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Solubility, Mechanical and Thermal Properties of Cassava Starch-Chitosan Film Incorporated with Red Cabbage Extract

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ABSTRACT

Plastics from synthetic petroleum for food packaging raise a concern in waste disposal and food safety. Therefore, biodegradable polymers or biopolymers have emerged as a viable alternative to non-biodegradable plastics in food packaging and preservation besides protecting the environment. In this work, the aim was to develop cassava starch-chitosan film containing red cabbage extract and to determine the effect of red cabbage extract on the properties of the film. The film was prepared by casting method and the film solubility, tensile strength, elongation at break and thermogravimetric analysis (TGA) were determined. The solubility of cassava starch-chitosan film was 58.3%, followed by 58.8%, 59.6% and 61.1% for cassava starch-chitosan films containing 5 ml, 10 ml and 15 ml red cabbage extract, respectively. The tensile strength of film containing 5 ml red cabbage extract was higher than cassava starch-chitosan film without red cabbage extract which are 0.533 MPa and 0.417 MPa, respectively. Meanwhile, elongation at break of the film without red cabbage extract increased from 22.20% to 30.33% with the increased of red cabbage extract. From TGA, the addition of red cabbage extract caused the film to decompose at high temperature, which boosts thermal stability compared to film without red cabbage extract. Overall, this study concluded that the incorporation of red cabbage extract improved the properties of cassava starch-chitosan film which potentially be employed as an alternative material in food packaging applications.

Keywords: Starch; Film; Red Cabbage; Tensile; Thermal

INTRODUCTION

Most materials used for food packaging are derived from fossil fuels which are non-biodegradable and cause an increase in solid waste disposal. Consequently, the rising environmental consciousness has driven the development of diverse biopolymers into environmentally friendly materials that can minimize the use of petroleum-based synthetic materials. Biopolymers are being actively developed as an alternative way in food packaging which are safe, non-toxic and biodegradable, make it suitable to preserve food while protecting the environment.

Starch is considered a potential choice as one of the natural polymers due to its abundance, biodegradable, renewable and least expensive. Starch mostly comprises amylase, a linear chain polymer, and amylopectin which is a polymer of glucose having a branched chain structure [1]. Starch is widely used in film and coating applications due to its film-forming ability [2]. In particular, cassava starch is a great choice in film packaging due to its odorless, tasteless, colorless, non-toxic and biodegradable characteristics [3]. However, starch based materials have drawbacks such as low moisture barrier and weak mechanical properties [4], which limit their applicability. To improve the properties of starch-based film, blending starch with additives and/or other polymers is recommended. Therefore, chitosan is one of the other polymers that can be blended to improve the moisture barrier characteristics and mechanical properties of starch film.

Chitosan is a deacetylated derivative of chitin, which has good biocompatibility, good biodegradability, low toxicity and good antibacterial properties [4]. The formation of stable hydrogen bonds between the chitosan and starch molecules promotes better barrier and mechanical properties of starch based film [2]. Furthermore, the hydroxyl groups of starch can interact with the amino groups of chitosan, to improve the compatibility of the two molecules in the gel matrix [5]. Chitosan matrices serve as carriers of active compounds such as nanomaterials, essential oil, fruit extracts, and other phytochemicals [6]. The antioxidant of chitosan can be further enhanced by incorporating natural antioxidants derived from plant polyphenols such as red cabbage extract.

Red cabbage extract contains anthocyanin which is a water-soluble pigment that provides red, purple, and blue colors to plants [7]. Recently, starch films have been reinforced with plant extracts rich in anthocyanins to develop active and intelligent packaging film. Research by Qin *et al.* [8] found that incorporating varying amounts of anthocyanin extract from Lycium Ruthenicum Murr (LRA) into a starch matrix had proven improvement in the moisture content, water vapor permeability, tensile strength and antioxidant property of the starch film due to hydrogen bonds formed between starch and LRA. Another study by Ribeiro Sanches *et al.* [9] found that the incorporation of red cabbage extract into sweet whey and starch film presented good mechanical properties, high antioxidant capacity, low solubility and low water vapor permeability. The film also exhibited antioxidant properties because of the significant existence of phenolic compounds and anthocyanins.

The thermogravimetric analysis of corn starch film containing anthocyanin from black bean seed coat and red cabbage had been studied by Prietto *et al.* [10]. They found that the film with the red cabbage anthocyanin showed a greater residual mass at 600 ^{o}C, indicating anthocyanin from red cabbage had a greater film stability at elevated temperature compared to the black bean anthocyanin. In other work by Silva-Pereira *et al.* [11], corn starch film with red cabbage extract has a higher mass loss at a lower temperature than the corn starch film, suggesting that the extract has a low thermal stability. Those findings show the incorporation of anthocyanins-rich extracts had improved the thermal stability of the film.

Anthocyanin extracted from red cabbage have also been proposed as smart packaging film by several authors [9], [12-14]. Plant extracts that contain anthocyanins can be used as smart devices that are vulnerable to pH variations which causes a reversible color transition. Besides the intelligent pH detector, the potential of anthocyanin from red cabbage extract as natural colorants for film packaging was interesting as it enhances film appearance and properties of the film. This research aims to investigate the effect of red cabbage extract on the mechanical properties, water solubility and thermogravimetric analysis of composite film of cassava starch and chitosan.

METHODOLOGY

Materials

Cassava starch (Cap Kapal ABC, Thailand), chitosan (Sigma Aldrich), acetic acid (R&M Chemicals) and glycerol (R&M Chemicals). Red cabbage was purchased from local market in Shah Alam, Selangor.

Preparation of Red Cabbage Extract

Red cabbage weighed 100 g was cut into pieces and placed in a beaker. 200 ml distilled water was added into the beaker and heated until boiling. Then, the heat is reduced to allow the mixture to simmer for 30 minutes. After that, the extracted red cabbage was filtered using cheesecloth and funnel. The red cabbage extract was kept at 4 ^{o}C before use.

Preparation of Film

Chitosan solution was prepared by dissolving 2.4 g chitosan in 1 %w/v acetic acid at room temperature and stirred at 200 rpm for 24 hours. Meanwhile, the starch solution was prepared by dissolving 4.8 g starch in 100 ml distilled water at 80 °C and stirred at 200 rpm for 30 minutes. Then, the chitosan solution and the starch solution were mixed and stirred for 15 minutes. The ratio 1:2 of chitosan and starch were chosen based on preliminary experiment which resulted smooth and easily peeled off film. Glycerol (1 %v/v) was added as plasticizer and the solution was mixed for 10 minutes. After cooling, red cabbage extract of different volumes namely RCE1 = 5 ml, RCE2 = 10 ml and RCE3 = 15 ml were added to the starch-chitosan solution and mixed with constant stirring for 10 minutes. The control film (SC) was prepared using the same conditions without incorporation of red cabbage extract. The film forming solutions were cast onto petri dish with 9 cm diameter. The petri dish was put on flat surface and 20 ml of each film forming solution sample was poured to ensure constant thickness of film. Then, it was dried at 60 °C in an oven for 24 hours. Dried films were peeled off and stored in desiccator prior to characterization.

Solubility of Film

Film was cut into 1 cm x 1 cm and was weighed using analytical balance (w_i). The film was immersed in 10 ml of distilled water in a beaker and left for 24 hours. Then the film sample was filtered, and undissolved film was dried in an oven at 100 °C for 1 hour. After drying, the sample was weighed again (w_f). The solubility was calculated by using Eq.(1).

$$\%\, solubility = \frac{w_i - w_f}{w_i} \times 100 \tag{1}$$

Mechanical Properties of Film

Tensile strength (TS) and elongation at break (E) of the films were determined by using Universal Testing Machine (Tinius Olsen H50KT) according to [15]. Film was cut into 10 mm x 50 mm for each sample and was mounted between the grips of the equipment for testing. The grip separation was initially set at 50 mm and the crosshead speed at 40 mm/min. Film thickness was measured by using a digital micrometer (Mitutoyo-Co, Japan) to estimate the cross-sectional area of the sample. The tensile tests were repeated in triplicate.

Thermogravimetric Analysis

Thermogravimetric analyzer (Mettler Toledo, TGA/SDTA581) was used to conduct the test. Sample weighed 20 mg was heated at a rate of 10 ^{o}C/min from ambient temperature to 600 ^{o}C, with a nitrogen flow rate of 30 ml/min.

RESULTS AND DISCUSSION

Solubility of Film

Solubility of film in water is an important property to consider for its desired application. For food coatings and food encapsulation, a high solubility are necessary, meanwhile films with a low solubility are usually used for food packaging [16]. As edible film, when the foods are consumed together with the film, it is necessary to have high solubility to facilitate the food melting in mouth or dissolving in water. Meanwhile as food packaging, low solubility is preferable because as primary packaging, the film should withstand moisture and maintain its integrity during storage [17]. Figure 1 depicts the solubility of cassava starch-chitosan film incorporated with different concentration of red cabbage extract. The solubility of SC film was 58.3% and the value was increased to 58.8%, 59.6% and 61.1%, respectively, when the red cabbage extract increased. Starch is hydrophilic because of the hydroxyl groups and can absorb large amounts of water molecules [18].

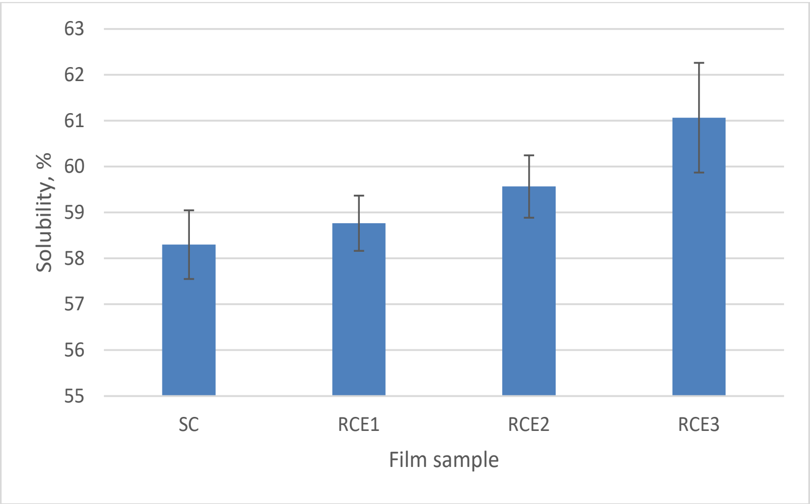

Figure 1: Solubility of starch-chitosan film incorporated with different concentration of red cabbage extract

Meanwhile, red cabbage extract is also hydrophilic, thus the increasing of red cabbage extract would increase the film's solubility because of the increase interaction of hydroxyl group between starch and red cabbage extract. Similar finding was obtained by Prietto et al. [10], the addition of extracted anthocyanin from black bean seed coat and red cabbage to corn starch films increased their water solubility as a result of an increase in hydrophilic sites for water absorption after interactions between the starch and anthocyanins. According to Yong & Liu [17], the water solubility of film often increases with increasing amount of anthocyanin due to more hydrophilic anthocyanin dissolved in water. For chitosan, the presence of amino and hydroxyl groups represent binding sites for water molecules in the chain of chitosan [19]. Thus, the hydrophilic nature of anthocyanin, starch and chitosan would contribute to the increased of solubility. Solubility ranged from 43.35% to 63.22% are good values for fruit applications [20]. The obtained solubility of the films in this study were in that range, so it is suitable to be applied for packaging of perishable food like fruits. Despite high solubility, the water resistance of film can be enhanced by incorporating hydrophobic substances such as lipid or essential oil into the film.

Tensile Strength and Elongation at Break of Film

Tensile strength is a measurement of how much stress a material can withstand before breaking. Based on Table 1, the tensile strength for SC film was 0.417 MPa and the tensile strength increased by 28% when 5 ml of the red cabbage extract was added (RCE1). The increased of tensile strength was expected due to strong hydrogen bonding between red cabbage anthocyanin molecules and the composite film matrix [8]. However, the tensile strength starts decreasing when the amount of red cabbage extract increased to 10 ml and 15 ml (RCE2 and RCE3). This was possibly because of high contents of red cabbage extract might form agglomerates, which interrupted the compactness of starch, as similarly found by Qin *et al.* [8] for cassava starch and L. ruthenicum anthocyanins (LRA) film. In a work by Silva-Weiss *et al.* [21], the addition of murta leaves extract decreased the tensile strength of chitosan-starch film. The authors found the linkages between the extract and chitosan-starch associations resulted increased of film volume and decreased of chains mobility. Therefore, it can be concluded that the increase amount of polyphenol rich extract including red cabbage had interrupt the structure of chitosan and starch which lead to weaken of tensile strength.

Table 1: Thickness, tensile strength and elongation at break of starch-chitosan film incorporated with different concentration of red cabbage extract

Sample	Thickness (mm)	Tensile Strength (MPa)	Elongation at Break (%)
SC	0.028	0.417±0.054	22.20±1.233
RCE1	0.029	0.533±0.066	24.73±1.898
RCE2	0.031	0.387±0.035	28.23±2.871
RCE3	0.033	0.321±0.056	30.33±2.279

Furthermore, the decreasing trend of tensile strength for RCE2 and RCE3 can be explained by plasticizing effect of red cabbage extract, which could weakening the interactions between polymers [10]. Similar trend was observed by Mei *et al.* [22] who found the decreased in tensile strength of sago starch films enriched with anthocyanin-rich torch ginger extract (TGE) could be attributed by the weakened interfacial adhesion or hydrogen bonds between hydrophilic sago starch and hydrophobic TGE. In addition, the tensile strength was inversely proportional to solubility of the films. This was probably related to the hydrophilic nature of starch-chitosan and anthocyanin molecules, which contributed to higher solubility, thus lowering the tensile strength.

Meanwhile for elongation at break, the values increased from 22.20% to 30.33% with the increased of red cabbage extract. This might be attributed to the plasticizing effect of extract which could penetrate into the film networks as found by Qin *et al.* [23]. Besides, in their research on starch/polyvinyl alcohol (PVA) films enriched with L. ruthenicum and red pitaya peel extract, the authors also explained that the formation of hydrogen bonds between extract and film matrix reduced the intermolecular forces among adjacent macromolecules, thus enhanced the mobility of polymeric chains. Moreover, elongation at break was related to the water absorption of the matrix [12]. Therefore, the higher solubility of the film resulted in the higher elongation at break as confirmed by the results obtained in this study.

Thermogravimetric Analysis of Film

The thermal property of film reflects their ability to resist decomposition at high temperatures. Thermogravimetric analysis (TGA) was performed to analyze the thermal stability of film. The thermogravimetric curve of the cassava starch-chitosan film (SC film) and cassava starch-chitosan film with 5 ml red cabbage extract (RCE1) are shown in Figure 2. Only TGA curve of RCE1 film was compared to the SC film because from the solubility and tensile strength, RCE1 film shows good resistance to water and higher strength rather than RCE2 and RCE3 films. As depicted from Figure 2, the SC film gives the lowest thermal stability, while the addition of red cabbage extract shifted the thermal stability of the films to 500 ^{o}C. Both films shows initial weight loss between 30 ^{o}C and 130 ^{o}Cwhich was due to evaporation of adsorbed water in the film [8]. The weight loss at this stage was 32.8% for SC film and 30.2% for RCE1 film. The decomposition of the SC film was from 130 °C to 350 °C with weight loss of 66.4%, meanwhile for RCE1 film was from 130 °C to 370 °C with weight loss of 59.8%. The RCE1 film was fully decomposed at 506.46 °C which higher than SC film at 356.32 °C. This indicates that the incorporation of red cabbage extract may boost the thermal stability of the cassava starch-chitosan film.

A study by Sadi & Ferfera-Harrar [14] reported that the combination of pistacia leaves extract (PE) with gelatin-montmorillonite (OM) and anthocyanins from red cabbage (ATH) has gradually slowed down the degradation process. The improved heat resistance of the films may be ascribed to the synergistic effects of additives, arising from intermolecular interactions within the matrix. Several factors could affect the thermal properties of a film that contains anthocyanins, including the polymer used, interactions between the film's various components and also the anthocyanins' source and composition itself [24].

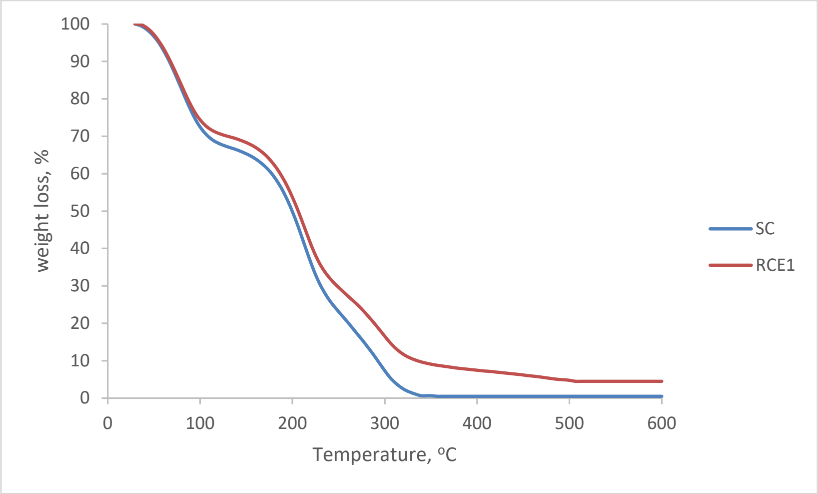

Figure 2: TGA curves of control film and RCE1 film

CONCLUSION

The combination of cassava starch and chitosan with the presence of the red cabbage extract increases the water solubility as compared to the control film. The film with incorporation of 5 ml of red cabbage extract (RCE1) exhibited the greatest tensile strength. For elongation at break, the values increased with the increased of red cabbage extract. The higher solubility of the film resulted the higher elongation at break and the lower tensile strength. The film incorporated with red cabbage extract was more stable due to high degradation temperature compared to control film. In summary, the incorporation of 5 ml red cabbage extract (RCE1) shows good water resistance, high tensile strength and high thermal stability of cassava starch-chitosan films. For future work, the interaction between the red cabbage extract and cassava starch-chitosan matrix can be analyzed through Fourier Transform Infrared (FTIR) study to support the solubility and mechanical properties of the film. The performance of cassava starch-chitosan film incorporated with red cabbage extract as food packaging can be evaluated as well as the antioxidant and antimicrobial properties of the film.

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