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Development of Intelligent Food Packaging from Red Cabbage Anthocyanin Pigment

Suzihaque, M.U.H, NurSyazwani Farzana Bt Mohd Zamroni

Abstract:-Corn starch, chitosan and red cabbage extract act as natural pH indicator to determine fruit spoilage by developing pH sensitive film and coating as the color changes based on pH of fruit. The film color changed from pink to purple and brownish with the changes of pH. pH indicator film and coating were assessed for their physical, chemical, mechanical and biological properties. The stability of the pigment was evaluated for 4 days with the presence and absence of light and with or without cooling effects. The film incorporated with red cabbage extract proven to have higher stability when stored at room temperature with the exposure to light. It also exhibits better color stability when kept under cold temperature in comparison to room temperature.

Keywords : Edible film, red cabbage, starch, pH sensitive, intelligent food packaging

I. INTRODUCTION

Freshness is one of the qualities that contribute to consumers. Generally, fruits and vegetables have high moisture that ranges from 75-95% and under normal atmospheric condition, it will dry rapidly as it loss rigidity and cell shrinkage that cause wilt and shrivel. To reduce moisture loss, good packaging is essential as to increase the shelf life and freshness of vegetables and fruits. [1]

Common materials used for food packaging are petroleum-based and non-renewable sources. Primary function of food packaging is to protect food from surrounding exposure that can cause spoilage. Spoilage of food includes discoloration, moldy, off-flavor and other that cause the characteristic of fresh food turns damage.

Plastics started to dominate food packaging market due to its mechanical resistance, heat resistance, shape versatility, degrees of rigidity and relatively low price.

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* Correspondence Author
Suzihaque M.U.H*, Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, 40450 Selangor, Malaysia. Email: suzihaque@uitm.edu.my
NurSyazwani Farzana Bt Mohd Zamroni, Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, 40450 Selangor, Malaysia.

Types of food packaging include transparent trays, perforated polyethylene film or nets, ventilated pouch, cartons and tray.

Plastics are made from polymers that contain heavy metals and organometallic compounds that encapsulated with polymer matrix to improve the characteristics and produces low production cost.[2]

Plastic bag has become one of the useful products worldwide amongst consumers due to its functional, lightweight, strong and hygienic way of transporting. It becomes useful for goods, foods and chemicals packaging. However, plastic is non-biodegradable which plastic bags can last for hundreds years in anaerobic environment and merely photodegrade but not completely.

The Malaysian Plastics Manufacturers Association (MPMA) claimed that the overall Malaysian consumes 300 plastic bags in a year. This will produce accumulated plastic waste by continuous and extensive disposal of petroleum derived polymers. So, alternative for plastic usage replacement need to be investigate in order to overcome concerns over non-biodegradable plastic usage.

One of the best alternatives to replace conventional plastic for food packaging is by inventing renewable and biodegradable film and coating from natural resources. Intelligent food packaging or also known as edible film and coating is packaging made from edible and natural components. The structure of thin layer film and coating used as food wrap without altering the original content or nutrient of food. This intelligent food packaging provides the improvement of gas and moisture barriers, mechanical properties, microbial protection and extend shelf life of wide range food product whether fresh or processed foods. [3]

Main contribution to prepare edible coating and film are classified into non-edible and edible biopolymers. Non-edible biopolymers are combination of starch with polyethylene, polyanhydrides, polyvinyl alcohol and polylactic acid (PLA). Natural resources from biopolymers to make edible film and coating are categorized into three sources which are polysaccharides, protein and lipid. Polysaccharides include starch, chitosan, alginate, xanthan gum and cellulose. Examples of protein are soy protein, sunflower, whey protein, wheat protein and corn zein while for lipids; bees wax, paraffin, shellac resin, free fatty acid and terpene resin. [4]

To improve properties of intelligent film and coating food packaging, there should be certain addition such as plasticizer. This is due to make the mechanical, biological and physical property of film and coating in a good quality[5].

In this research, red cabbage is used as main material to indicate strawberry spoilage as fresh strawberries are popular choice of berry worldwide. Corn starch, chitosan and red cabbage act as natural pH indicator to determine strawberry spoilage by developing film and coating as the color changes based on pH of fruit. Different parameters will be compared on the film and coating such as pH, tensile strength, FTIR, antimicrobial and color.

II. METHODOLOGY

A. Red Cabbage Anthocyanin Pigment Extract Preparation

About 150.0 g of red cabbage was crushed and diluted with 100 mL ethanol. The extracted sample was stored for 24-hour at 70°C in an oven. The material was filtered using a filter paper to obtain the extract.

B. Production of starch and chitosan-film solution

For the production of potato starch film solution, 4 g of starch, 4 ml of glycerol and 100 ml distilled water was stirred at the temperature of 70-80°C until the solution became translucent. Chitosan film-forming solution was prepared by dissolving 2 g chitosan, 30 ml acetic acid and 20 ml NaOH in 50 ml distilled water, and stirred for 24-hours at room temperature.

C. Production of pH indicator film and coating

The final step to produce the film was prepared by mixing Chitosan and Starch film solution with 10 ml red cabbage. About 20ml of film solution was casted on a petri dish and placed in an oven for 2 days at 40°C. The film solution was also used for coating strawberries.

D. Deterioration study of strawberry as the indicator

To application tests was conducted on fruit products where films were cut into rectangles and used as indicators to monitor the freshness of the fruit. Strawberry was used as a sample for the tests. The coated and film strawberries were kept on cold and room temperature for seven days to observed the color changes and the effect of temperature changes.

E. Determination of Film thickness

Film thickness was determined by a micrometer at the nearest 0.0001 mm at 3 random positions on the film area. Three measurements were taken at a nonspecific spots for each sample. The average thickness was calculated for each sample and used in the measurement of tensile strength.

F. Determination of Color measurement

The film colour was determined by a Minolta colorimeter (CR 300; Minolta, Japan). Chroma meter was used to measure the parameter of film colour where a* indicates redness-greenness, b* indicates yellowness-blueness and L* indicates lightness were used to determine the color differences. The sensitivity to the presence and absence of light on films were measured for 3 days. The color change data were obtained on each film and color difference (ΔE) was determined by the following equation.

$$\Delta E = \left((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{1/2} \quad \text{-[1]}$$

Where: $\Delta L^* = L^* - L_o^*$; $\Delta a^* = a^* - a_o^*$; $\Delta b^* = b^* - b_o^*$

G. Determination of Mechanical characteristics of films

The tensile stress and strain of the films were detrmined by using Universal Testing Machine using ASTM D1708-10 method which was used to determine the tensile strength of the plastics. This test was supported with a 2.5 kN load cell at a rate strain of 50 mm/min. The films were cut to smaller pieces of 20x50 mm.[6] Average thickness of the three film strips measurement was used to determine the cross section area of the sample.

III. RESULTS AND DISCUSSION

A. The examination of film and coating on strawberry

Fig. 1 shows the film condition after drying for two days at 40°C in an oven. The film in Fig. 1 was the preliminary study for development of the film. The first film in pink showed in Fig. 1 was at pH 5. Anthocyanin of red cabbage acts as natural pH indicator as the color turned red in acidic. The colour will changed to purple, blue, green and then finally turn to yellow when it becomes alkaline [7]. In Fig. 1(a), the film showed pink but there were white spots on the surface of the film due to uneven starch mixing when making the starch solution. This will affect elongation test as it caused brittleness. The color of the film in Fig. 1(b) should be in pink color instead of brownish which was in pH 2-3. The texture of this film was oily and spoiled due to mixing with other sample during drying that changed its color. Fig. 1(c), it showed purple film in pH 6-7. The texture of the film were in good state but had uneven color distribution on the film surface. These three different colors of films were used for color test in the presence and absence of light and different temperature effects.

Fig. 2 showed the initial and final observation of coated strawberries under room and cold temperature for seven days. As for Fig. 3 and Fig. 4, the strawberries were wrapped with three different color films under room and cold temperature for four days. Strawberries were used as samples it has very short shelf life as it is prone to texture softening, mechanical injury and infections caused by pathogens [7]. Strawberries are acidic and the pH is range 3.3 to 3.6. There were no obvious differences between the film and samples coated after a day of storage. The conditions of all strawberries were in good condition after one week for all temperatures. However, the color of the coated strawberry became faded under room temperature and the color of strawberry under cold temperature was slightly faded. This was because color changes of fruit was from synthesis of carotenoid and anthocyanin and degradation of chlorophyll [8]. The scent of coated strawberries was sweet until day 7 as coating could slow down fruit deterioration, storing strawberry under cold or freezing temperature. Strawberries without coating could causes quality deterioration because of structural collapse [9]. The pH of strawberries decreased during storage. In Fig. 3(b), the film wrapped with strawberries turned red at the last day of storage. It showed that the strawberries were acidic. For Fig. 4(b), it can be seen that the films changed to brown after 3 days. These might due to protein denatured in red cabbage.

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These observations showed that the optimum storage temperature for strawberries were in cold condition. The incorporation of chitosan on strawberries lead to protective effect and reduces the decay of strawberries of 15% [7].

Fig. 1: (a) Pink, (b) brownish, (c) purple films

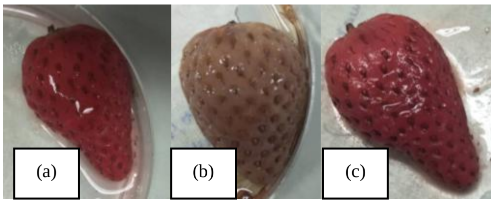

Fig. 2: Coated strawberries (a) Day 0, (b) Day 7 (room temperature), (c) Day 7 (cold temperature)

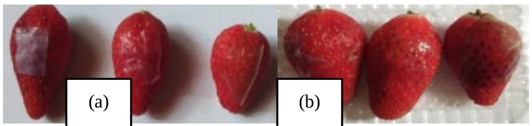

Fig. 3: Film at Cold temperature (a) Day 0, (b) Day 3

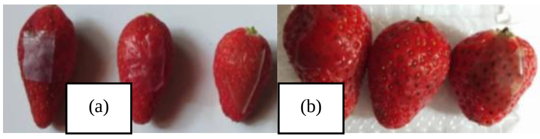

Fig. 4: Film under Room temperature (a) Day 0, (b) Day 3

B. FT-IR Spectroscopy

FT-IR equipment can detect the interaction in polymeric mixture. FT-IR was used to determine the possibility interactions between the components and also the type of molecular bonds. Fig. 5 showed the FT-IR spectra for one sample of starch/red cabbage extract/chitosan film where x-axis is wavenumber and y-axis is transmittance. The sample analysis exhibits characteristics absorbance patterns at wavelength between 4000 and 607 cm^{-}. The results dictated all major functional group exist in infrared spectra of the film. Film spectrum showed a classic amide I (C=O) stretch bend at 1647 cm^{-} where the characteristic of chitosan is presence, while at 1556 cm^{-} has stretch bend of C=C rings which indicates the aromatic compounds in the extract. FT-IR spectrum for film indicates a large absorption range at a maximum at 1044 cm^{-} corresponding to aromatic ring C-H deformation. This peak represents the vibrational modes of amylose and amylopectin from starch components. This analysis also showed the presence of red cabbage extract as hydroxyl group located at range 3294 cm^{-}.

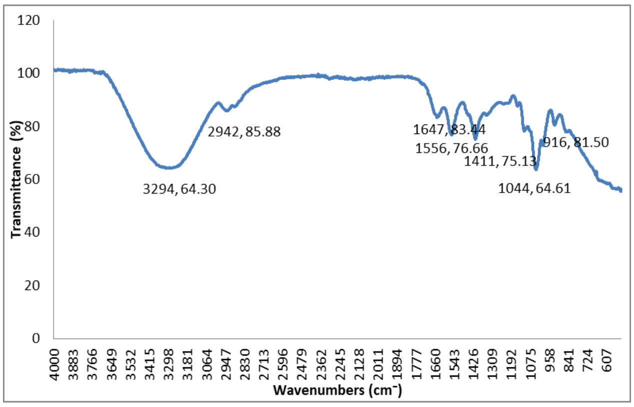

Fig. 5: FT-IR spectra of starch/chitosan/red cabbage extract film

C. Determination of Color stability

The color characteristic of edible film is an important physical characteristics as it effects the appearance of the products [8]. Three essential aspects in food acceptance are color, texture and flavour. The brighter the film, the better quality of the edible films [9]. The pH-sensitive films were measured for their stability of color as a function of temperature, time and lighting. Changes in the anthocyanin content is parallel with the value changes of color parameters. The film were stored under sunlight and in dark for three consecutive days. The change of the film color during storage were calculated and compared with the initial color of the films. The color of the films that stored in dark place remains constant visually for three days while color of films kept under sunlight became slowly faded.

During the storage time, most of the color saturation, c* decreased as pH increased. But some values of c* increased when pH increased[10]. The high value pf L* indicates high brightness in the pH films. The chroma a* values opposed to the relation of pH which dictates the higher the value of a*, the lower the pH. The result indicates that red color has a higher intensity at lower pH variations for anthocyanins. Films with red cabbage anthocyanins have more negative values of b* showed a prominent blue intensity. On the other hand, ΔE value above than 5 can be easily detected with human eyes [10]. Therefore, films incorporated with red cabbage anthocyanins showed to have limitation at pH 6 and 7.

To identify the effect of temperature on films, three different colors films were used which were pink, brownish and purple films. Fig. 6 and 7 showed the graph of total color difference of under the presence and absence of light. In the presence of light, brownish coloured film showed high color stablity than other films as there was just slight difference color changes, while pink colored film showed greater difference on color change. For films kept in the absence of light, total color differences of three samples increased. Brownish film showed to be more stable than other colored films. Since brownish film was at the lowest pH, it showed that anthocyanins was stable at lower pH and more unstable at higher pH conditions [11]. Table I showed the results of colour difference for red cabbage extract film. From the table, the film displayed bright purple colour at day 1, and turned into light purple colour after 24 hours.

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After the second day, the film changed to a dark purple-blue colour and finally appeared in purple-green colour at the last day of storage. [12] Value of colour difference of both of the films did not show great difference. Hence, this comes to a conclusion that film may have good colour variation depending on pH value which potrays good visual colour variability [13].

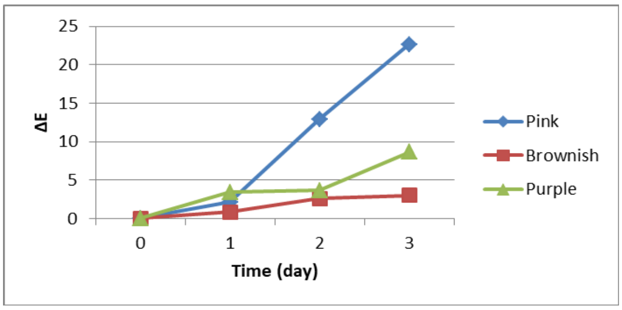

Fig. 6: Total color difference under the presence of light

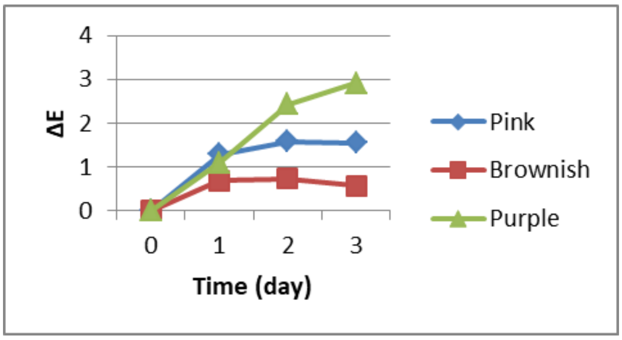

Fig. 7: Total color difference under the absence of light

Table I: Color difference of bio-indicator edible film from red cabbage extract

Day	ΔE	pH
0	0	5.8 ± 0.1
1	13.66 ± 0.43	5.85 ± 0.13
2	17.42 ±1.13	6.12 ± 0.25
3	22.47 ±1.88	7.12 ± 0.21

As the anthocyanin color changes, the molecular structure of the anthocyanin changes with pH changes. At acidic conditions the predominant flavylium cation, contributes to purple and red colors at pH 1–3. At pH of 4–5, pseudo-base carbinol is the predominant form which caused by the hydration of the molecule showed to be colorless. When the pH increased to 6–7, it rendered the quinoidal structure of basic purple color. The anionic structure formed at pH 7–8 with a blue color. At pH 8–9 range, the central ring opens, formed a yellow colored chalcone. [14] The films with the red cabbage anthocyanin indicates better color stability, even at room temperature, as acylated anthocyanin transmits greater stability to the molecule.

D. Determination of film thickness and mechanical characteristics of

The tensile strength of the film was evaluated for its mechanical properties for instance the maximum force and elongation at break; and the relative increase in sample length at break point. Usually, the films with higher tensile strength generally have lower elongation according to their structure [15].

Table II shows the results of tensile strength and elongation of the pH sensitive films where the mechanical values do not meet the Japanese Industrial Standard for elongation of minimum tensile strength and elongation are at 3.92 MPa and 70% respectively [16]. The addition of anthocyanin with solid concentration is proportional increased with the thickness of the film. Addition of glycerol concentration also resulted in the increases of film thicknes. Tensile strength tends to decrease with increasing glycerol concentration [17]. The molecules formed a 3-D network organized with intermolecular interactions when the film was formed only with starch after gelatinization,. The presence of anthocyanin, however, may weaken the intermolecular interactions and thus affect the mechanical properties of the films. [18].

Elongation at break is the ability of the film to extend before breaking [18]. Concentration, type of base material and solvent in film production affect the elongation and tensile of the film [19]. The elongation of the films however was found to be unaffected with the presence of anthocyanins.

Table II: Tensile strength and elongation of two films

Parameters	Film 1	Film 2
Thickness (mm)	0.145	0.145
Tensile strength (MPa)	0.345	0.230
Elongation (%)	26.3	21.6

IV. CONCLUSION

Starch/chitosan/red cabbage extract film have shown good results to be a potential development of intelligent packaging. Film with red cabbage extract has high contribution as a pH sensitive film due to its reactivity in color variations. This pH-sensitive film however had thin and flexible structures with rough surfaces. Based on the results obtained, this film had greater prospective for the evolusion of intelligent packaging due to its stability during storage and extraordinary color variation between pH changes. Its characteristic, rather unpleasant smell of red cabbage constitutes a certain limitation. Overall, this pH indicator film would be optimal for intelligent packaging applications.

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AUTHORS PROFILE

Suzihaque M.U.H is a senior lecturer at the Faculty of Chemical Engineering, Universiti Teknologi MARA. She received her first degree and Master in Chemical Engineering from the Universiti Teknologi Malaysia. She completed her PhD at the University of New South Wales, Australia. Her research interest would be mainly on food drying, food preservation and food processing.