxic, easy to prepare, and economical when compared to chemosynthetic dyes (Choi et al., 2017; Zhang et al., 2014). Recently, more researches have focused on curcumin (CR), which is extracted from the curcumin. It is a biologically active member of curcuminoids and widely used as a spice and colorant (M. et al., 2017). CR is a lipophilic phytochemical that has been found to possess pH-dependent solubility(W. L. et al., 2019). Musso, Salgado, and Mauri (Y. S. et al., 2017) found that the use of an ethanol-water mixture as solvent for CR could intensify the color response capacity of CR/gelatin films against pH changes.

The use of colorimetric indicators requires a membrane as a reaction medium between reagents and analytes in a sensor manufacture. The use of bacterial cellulose as an edible membrane can be an option because it is made from natural materials, environmentally friendly and safe for consumption (A. L. et al., 2020). One of the commonly known bacterial cellulose products is nata de coco (H. D. et al., 2018). This study aims to determine whether the edible freshness sensor can be applied as an indicator of the freshness of mackerel fillets, carried out various tests of parameters of the freshness level of mackerel fillets, and the relationship between changes in the color of the sensor and various parameters of the freshness level of mackerel fillets.

1.1 Materials and Method

The materials used in this study were mackerel fillet (Rastrelliger spp) and curcumin purchased at the Modern Market in Depok Indonesia, unsweetened nata de coco purchased at the marketplace, aquades, 96% ethanol, chitosan and acetic acid. The membrane cellulose is made from basic ingredients of nata de coco using the mixing and casting method and then drying the sample. The mixing method is mixing the ingredients using a hot plate stirrer or magnetic stirrer. The mass of acetic acid as an additive was varied from 15 ml, 20 ml and 25 ml, while the mass of nata de coco and chitosan used remained at 16 grams and 0.2 grams. For pH testing, 1 g of the sample was crushed and dissolved in 20 mL of distilled water and homogenized. The acidity level was measured with a pHmeter that had been previously calibrated with standard buffers 4, 7, and 10.

1.2 Result and Discussion

The first stage has successfully made a membrane as an indicator label media. The membrane is made from basic ingredients of nata de coco using the mixing and casting method and then drying the sample, as shown in Figure 1. The mixing method is mixing the ingredients using a hot plate stirrer or magnetic stirrer. The mass of acetic acid as an additive was varied from 15 ml, 20 ml and 25 ml, while the mass of nata de coco and chitosan used remained at 16 grams and 0.2 grams. Curcumin extract is made from 50 grams of curcumin that has been mashed using a blender then added 10 ml of Ethanol, after being smooth squeezed to get extract from curcumin.

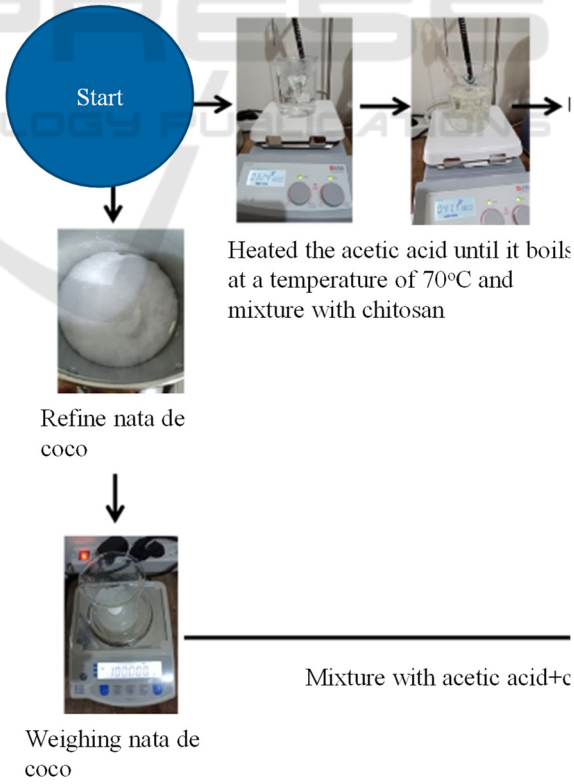

Figure 1: The process of membran made based nata de coco.

If observed directly, all the resulting samples show a visual like plastic. Plastic is usually used to package fish like many we find in supermarkets. Therefore, the membrane used for labeling this indicator must have plastic-like properties. The sample with 15 ml of acetic acid variation showed a flat, transparent, odorless but brittle visual as shown in Figure 2. While the 20 ml and 25 ml variation of acetic acid showed a stronger sample when pulled. However, the sample with 25 ml of acetic acid variation showed a strong sour smell. This happens because of the high content of acetic acid as a mixture in the manufacture of samples.

Figure 2: The result of membrane with various acetic acid 15 ml.

To determine the properties of the resulting sample more accurately, sample characterization was carried out which included weigh, thickness, transparency testing and microscope observations. Tests were also carried out on the three types of plastic commonly used in the market as a comparison (plastic A, plastic B and plastic C). Table 1 show that characteristic of sample membrane with composition nata de coco, chitosan and acetic acid, we abbreviate nata de coco with NDC, Chitosan with CH and Acetic acid with AA.

Table 1: The characteristic of sample membrane.

	Weight (gr/m^2)	Thickness (micron)	Transparency (%)
Membrane 1 (NDC+CH+15 ml AA)	29.6	25.8	89.24
Membrane 2 (NDC+CH+20 ml AA)	30.1	27.1	95.52
Plastic A	31.8	27.8	-
Plastic B	46.2	30.1	-
Plastic C	37.4	29.3	97.16

The samples that were characterized were only samples with variations of 15 ml and 20 ml of acetic acid while 25 ml were not tested. The results of the basic weight test of the sample with a variation of 15 ml of acetic acid showed a weight of 29.6 gr/m^2, which means that every 1 m^2 weighs 29.6 grams. The basic weight of the sample with a variation of 20 ml of acetic acid showed heavier results, namely 30.1 gr/m^2. These results show a weight that is almost the same as plastic packaging on the market, namely plastic A. The results of testing the thickness of the sample with a variation of 15 ml of acetic acid showed a thickness of 25.8 microns while the thickness of the sample with a variation of 20 ml of acetic acid showed thicker results, namely 27.1 micron. These results show a weight that is almost the same as plastic packaging on the market (plastic A) of 27.8 microns.

The sample transparency test was characterized using a UV-Vis spectrometer. The results obtained from testing using a UV-Vis spectrometer are the values and graphs of transmittance at certain wavelengths. Materials that are able to transmit more light are transparent materials. Therefore, materials that have a high transmittance value are related to materials with a high level of transparency (H. D. et al., 2018). Tests were also carried out on the type of plastic (plastic C) commonly used in the market as a comparison. The test results of the UV-Vis spectrometer are as shown in Figure 3. The level of transparency of the sample is visually shown in the Figure 4. The membrane sample with a variation of 20 ml of acetic acid had a higher transparency value than other methods. The value of the transparency of the membrane sample is also the closest to the value of the transparency of the plastic.

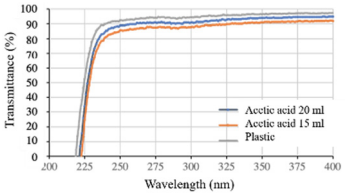

Figure 3: The result of spectrometer uv-vis test.

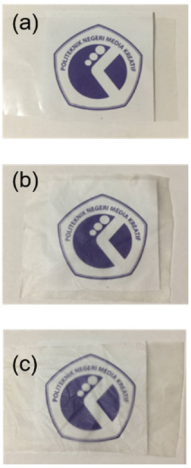

Figure 4: These two figures have been placed side-by-side to save space. Justify the caption.

Furthermore, the process of immobilization of curcumin extract on the membrane. The membrane used was a membrane with a composition of nata de coco, chitosan and 20 ml of acetic acid. Curcumin extract is made from 50 grams of curcumin that has been mashed using a blender then added 10 ml of Ethanol, after being smooth squeezed to get extract from curcumin. Preparation of curcumin extract as shown in Figure 5.

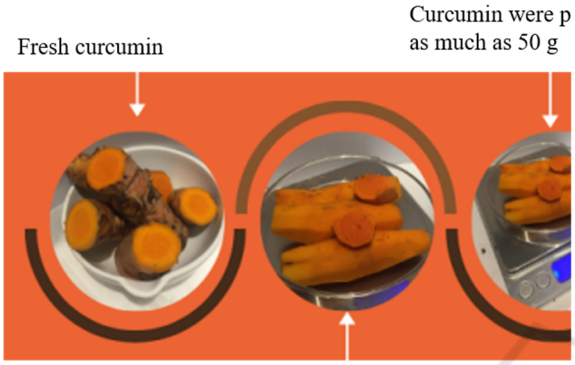

Figure 5: Preparation of curcumin extract.

Next, make an indicator label by immobilizing the curcumin extract on a piece of membrane with a size of 2cm x 1cm for 30 minutes and dry it. After the sample was dry, the membrane was put into a closed container with plastic wrap containing 10 ml of NH_4OH solution, then do the same with the solution to measure the pH. Then monitor both for 30 minutes-1 hour once in 24 hours, the results are as shown in Figure 6.

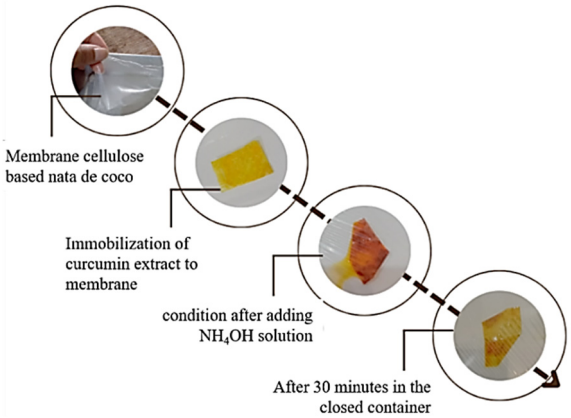

Figure 6: Preparation of curcumin extract.

Then the results of the curcumin extract were carried out by varying the pH using acetic acid and NaOH, by inserting 2 ml of curcumin extract into 5 small bottles then 2 bottles being adjusted to pH = 3 and pH = 4 with the addition of acetic acid and 3 bottles adjusting the pH to pH = 10, pH = 11 and pH = 12 with added NaOH. This stage serves to make an indicator solution.

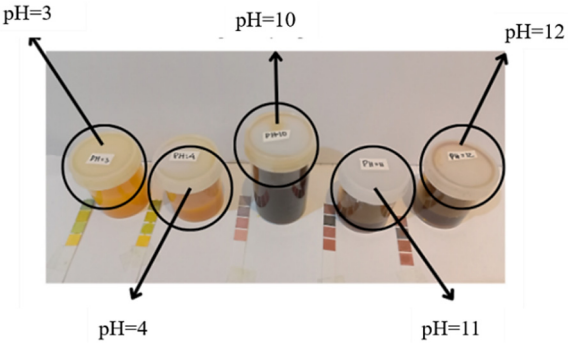

Figure 7: Preparation of curcumin extract.

Next, test the indicator label of the curcumin extract by cutting the cellulose membrane with a size of 3cm x 2cm, then dripping 15 drops of curcumin extract then let stand for 30 minutes and dry. The test was carried out using mackerel. Fresh mackerel fish (fish (*Rastelliger spp*) was stored with an indicator label in a closed container and then the pH was measured for some time. Color of indicator labels stored with fish for 24 hours was shown in Figure 8.

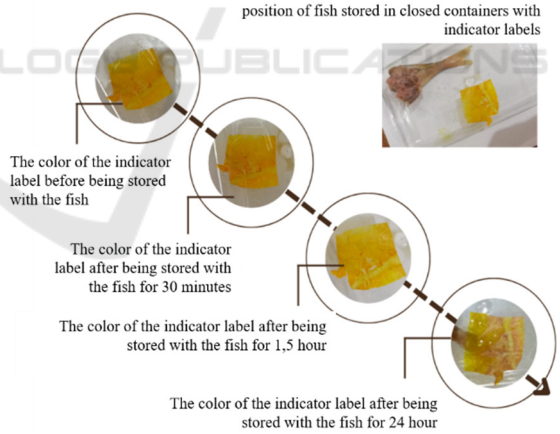

Figure 8: Color of indicator labels stored with fish for 24 hours.

The color change on the label that is put into a container containing fish after rotting is the same as the color change on the label that is dripping with NH_4OH. This shows that the curcumin indicator label can work in responding to the decline in fish quality. The color change in the curcumin extract solution when the pH was varied using acetic acid and NaOH, to determine whether curcumin extract

could be an indicator of freshness to fish. The pH value of mackerel fillet was determined using a pH meter. The results of pH observations can be seen in Table 2.

Table 2: The result of pH test.

Hours	pH
0	6
0.5	6.1
1.5	6.6
4	6.7
9	6.8
12	6.9
16	7
18	7.5
21	7.5
24	8

Along time the storage of fish fillets bloating has decreased in good quality microbiological, chemical, physical and organoleptic. Based on the results of color sensor observations freshness of edible on mackerel fillet packaging on room temperature storage, freshness sensor color edible changes along with changes in the freshness level of mackerel fillets. Sensor color the freshness of the edible light yellow at the time of fillet fresh mackerel, until brown when it is rotten or cannot be consumed. This is because the number of microbes in fish fillets stored at room temperature has increased with the length of storage time (A. L. et al., 2020). Enhancement The number of microbes will produce volatile nitrogen base compounds or also called total volatile nitrogen bases (TVB-N), which mostly consist of trimethylamine (TMA), dimethylamine (DMA), and ammonia. The compound can be used to determine the freshness of fish, the maximum limit of TVB-N in fish that can be consumed (Bhadra et al., 2015). Enhancement TVB-N concentration resulted in an increase in pH on fish and the atmosphere around the sensor becomes alkaline, resulting in a change in the color of the sensor edible freshness (P. A et al., 2007). Mackerel fillet texture value experienced decreased during storage at room temperature. A decrease in the texture value indicates the presence of decrease in fish quality. When fish experience decrease in quality, fish meat will soften due to remodeling of the muscle tissue by enzyme activity in protein hydrolysis (Wibowo et al., 2014). In addition, the results of the organoleptic assessment of odor and the appearance of the color of the fish meat stored in room temperature decreases with time storage time.

2 CONCLUSION

Curcumin based edible freshness sensor with membrane nata de coco bacterial cellulose can be applied on the packaging of mackerel fillet as an indicator freshness. The edible freshness sensor is light yellow when the mackerel fillet is fresh and brown when the mackerel is rotten. The pH value was observed to increase as the freshness level of the fish decreased.

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