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# Effect of Antioxidant Concentrations and Relative Humidity on Mechanical Properties of Cassava Starch/ Gelatin Films

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#### Abstract

In this research, the new antioxidant active food packaging has been developed and evaluated. Antioxidants (quercetin and tertiary butylhydroquinone (TBHQ)) were added (0, 20, 50 and 100 mg / 200 ml film solution) in cassava starch/gelatin (7:3 w/w) blended films containing glycerol (30 g/ 100 g starch/gelatin mixture) as a plasticizer. The film solution was casted and dried at 23°C for 24 hours. Effects of quercetin and TBHQ concentrations and relative humidity (36 and 52 %RH) on mechanical properties of cassava starch/ gelatin films were examined. At 36 %RH, increasing concentration of quercetin increased tensile strength and reduced elongation at break of the film blends. The increase of TBHQ content decreased tensile strength but did not significantly affect elongation at break of the films. Cassava starch/gelatin blended films containing quercetin showed higher tensile strength but lower elongation at break than film with TBHQ. Film containing 50 mg quercetin showed the highest tensile strength. All films stored at 52% RH gave higher elongation but lower tensile strength than films at 36% RH condition. At 52 %RH, increasing of quercetin and TBHQ concentrations decreased tensile strength of cassava starch/gelatin films. Elongation at break of film increased with increasing TBHQ concentration but did not have significantly difference with increasing quercetin.

Keywords: Cassava starch/gelatin film; quercetin; TBHQ; mechanical properties.

#### Introduction

The development of biodegradable films based on biopolymers has attracted attention mainly due to their friendliness to the environment and their potential substitution for some petrochemicals in food packaging industry. The biodegradable films generally produced from renewable natural and abundant biopolymeric materials such as polysaccharides, proteins, lipids or the combination of these components. Some biodegradable films based on the blends of polysaccharides and proteins such as methylcellulose–wheat gluten (Debeaufort *et al.*, 1994), soluble starch–gelatin (Arvanitoyannis *et al.*, 1997), hydroxypropyl starch–gelatin (Arvanitoyannis *et al.*, 1997), hydroxypropyl starch–gelatin (Arvanitoyannis *et al.*, 1997), pullulan–starch (Biliaderis such as starch–methylcellulose (Arvanitoyannis *et al.*, 1999), pullulan–starch (Biliaderis, 2002), CMC-rice starch (Li *et al.*, 2008) were investigated. Depending on the interactions between components, these formulas can improve the mechanical properties and gas/moisture barrier properties in some cases.

Antioxidants are widely used as food additive to improve oxidation stability of lipid and to prolong shelf-life, mainly for dried products and O<sub>2</sub>-sensitive foods. Synthetic phenolic antioxidants (SPAs), such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and tertiary butylhydroquinone (TBHQ), are commonly used because of their chemical stability, low cost and availability. However, their safety has been questioned. There is much interest among food manufacturers in natural antioxidants (such as tocopherol, ascorbic acid and quercetin) to act as replacements for synthetic antioxidants currently used (Phoopuritham et al., 2007). Recently, antioxidants have been suggested for integration in polymer films to exert their antioxidative effect (Pascat, 1986). Hargens et al. (1995) used tocopherols in edible film to control of warmed over favor and improve precooked meat quality. Oussalah et al. (2004) added essential oils in milk protein-based film. Lopez-de-Dicastillo et al. (2007) developed the EVOH-based film containing natural antioxidants (catechin and quercetin). However, a few information on the effect of antioxidants on cassava starch based films and their mechanical properties are available. Rachtanapun *et al.* (2006) reported that antioxidants (propyl gallate (PG), butylhydroxyanisole (BHA) and butylhydroxytoluene (BHT)) had no effect on tensile strength, %elongation and folding endurance of rice flour/cassava starch blended film. In previous study, cassava starch/gelatin film has been successfully prepared and determined its mechanical properties (Tongdeesoontorn et al., 2009). Since research on the properties of cassava starch/gelatin film incorporated with antioxidant have not been investigated, the objective of this study was to evaluate the effect of antioxidants (quercetin and TBHQ) and relative humidity on mechanical properties of cassava starch/gelatin film with plasticizer.

# **Materials and Methods**

## Materials

Cassava starch (Bangkok Inter Food Co., LTD., Thailand) was employed to obtain the film. Gelatin and glycerol were purchased from Sigma (Sigma-Aldrich, Germany) and Merck (Germany), respectively. Quercetin and tertiary butylhydroquinone (TBHQ) were obtained from Alfa Aesar (Siracusa, Rocculi, Romani & Rosa) and Fluka (Switzerland), respectively. *Film preparation* 

Cassava starch/gelatin film casting method was modified from method in previous study (Tongdeesoontorn *et al.*, 2009). Film solution was prepared by dispersing 7 g of cassava starch and 3 g of gelatin in distilled water (200 ml) with various quercetin and TBHQ content (0, 20, 50, 100 mg). Glycerol (30 g/ 100 g cassava starch/gelatin mixture) was added as plasticizer. Film solution was heated to  $80^{\circ}$ C with constant stirring to obtain starch gelatinization. Film-forming solution was casted on a flat 30 x 30 cm Teflon plate. The films were dried at room temperature (23°C) for 24 hours.

#### Mechnical properties

Films were cut into 100 x 25.4 mm strips and preconditioned in the environmental chamber at 36 and 52 % RH for 48 h. Tensile strength (TS) and elongation at break of films were determined using universal testing machine (Hounsfield, England) according to ASTM D 882-91. The initial gauge length was 50 mm and crosshead speed was 50 mm/min. Twenty replicated of each film type were tested.

#### Statistical analysis

Statistical significance was determined by one-way analysis of variance using SPSS 10.0 for Windows. Differences at P<0.05 were considered to be significant. A Duncan test for comparison of multiple means was used.

## **Results and Discussion**

Cassava starch /gelatin (7:3) was used in this study to form a film which showed good mechanical properties as described in previous study (Tongdeesoontorn *et al.*, 2009). Antioxidants (quercetin and TBHQ) were added into the film for determining the effect of quercetin and TBHQ concentrations on mechanical properties of cassava starch/gelatin film. Tensile strength (TS) of cassava starch/gelatin film with various quercetin and TBHQ concentrations were shown in Figure 1 (A) and (B), respectively.

At 36 %RH, TS of cassava starch/gelatin film with quercetin was higher than control cassava starch/gelatin film. It might be due to a possible interaction between quercetin and cassava starch/gelatin, which strengthened the film network. Hydroxyl group of quercetin possibly acted as hydrogen donor and hydrogen bonds could be formed between quercetin and starch/ gelatin molecules. For film containing TBHQ, a decrease in TS could be probably caused by incompatibility of TBHO and starch/gelatin molecules, resulting in the lessened integrity of film structure. This result agreed with TS of fish skin gelatin film incorporated with BHT and  $\alpha$ -tocopherol (Jongjareonrak *et al.*, 2008). It related to elongation at break of the films as shown in Figure 2. Cassava starch/gelatin film with TBHQ gave higher EAB than film without antioxidant (control). Conversely, film with quercetin gave lower EAB than control film. However, increasing quercetin content increased EAB of the film blends. Whereas increasing TBHQ content did not significantly affect EAB of the film. Comparison of mechanical properties of film with quercetin and TBHQ, cassava starch/gelatin blended films containing quercetin showed higher tensile strength than film with TBHQ. Nevertheless, cassava starch/gelatin film with TBHQ was more flexible than the film with quercetin. Film containing 50 mg quercetin / 200 ml film solution showed the highest TS and film containing 100 mg TBHQ / 200 ml film solution showed the highest EAB. However, the results were disagreed with rice flour/cassava starch film containing antioxidants (PG, BHA, BHT) which type of antioxidants had no effect on mechanical properties of the film (Rachtanapun et al., 2006).

Effect of relative humidity (36% and 52% RH) on mechanical properties of the film blends was also investigated. All films stored at 52% RH gave higher EAB but lower TS than films at 36% RH condition because water worked as a plasticizer by binding with hydroxyl group (OH) of starch chain and reduced the intermolecular bonds and increased mobility in polymer chains. This result agreed with Rachtanapun and Wonchaiya (2008) who studied on effect of relative humidity on mechanical properties of chitosan-methylcellulose film. At 52 %RH, increasing of quercetin and TBHQ concentrations decreased tensile strength. Increasing of TBHQ content increased EAB of cassava starch/gelatin films due to plasticizing effect of increasing absorbed water in film (Mathew and Dufresne, 2002; Suppakul *et al.*, 2006; Rachtanapun and Wonchiaya, 2008). On the contrary, the increase of quercetin concentration had no significantly difference of EAB of the film.

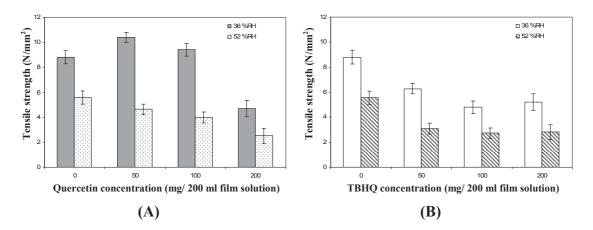


Figure 1 Tensile strength (TS) of cassava starch/gelatin film with various (A) quercetin and (B) TBHQ contents at 36 and 52 %RH.

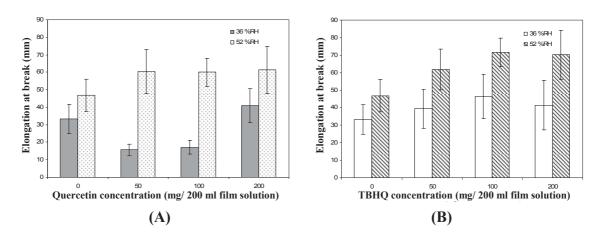


Figure 2 Elongtion at break (EAB) of cassava starch/gelatin film with various (A) quercetin and (B) TBHQ contents at 36 and 52 %RH.

#### Conclusion

Mechanical properties of cassava starch/gelatin film were generally affected by the incorporation of quercetin and TBHQ as well as relative humidity. Cassava starch/ gelatin film with quercetin showed higher tensile strength but lower elongation at break than control film. Conversely, film containing TBHQ showed lower tensile strength but higher elongation at break (except at 200 mg/ 200 ml film solution) than control film. Cassava starch/gelatin blended films containing quercetin showed higher tensile strength than film with TBHQ. Nevertheless, cassava starch/gelatin film with TBHQ showed higher elongation than the film with quercetin. Tensile strength decreased significantly with increasing quercetin and TBHQ concentrations. Elongation at break increased with increasing quercetin, whereas the increase of TBHQ had no significantly difference of film elongation at break. At higher relative humidity, cassava starch/gelatin film containing quercetin and TBHQ showed lower tensile strength but higher elongation at break. Increasing quercetin and TBHQ concentrations decreased tensile strength but increased elongation at break.

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# References

- Arvanitoyannis, I., and Biliaderis, C. G. (1998). Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends. *Food Chem.*, *62*(3), 333-342.
- Arvanitoyannis, I. and Biliaderis, C.G. (1999). Physical properties of polyol-plasticized edible blends made of methyl cellulose and soluble starch. *Carbohyd. Polym.*, *38*, 47-58.
- Arvanitoyannis, I., Nakayama, A., and Aiba, S. (1998). Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water. *Carbohyd. Polym.*, *36*(2-3), 105-119.
- Arvanitoyannis, I., Psomiadou, E., Nakayama, A., Aiba, S., and Yamamoto, N. (1997). Edible films made from gelatin, soluble starch and polyols, Part 3. *Food Chem.*, 60(4), 593-604.
- Bae, H. J., Darby, D. O., Kimmel, R. M., Park, H. J., and Whiteside, W. S. (2009). Effects of transglutaminase-induced cross-linking on properties of fish gelatin-nanoclay composite film. *Food Chem.*, 114(1), 180-189.
- Biliaderis, C. G., Lazaridou, A. and Arvanitoyannis, I. (1999). Glass transition and physical properties of polyol-plasticised pullulan–starch blends at low moisture *Carbohyd. Polym.*, 40, 29-47.
- Debeaufort, F., Voilley, A. and Meares, P. (1994). Water vapor permeability and diffusivity through methylcellulose edible films. *J. Membrane Sci.*, 91(1-2), 125-133.
- Hargens-Madsen, M., Schnepf, M., Hamouz, F., Weller, C. and Roy, S. (1995). Use of edible films and tocopherols in the control of warmed over flavor. *J. American Diet. Assoc.*, 95, A-41.
- Jongjareonrak, A., Benjakul, S., Visessanguan, W., and Tanaka, M. (2008). Antioxidative activity and properties of fish skin gelatin films incorporated with BHT and [alpha]-tocopherol. *Food Hydrocolloid.*, *22*(3), 449-458.
- Lazaridou, A. and Biliaderis, C. G. (2002). Thermophysical properties of chitosan, chitosan– starch and chitosan–pullulan films near the glass transition. *Carbohyd. Polym.*, 48, 179– 190.
- Li, B., Kennedy, J. F., Jiang, Q. G., and Xie, B. J. (2006). Quick dissolvable, edible and heatsealable blend films based on konjac glucomannan Gelatin. *Food Res. Int.*, *39*(5), 544-549.
- Li, Y., Shoemaker, C. F., Ma, J., Shen, X., and Zhong, F. (2008). Paste viscosity of rice starches of different amylose content and carboxymethylcellulose formed by dry heating and the physical properties of their films. *Food Chem.*, *109*(3), 616-623.
- Lopez-de-Dicastillo, C., Hernandez-Munoz, P., Gavara, R. and Catala, R. (2007) Development of packaging films containing natural antioxidants. Characterization of their activity on simulant and real foods. 5th International Packaging Congress & Exhibition. IZMIR, Turkey, pp. 213-221.
- Mathew, A. P. and Dufresne, A. (2002) Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. *Biomacromol.*, 3, 1101-1108.
- Oussalah, M., Caillet, S., Salmieri, S., Saucer, L. and Lacroix, M. (2004). Antimicrobial and antioxidant effects of milk protein-based film containing essential oils for the preservation of whole beef muscle. *J. Agr. Food Chem.*, *52*, 5598-5605.
- Pascat, B. (1986). Study of some factors affecting permeability. London: Elsevier.

- Phoopuritham, P., Thongngam, M., Yoksan, R.and Suppakul, P. (2007). Properties of antioxidant cellulose ether films containing selected plant extracts. 5th International Packaging Congress & Exhibition. IZMIR, Turkey, pp. 659-668.
- Rachtanapun, P., Kaewsuwan, N., Khantaprab, P. and Sirivatanapa, V. (2006) Effect of antioxidants on mechanical properties of blended rice flour/cassava starch film and releasing of antioxidants from film. Thailand Research Expo 2006, September 8-13, 2006, Central Plaza, Bangkok.
- Rachtanapun, P. and Wongchaiya, P. (2008). Effect of relative humidity on mechanical properties on blended chitosan-methylcellulose film. Mae Fah Luang Symposium. Chiang Rai, Thailand, p. 50.
- Ribeiro, B., Valentao, P., Baptista, P., Seabra, R. M., and Andrade, P. B. (2007). Phenolic compounds, organic acids profiles and antioxidative properties of beefsteak fungus (Fistulina hepatica). *Food Chem. Toxicol.*, 45(10), 1805-1813.
- Siracusa, V., Rocculi, P., Romani, S., and Rosa, M. D. (2008). Biodegradable polymers for food packaging: a review. *Trends Food Sci. Tech.*, 19(12), 634-643.
- Suppakul, P., Chalernsook, B., Ratisuthawat, B., Prapasitthi, S. and Munchukangwan, K. (2006) Plasticizer and Relative Humidity Effects on Mechanical Properties of Cassava Flour Films. The 15<sup>th</sup> IAPRI World Conference on Packaging. 3 5 October 2006. Tokyo, Japan.
- Tongdeesoontorn, W., Mauer, L., Wongruong, S. and Rachtanapun, P. (2009). Effect of gelatin and carboxymethyl cellulose concentration and relative humidity on cassava starch based film properties. The forth China-Europe symposium on processing and properties of reinforced polymers. Guilin, China, p. 104.