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Properties of fish skin gelatin film incorporated with seaweed extract

Saowapa Rattaya [a], Soottawat Benjakul [a,*], Thummanoon Prodpran [b]

[a] Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, 15 Knachanawanich Road, Hat Yai, Songkhla 90112, Thailand
[b] Department of Material Product Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

Fish skin gelatin films incorporated with 6% oxygenated seaweed (*Turbinaria ornata*) extract (based on protein content) with pHs 9 or 10 were prepared and characterized in comparison with the control film (without seaweed extract). Films incorporated with seaweed extract at both pHs exhibited the higher elongation at break (EAB) than the control film ($p < 0.05$). However, no differences in tensile strength (TS) and transparency between films without and with seaweed extract were observed ($p > 0.05$). Water vapor permeability (WVP), and film solubility decreased as seaweed extract was incorporated, regardless of pH ($p < 0.05$). This was associated with the formation of non-disulfide covalent bond in the film matrix, most likely induced by the interaction between oxidized phenols in seaweed extract and gelatin molecules. Coincidentally, the second transition temperature of gelatin film shifted from 170.54 to 178.36 °C when incorporated with 6% seaweed extract at pH 10. Film without seaweed extract had smooth surface while the rougher surface was noticeable in film incorporated with seaweed extract for both pHs. Thus, the addition of seaweed extract had the impact on the property of fish skin gelatin film, most likely due to the enhanced formation of protein cross-links.

1. Introduction

Plastic packaging or synthetic films has been widely used, due to their good mechanical properties and effectiveness as a barrier to oxygen and water (Gómez-Estaca et al., 2009; Gómez-Guillén et al., 2009). However, most synthetic films are petrochemical-based and non-biodegradable, leading to environmental pollution and serious ecological problems (Tharanathan, 2003). Therefore, edible film from natural polymer has become an ecologically important alternative to the film from commonly used synthetic polymer (Piotrowska et al., 2008). Edible films can enhance food quality by acting as moisture, gas, aroma and lipid barriers, providing protection to a food product after the primary package is opened. Furthermore, such films are biodegradable and can even be eaten with food, which will reduce pollution of traditional non-biodegradable plastic films (Kim and Ustunol, 2001). Edible films can be made from natural polymers including, proteins, polysaccharides, lipids or the combination of these components (Tharanathan, 2003). Protein-based films generally exhibit the poor water barrier property. However, films composed of lipids are more moisture resistant (Gontard et al., 1994).

Gelatin obtained by partial degradation of collagen has gained more attention as a new material for edible films (Jongjareonrak et al., 2006; Gómez-Guillén et al., 2009). With the restriction of uses of gelatin from land animals, fish gelatin is acceptable for Islam, and can be used with minimal restrictions in Judaism and Hinduism. Nevertheless, gelatin from marine sources showed the lower functional properties than that of mammalian (Leuenberger, 1991). Chemical and physical treatments can be applied to modify the polymer network through cross-linking of the polymer chains (Cao et al., 2007). Chemical cross-linking agents and enzyme used include gossypol, formaldehyde, glutaralaldehyde (Marquie et al., 1995; de Carvalho and Grosso, 2004; de Carvalho et al., 2008), and transglutaminase (Mariniello et al., 2003). Nevertheless, some cross-linking agents have the toxicity and high cost (Bigi et al., 2002; Cao et al., 2007). Therefore, a natural cross-linking agent with no toxicity is of great interest for improving the properties of films, especially protein based film.

Seaweeds or marine macroalgae are potential renewable resources in the marine environment. About 6000 species of seaweeds have been identified and are grouped into different classes including green (Chlorophytes), brown (Pheophytes) and red (Rhodophytes) algae (Abugoch et al., 2003). Total global seaweed production of the world in the year 2004 was greater than 15 million metric tones (FAO, 2006). However, algae grown in Thailand are still underutilized. Only small portion has been used as food, animal feed, fertilizers, and for the production of hydrocolloids (Aungtonya and Liao, 2002). Seaweed extracts are considered to be a rich source of phenolic compounds (Athukorala et al., 2003; Heo et al., 2005). Strauss and Gibson (2004) reported that the phenolic compounds from coffee beans, tea leave and tubers can serve

* Corresponding author. Tel.: +66 74 286334; fax: +66 74 212889.
E-mail address: soottawat.b@psu.ac.th (S. Benjakul).

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as cross-linkers of gelatin. Cross-linking effect of phenolic compounds of plant extracts in gelatin based film was reported (Gómez-Guillén et al., 2007). Therefore, the incorporation of phenolic compounds from natural sources, especially from seaweed may improve functional properties of gelatin film. Additionally, seaweed extract could be a novel cross-linker in gelatin film, which could yield the resulting film with different properties, in comparison with the toxic cross-linking compounds, especially aldehydes. Gelatin film incorporated with seaweed extract can be used as the edible film, whereas the film added with toxic cross-linkers are recognized unsafe for consumption. The objective of this study was to prepare and characterize fish skin gelatin film incorporated with seaweed (*Turbinaria ornata*) extract used as protein cross-linker.

2. Materials and methods

2.1. Chemicals/enzymes

Potassium chloride, urea and sodium dodecylsulfate (SDS) were purchased from Univar (Worksafe, Australia). Glycerol and α-chymotrypsin (55 units/mg solid) were purchased from Wako Pure Chemical Industry, Ltd. (Tokyo, Japan). Methanol was obtained from Merk (Darmstadt, Germany). β-mercaptoethanol (β-ME) was purchased from Sigma Chemical Co. (St. Louis, MO, USA).

2.2. Preparation of seaweed extracts

Brown seaweed (*T. ornata*) was collected from Samui Island, Suratthani Province, Thailand in June–July 2007. Seaweed was transported to the Department of Food Technology, Prince of Songkla University within 6 h. Upon arrival, seaweed was washed with tap water and dried using a hot-air oven at 35 °C until the final moisture content of 10% was obtained. Dried seaweed was then ground and sieved to obtain the diameter of around 0.5 mm. To prepare the seaweed extract, seaweed powder (5 g) was mixed with 150 ml of methanol following the method of Terada et al. (1987). The mixture was homogenized at 10,000×*g* for 2 min using a homogenizer (model T25 basic, ULTRA TURREX®, Selangor, Malaysia). The homogenate was then stirred continuously at room temperature for 30 min. The mixtures were centrifuged at 5000×*g* for 10 min at room temperature using a Sorvall Model RC-5B Plus refrigerated centrifuge (Newtown, CT, USA) to remove undissolved debris. The solvent in the extract was removed by a rotary evaporator (Model Rotavapor-R, Brinkmann, Switzerland) at 40 °C.

2.3. Preparation of fish skin

Bigeye snapper (*Priacanthus tayenus*), off-load approximately 48 h after capture, were obtained from the dock in Songkhla, Thailand. Fish were stored in ice with a fish/ice ratio of 1:2 (w/w) and transported within 1 h to the Department of Food Technology, Prince of Songkla University, Hat Yai. Upon arrival, fish were washed with tap water. The skins were then removed, cut into small pieces (0.5 × 0.5 cm^2) and stored at −20 °C until use.

2.4. Extraction of fish skin gelatin

Gelatin was extracted from fish skin according to the method of Kittiphattanabawon et al. (2005) with a slight modification. Skins were soaked in 0.025 M NaOH with a skin/solution ratio of 1:10 (w/v) with a gentle stirring. The solution was changed every 1 h for 2× to remove non-collagenous protein and pigments. Alkaline-treated skins were then washed with tap water until neutral or faintly basic pH of wash water was obtained. The skins were then soaked in 0.05 M acetic acid with skin/solution ratio of 1:10 (w/v). The solution was changed every 40 min for 3× with a gentle stirring to swell the collagenous material in fish skin matrix. Acid-treated skins were washed as previously described. The swollen fish skins were soaked in distilled water (45 °C) with a skin/water ratio of 1:10 (w/v) for 12 h with a continuous stirring to extract the gelatin from skin matter. The mixture was then filtered using two layers of cheesecloth. The resultant filtrate was freeze-dried (Dura-Top™ μp, FTS system, New York, USA) with drying pressure of 50 mbars and the vaporized temperature of 25 °C. The dry matter was referred to as gelatin.

2.5. Film preparation

Freeze dried gelatins were dissolved with distilled water to obtain the final protein concentration of 2% (w/v) as determined by the Biuret method (Robinson and Hodgen, 1940). The solution was added with glycerol at 50% (w/w) of protein content. Film forming solution (FFS) was stirred gently until the homogeneity was obtained and incubated at 60 °C for 30 min (Jongjareonrak et al., 2006). FFS was then adjusted pHs to 9 or 10 using 1 M NaOH.

Methanolic extract of *T. ornata* was dissolved with deionized water. The solution (10 mg/ml) containing phenolic compounds at level of 15.66 ± 0.12 μg catechin/ml determined by Folin–Ciocateu assay (Slinkkard and Singleton, 1997) was adjusted to pHs 9 or 10 using 0.1 M NaOH. The solutions were oxygenated for 30 min. Oxygenated extracts were then added into FFS with the corresponding pH (9 or 10) to obtain a concentration of 6% (w/w) (based on protein content). The mixtures were stirred at room temperature for 1 h. FFS obtained (4 *g*) was cast onto a rimmed silicone resin plate (5 × 5 cm^2) and air blown for 12 h at room temperature prior to further drying at 25 °C and 50% relative humidity (RH) for 24 h in an environmental chamber (WTB Binder, Tuttlingen, Germany). The resulting films were manually peeled off and used for analyses.

2.6. Determination of film properties

The films were conditioned for 48 h at 25 °C and 50% RH prior to testing, except for DSC study, films were conditioned over silica gel at 25 °C for 3 weeks before testing. After being conditioned, the films were subjected to the following determinations.

2.6.1. Film thickness

The thickness of film was measured using a micrometer (Gotech, Model GT-313-A, Gotech Testing Machines Inc, Taiwan). Nine random positions of each film of nine films were used for thickness determination.

2.6.2. Mechanical properties

Tensile strength (TS) and elongation at break (EAB) were determined as described by Iwata et al. (2000) with a slight modification using the Universal Testing Machine (Lloyd Instruments, Hamsphire, UK). Nine samples (2 × 5 cm^2) with initial grip length of 3 cm were used for testing. Cross-head speed was 30 mm/min and load cell used was 100 N.

2.6.3. Color and film transparency

Color of the film was determined as L^*, a^* and b^* using CIE colorimeter (Hunter Associates Laboratory, Inc., Reston, VA, USA). The films were subjected to the transmittance measurement at 200, 280, 350, 400, 500, 600 and 800 nm using the UV-16001 spectrophotometer (Shimadzu, Kyoto, Japan) as described by Han and Floros (1997). The transparency value of the films was calculated at 600 nm by the following equation: