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Development of smart colourimetric starch–based indicator for liberated volatiles during durian ripeness

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ABSTRACT

The mechanical, physical and barrier properties of colourimetric starch–based films (CSBFs) were developed by adding natural polymers (chitosan, citric acid, carboxymethylcellulose, and kraft fibre). Novel volatile compound indicator films were prepared from starch (as a film matrix with 30% *w/w* sorbitol) using the casting method and adding natural polymers, and pH–dye (methyl red and bromothymol blue as indicators). CSBFs mixed with 0.1% chitosan improved the mechanical and barrier properties with a significant decrease in water vapour transmission rate, water solubility, and oxygen transmission rate, as well as improved tensile strength. Trials using liberated fruit aromas verified that CSBFs resulted in visible colour changes in the presence of mixed sulphur and ethyl alcohol aromas. Colour change in terms of the total colour difference of CSBFs was related to mixed sulphur and ethyl alcohol levels, thereby enabling CSBFs could be used to monitor real–time ripeness of durian volatiles.

1. Introduction

Intelligent packaging is a concept that detects, records, and indicates the condition of packaged products to provide information, enhance safety, and improve quality. Intelligent packaging devices are classified as data carrier tags (such as barcode labels and radio frequency identification (RFID)) and package indicators (such as time–temperature indicator, gas indicator, and bio–sensors) (Yam, Takhistov, & Miltz, 2005). Indicator systems usually provide qualitative information through visual colourimetric changes. An ideal indicator for packaging should be inexpensive and should not require an expensive piece of analytical instrumentation (Mills, 2005). These intelligent devices may be incorporated in packaging materials or attached to the inside or outside of a package (Brody, Bugusu, Han, Sand, & McHugh, 2008).

Colour–based pH indicators can potentially be used as secondary metabolite indicators, especially volatile compounds, because aromas can induce pH changes (Kerry, O' Grady, & Hogan, 2006). The fundamental characteristic of colour–based pH indicators is that they change colour when placed in an acidic or basic environment. According to Smolander (2003), colour changes of pH dyes can be employed to detect acidic/basic volatile compounds and display an irreversible change in visual appearance. Two achievement colourimetric pH indicators have been proposed as a prototype for detecting freshness using chitosan suspensions containing anthocyanin applied on card paper (Maciel, Yoshida, & Franco, 2012), and chitosan film containing anthocyanin (Yoshida, Maciel, Mendonca, & Franco, 2014).

In addition to detecting spoilage, pH dyes reacting in the presence of CO_2 have been used to construct intelligent packaging concepts that indicate the deterioration of traditional fermented vegetable foods in Korea (kimchi) (Hong & Park, 2000), and Thai dessert 'Golden Drop' (Nopwinyuwong, Trevanich, & Suppaku, 2010). In 2012, Lang & Hübert developed an apple-ripeness–indicator-label to measure volatile compounds produced by apple fruit during storage. Smolander et al. (2002) developed an agarose–immobilised myoglobin–based freshness indicator for unmarinated or preserved broiler pieces that detected hydrogen sulphide produced during spoilage. Moreover, a chemical indicator for monitoring the microbial breakdown product in the headspace of packaged fish has been developed (Pacquit et al., 2007).

Although some researches have performed on fruit ripeness indicators by monitoring ethylene, fruit produce ethylene in small amounts <1–10 μL ethylene/kg/h. Moreover, fruit undergo respiration processes and produce water vapour, which makes ethylene difficult to detect (Klein, Riley, DeCianne, & Srinavakul, 2006). Fruit have a complex mixture of large exotic volatile compounds that could be ripeness markers, especially durian which is one of the major agricultural crop in Thailand. Durian is appreciated fruit by consumers due to its unique volatiles with high nutritional values (Ketsa & Daengkanit, 1998). Our previous study has shown that the predominant aroma–active compounds in durian were sulphur–containing compounds, which they have been changing during post–harvested storage, and these compounds are related to the physicochemical qualities of durian fruit (Niponsak, Laohakunjit, & Kerdchoechuen, 2014). Although the ripeness judgment of fresh–cut

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durian is very complicated, very few reports showed the developed accurate methods which could evaluate real–time ripeness of fresh–cut durian. However, real–time sulphur indicator as in SO_2 form has been developed based on different sensing mechanisms, but the technology for detecting sulphur–containing compound complexes of fruit is limited.

Most of the colourimetric indicators are produced from plastic polymers (Maciel et al., 2012; Smolander, 2003). Presently, biodegradable materials derived from natural resources can be used as interesting potential substitutes for traditional non–biodegradable plastic polymers due to their low cost, easy availability from reproducible resources, and biodegradability (Janjarasskul & Krochta, 2010). Biodegradable films, by acting as barriers to control the transfer of moisture, oxygen, lipids and flavour, can be used as self–standing films for indicators. Several studies have reported the use of polysaccharides from different sources to prepare films with different properties, and indicated that these carbohydrates are promising materials (Avérous & Boquillon, 2004; Ghanbarzadeh, Almasi, & Entezami, 2010). Carbohydrates; for instance, starch (cassava starch, rice starch, and corn starch) could retain aroma compounds and specific molecules, such as sulphur compounds, and alcohol on their amylose–amylopectin helix interaction between starch and particular molecules. Starch also forms a well film with good gas/water barrier properties (Guichard, 2002). However, one of the main problems associated with starch polymers is their inherent sensitivity to humidity due to the hydrophilic and hygroscopic nature of starch and its plasticizers (Mathew & Dufresne, 2002). The need for improved water–resistant properties of starch based film would be further developed with the additions of natural or modified polymers, such as chitosan (Bonilla, Talón, Atarés, Vargas, & Chiralt, 2013), carboxymethylcellulose (Jansson & Jarnstrom, 2005), cellulose–based organic fillers (Avérous, Fringant, & Moro, 2001), and citric acid (Yoon, Chough, & Park, 2006). The number of packaging fruit with freshness detection is still very little, however new freshness indicator concepts and commercial products are likely to be patented and become available in the near future.

The goal of this research was to develop an innovative colourimetric starch–based volatile compound indicator by adding various substances, including chitosan, citric acid, carboxymethylcellulose and kraft fibre. Chemical reactions of colourimetric starch–based indicators with volatile compound models, physical, mechanical, and barrier properties of indicators were also evaluated. Moreover, colourimetric starch–based indicators were evaluated for monitoring the ripeness of fresh–cut durian.

2. Materials and methods

2.1. Materials

Commercial cassava starch (Fish Brand, Thailand, Food grade) and chitosan (MW 800,000; 85% deacetylation, Sigma–Aldrich, USA) were used as the film–forming matrix. Distilled water was used as the solvent to prepare the film–forming solutions. Sorbitol (Merck, Germany) was used to improve the mechanical properties of the film. Citric acid (Analytical grade, Ajex Finechem, Australia), carboxymethylcellulose (CMC) (Food grade, Ingredient Center, Thailand), and kraft fibre (Thai Paper Co., Ltd., Thailand) were used to improve the water barrier. Diethyl disulphide (purity > 99%, Sigma–Aldrich, USA), dipropyl disulphide (purity > 98%, Sigma–Aldrich, USA), ethyl alcohol (purity > 99%, Macron Chemicals, USA), acetic acid (purity > 99.8%, QReC, New Zealand), and ethyl acetate (HPLC grade, Fisher Scientific, UK) were used as detected volatile compound models (according to the report by Niponsak et al., 2014), and for testing the properties of the films. Methyl red (Panreac, Panreac Quimica, EU) and bromothymol blue (Ajex Finechem, Australia) were used to prepare the dye mixture. Silica gel and sodium chloride (NaCl, Univar, New Zealand) were used to prepare saturated salt solutions to fix the RH at <2%, and 75% for water vapour permeability measurements, and film conditioning prior to analysis.

2.2. Development of colourimetric starch–based film indicators

2.2.1. Colourimetric starch–based film indicator formation

Cassava starch (5% *w/w*) was mixed with distilled water, and the aqueous starch dispersion was heated and stirred on a hotplate until it reached complete gelatinization. Sorbitol was slowly added to the starch solution (starch: sorbitol ratio at 1: 0.30) when the dispersion was cooled down. The indicator solutions were prepared by mixing methyl red (0.3% *w/v*) in ethanol (50% *v/v*) and bromothymol blue (0.3% w/v) in ethanol (50% *v/v*) at ratios of 3:2.

The additive and indicator substances were added to the film–forming solution, resulting six film–forming dispersions: Control (without pH dye), colourimetric starch–based film (without additives) (CSBF), CSBF mixed with 0.1% and 1.0% chitosan (CSBF + 0.1% chitosan and CSBF + 1.0% chitosan (chitosan solution was prepared with 1.0% acetic acid); mass ratio of CSBF:chitosan was at 1:1), CSBF mixed with citric acid (CSBF + 0.1% citric acid and CSBF + 1.0% citric acid), CSBF mixed with CMC (CSBF + 0.1% and 1.0% *w/v* CMC), and CSBF combined with kraft fibre (CSBF + 0.1% and 1.0% kraft fibre). All of the film–forming indicator solutions were homogenized using a homogenizer (T25 basic, IKA®, Germany) at 10,000 rpm for 10 min, and degassed at room temperature to remove air bubbles using a sonicator (D–78224 Singen/Htw, Elma, Germany). In order to obtain the developed films, each of the film–forming dispersions (40 g) was cast on an 8.0 × 12.5 cm horizontal flat polystylene plate. After oven drying for 15 h at 50 °C, the films were conditioned at 30 °C and 75% RH in cabinets containing saturated solutions of NaCl prior to analysis.

2.2.2. Physical properties

2.2.2.1. Colour. The colours of the colourimetric starch–based films were measured using a Hunter Lab colourimeter (Miniscan EZ, Hunter Associates Laboratory, Inc., Reston, USA). Prior to analysis, the colourimeter was calibrated to a standard black and white plate. Triplicate measurements were performed on each of the film samples by measuring at five random positions. Measurements were analyzed using the CIE L^* a^* b^* system. The parameter L^* represents the lightness of the colour from 0 (dark) to 100 (light), a^* is the greenness/redness parameter (negative a^* is green and positive a^* is red), and b^* is the blueness/yellowness (negative b^* is blue and positive b^* is yellow). The a^* and b^* parameters both move along the two axes that form a plane orthogonal to L^* and do not have specific numerical limits. The angular coordinates of the hue angle ($h^{\bigcirc}$) were calculated as follows:

$$h^\circ = \tan^{-1}(b*/a*) \text{ when } a*>0 \text{ and } b*>0$$

$$h^\circ = 180^{\bigcirc} + \tan^{-1}(b*/a*) \text{ when } a*<0$$

$$h^\circ = 360^{\bigcirc} + \tan^{-1}(b*/a*) \text{ when } a*>b* \text{and } b*<0.$$

The parameter h° refers to the dominant wavelength, which starts with 0° and increases counterclockwise.

2.2.2.2. Moisture content. Moisture contents of the colourimetric starch–based film were determined by measuring the weight losses of the film samples after drying in an oven at 105 ± 1 °C until a constant weight (dry sample weight) was obtained. Samples were analyzed in triplicate. Moisture content (%) was calculated as follows:

Moisture content (%) = [(Wet sample weight − Dry sample weight) / Wet sample weight] × 100.

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