Application of Anthocyanin Extracted from Red Cabbage as a Natural Dye in The Smart Food Packaging Technology

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**Abstract.** Smart packaging in the food industry is an emerging technology for fulfilling food safety and quality. In this research, we proposed the application of anthocyanin extracted from red cabbage as a natural dye for smart food packaging applications due to the structural transformations of anthocyanins associated with a color change in the function of pH. This natural dye was extracted from red cabbage using the boiling method. The highest absorbance of the anthocyanin extract in the various pH environment was determined using UV-vis characterization. The red cabbage extract with a pH of 2 in the various concentrations of 2%, 4%, 6%, 8%, and 10% was soluted to the film label made from PVA (Polyvinyl Alcohol) and carrageenan. The thickness, tensile strength, and elongation of the film were discussed as the physical properties of the film label. The FTIR spectra of the film were also discussed to guarantee the anthocyanin in the film composition. Film labels with 6%, 8%, and 10% concentration of the dye had a bright and produced a striking color change after being applied as an indicator of shrimp freshness.

1. Introduction

Currently, the selection of a product, especially food, cosmetic, or drug products is not only seen from its attractive packaging but also the feasibility of the product for consumption [1]. The expiration date will definitely be seen by consumers before buying. In fact, not all products are suitable for consumption even though they have not reached the expiration date. This can be caused by many things, such as improper storage process, damaged/leaked packaging, or due to transportation resulting in damage to the product. Smart packaging is the best solution to solve this problem.

Smart packaging is one of the new technologies in the packaging sector. In contrast to conventional packaging which only provides information about the product itself (such as manufacturer, expiration date, composition), smart packaging can inform changes that occur in the product or its environments such as temperature, pH, and microbial growth. Not only that, but smart packaging can also provide the latest information on products through internet technology (internet of things), for example, information that can be accessed through the RFID (Radio Frequency Identification) label on the packaging [1, 2].

Smart packaging is very necessary for food packaging. One example of a smart packaging application is packaging that can detect changes in food products in the form of sensors, such as the Time-Temperature Indicator (TTI), gas indicator, or food freshness indicator. Other applications are packaging that can actively increase the shelf life of the product, for example, packaging that can absorb CO2, water, ethylene gas, or other compounds that can cause food products to spoil quickly; or packaging that actively releases certain gases or substances to increase shelf life; and antimicrobial packaging. [2, 3, 4]

Smart packaging applications for several food products have been widely studied [9]. Among them is silica gel as a moisture absorber, silver-based antimicrobial packaging, chip-shaped CO2 release, oxygen indicator with the O2SenseTM brand, or TTI produced by OnVuTM [3]. However, smart packaging still needs to be investigated further, for example by using natural ingredients so that it does not cause harm/toxic to the human body. One example of natural ingredients that exist in plants is anthocyanins. Anthocyanins in plants are color carriers such as red, orange, purple, or blue colors in flowers, fruits, vegetables, and leaves. Anthocyanins are very sensitive to changes in pH and show different colors under acidic, neutral, or alkaline conditions. [4, 5]

One of the potential materials for color carrier matrices in smart packaging labels is a mixture of PVA and Carrageenan because both can form films with good membranes [8]. In making PVA-based smart labels using color indicators, it is necessary to have a dye that has certain stability that can be influenced by factors such as storage temperature and the material to be packaged. Anthocyanins are water-soluble pigments. Anthocyanins are usually found in plants and fruits. Red cabbage is a source of natural dyes. Red cabbage is a plant that contains a lot of anthocyanins. Anthocyanins extracted from red cabbage are sensitive to heat and light, so they can be used as color indicators on smart labels to detect product damage due to high temperatures. This plant is used as the main ingredient of natural dyes in this study. [5,6]

1. Methods
   1. *The Anthocyanin Extraction from Red Cabbage and UV-Vis Characterization*

The red cabbage was boiling in the distilled water at a temperature of 80ºC to 100ºC. The anthocyanin content in the red cabbage will release into the water in high temperatures for 7-10 minutes until the entire surface of the leaves is white. The ratio of red cabbage to distilled water was determined with a 1:3 composition. In this process, the authors used 600 ml of distilled water with 200 g of red cabbage. The whole extract was centrifuged to separate the extract from the precipitate and then get steamed for more concentration.

The buffer solution was added to the red cabbage extract to change the pH from pH=2 to pH=11 and then characterized by UV-vis spectrophotometry. This test was conducted to determine the maximum absorption value of the sample solution of red cabbage anthocyanin extract.

* 1. *Label Film Making and Its Characterization*

The matrix solution was prepared by mixing PVA (Polyvinyl Alcohol) and Carrageenan solution at a ratio of 3:2 (w/w) with a hotplate magnetic stirrer. In this research, we add 2 g of PVA (Polyvinyl Alcohol) in the 50 ml boiling water for 30 minutes to get the homogeneous solution. In the other glass, we add 1.5 g of Carrageenan in the 50 ml boiling water for 30 minutes too. The next step was mixing the PVA (Polyvinyl Alcohol) and Carrageenan solution in one beaker glass and adding 3 ml of glycerol to the solution and heating it for 15 minutes.

We various the red cabbage extract in the same matrix solution. In every 100 ml of matrix solution, we add 0 ml, 2 ml, 4 ml, 6 ml, 8 ml, and 10 ml red cabbage extract to get various film solutions. The film solution was poured into a 20 cm x 10 cm of Flexi glass and left for 3 hours and then placed in an oven at 50ºC for 24 hours. After 24 hours the film was removed from the oven, then stored in a desiccator for approximately 3 hours, then remove the entire film from the mold by scraping it using a cutter.

The thickness, tensile strength, and elongation of the film were determined to get the physical characterization. The chemical bond in the film was also determined by FTIR characterization. In the initial application, the authors applied smart packaging labels to detect the freshness of shrimp. The color changes of the label were observed on fresh and rotten shrimp.

1. Result and Discussions
   1. *UV-Vis Characterization*

Fig 1 showed the UV-Vis of the red cabbage extract. The maximum absorption value was at pH=2. This is evident with wavelengths from 450-600 nm, the maximum absorption peak is at a wavelength of 520-521 with an absorbance value of 0,7. Therefore, when the sample was stored in the open area, the absorbance will be the maximum value.

The extract solution with pH = 2 was then used as a dye for film labels by mixing red cabbage anthocyanin extracts with concentrations of 0%, 2%, 4%, 6%, 8% of the total solution, into PVA and carrageenan solutions, which were then printed to create film labels.

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| **Figure 1.** UV-Vis Spectra of Red Cabbage Extract |

* 1. *Physicsl Properties of The Label Film*

The result of the physical properties of label film was shown in Table 1.

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| **Table 2.** Physical properties of Label Film | | | |
|  | **Thickness (cm)** | **Tensile Strength**  **(kg f/cm2)** | **Elongation (%)** |
| *Matrix* | 0,0053 | 144,8 | 0,16 |
| *Matrix + 2 ml dye* | 0,0069 | 50,4 | 0,27 |
| *Matrix + 4 ml dye* | 0,0088 | 24,3 | 0,23 |
| *Matrix + 6 ml dye* | 0,0095 | 23,6 | 0,36 |
| *Matrix + 8 ml dye* | 0,0084 | 22,3 | 0,39 |
| *Matrix + 10 ml dye* | 0,0088 | 24,0 | 0,39 |

Of the six formulas that have been tested, the PVA + Carrageenan + 6% dye sample has the largest thickness of 0.0095 cm, while the smallest thickness is PVA + Carrageenan + 0% dye sample with a thickness of 0.0053 cm. In this test, the percentage of dye variation from red cabbage anthocyanin extract was not very influential. In the manufacture of films based on PVA and carrageenan used a plasticizer, namely glycerol. Glycerol has the advantage of being a plasticizer because of its high boiling point so that no glycerol evaporates in the process.

In removing the film label from the Flexi glass, the film label that is the easiest to remove is the concentration without dye. And when added with dye, the film label is easily removed and the results are perfect, with dye concentrations of 2%, 4%, and 6%. With more than 6% addition of red cabbage anthocyanin extract, the film label is easy to tear (brittle).

The strongest tensile strength test was Matrix solution without dye with a tensile strength of 144.8 kg f/cm², while the weakest tensile test was Matrix solution + 8% dye with a tensile strength of 22.3 kg f/cm². This tensile strength test is influenced by the concentration of dye made from red cabbage anthocyanin extract which is added, the higher the percentage of extract given to the film solution, the weaker the attraction. The tensile strength of this film label tends to decrease, this is probably due to the presence of water content in the dye which interferes with the manufacture of the film by PVA polymer and carrageenan.

The highest elongation or percent elongation of the resulting film was Matrix solution + 10% dye with an elongation value of 0.39% while the lowest was Matrix solution without dye with the elongation value is 0.16%, the greater the elongation value, the more elastic the film. The elongation of this film label tends to increase, the more dye added, the greater the percent elongation.

* 1. *FTIR Characterization*

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| **Figure 2.** The FTIR Spectra of the Label Film Indicator |

Red cabbage contains compounds belonging to the flavonoid group, namely anthocyanins which play a role in various red and blue colors in plants. Chemically, anthocyanins are derivatives of a single aromatic structure, namely cyanidin, where all types of anthocyanins have differences based on the bond of the aromatic ring.

The C-C chemical bonds appear in the FTIR spectrum with wavenumbers of 557.81 cm-1, 595.90 cm-1, 666.29 cm-1, which indicates chain group bonding (R). Aromatic structural bonds were detected in the C=C bond at wavenumbers 1632.93 cm-1, 1712.96 cm-1, and the C-H bond at 3358.91 cm-1. The C-O bond was detected at a wavenumber of 1221.68 cm-1.

The PVA is a polymer made from the hydrolysis of poly(vinyl acetate) with alcohol to produce PVA. The chemical structure of PVA is shown in the following figure. From the chemical formula, it can be seen that the chemical bonds in PVA are in the form of C-C, C-O, C-H, and O-H bonds. The C-C, C-O, C-H, and O-H chemical bonds in PVA and carrageenan appear on the FTIR spectrum of the packaging labels for both Matrix solution (PVA+ Carrageenan) and Matrix solution with dye (10% red cabbage extract +PVA+ Carrageenan).

There is an absorption peak at wave number 1221 cm-1 which only appears in the anthocyanin dye of red cabbage extract and PVA film label + carrageenan + 10% dye. This indicates that on the film label PVA + carrageenan + dye 10% contains red cabbage anthocyanin extract. There is an absorption peak at wave number 2941.40 cm-1 in which only appears on the PVA film label + carrageenan and PVA film label + carrageenan + 10% dye. This indicates that the bond is a characteristic of chemical bonds in PVA and carrageenan.

* 1. *The Color Changes of Smart Packaging Labels as a Freshness Indicator of The Shrimp*

The first picture shows the condition of the film label before the test, seen directly on the film label with variations of red cabbage anthocyanin extract dye with concentrations of 2%, 4%, 6%, and 10% before testing. There is a color gradation that becomes more concentrated with an increasing concentration of red cabbage extract. However, the concentrations of 6%, 8%, and 10% have almost the same color density. The film labels with concentrations of 2% and 4%, which show the color is not concentrated and tends to be pale.

The second picture shows the condition of the film label after testing. The test was carried out by attaching a label to the lid of the jar (bottle), which was filled with initially fresh prawns. The test was carried out at room temperature with the jar tightly closed and left for 24 hours. The result is that the shrimp jam emits a foul odor and changes in the color of the shrimp, the film label attached to it changes its color, as seen from Figure 2. The film label with a concentration of red cabbage anthocyanin extract dyes of 6%, 8%, and 10% gives the clear and visible color changes before and after application. Meanwhile, the color changes of film labels with 2% and 4% concentration aren’t clear.

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| (a) |
| (b) |
| **Figure 2.** Thecolor changes of smart packaging labels with various concentrations of the dye as a freshness indicator of Shrimp: (a) before applied and (b) after applied for 24 hours at room temperature |

1. Conclusion

Film labels made from anthocyanin extracted from red cabbage with pH = 2 showed the maximum absorbance in the UV-Vis characterization. The concentration of the of red cabbage extract 6%, 8%, and 10% produce a solid and bright color in the film. Moreover, the color change after being applied as an indicator of shrimp freshness gives a clear color change. The FTIR spectra showed that red cabbage extract was still detected in the sample of the packaging film label. Film labels with concentrations of red cabbage extract 6%, 8%, and 10% had uniform thickness, tensile strength, and elongation test results.

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