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Improvement of Mechanical Properties of Peanut Protein Films by Chemical Modification

Yun Joong Kwon, Chin-Chi Liu* and Elena Castell-Perez*

Dept. Food Science and Biotechnology, Kyonggi University
**Dept. Biological and Agricultural Engineering, Texas A&M University*

Abstract

Peanut protein films were prepared by casting heated alkaline solutions in the presence of glycerol (1.0 g/g of protein) as a plasticizer. To improve the mechanical properties of peanut protein films, formaldehyde and propyleneglycol alginate (PGA) were added to the film-forming solutions and their effects on film tensile strength (TS) and elongation were investigated. Formaldehyde resulted in improvement of TS, while reducing % elongation. Treatment with PGA increased TS by 60% with slight increase in % elongation. Since PGA is not only safe for human consumption but also effective in alkylating proteins, the PGA treatment seems promising for the preparation of protein-based edible films.

Key words: edible film, peanut protein, propyleneglycol alginate, chemical modification

Introduction

Edible films and coatings based on proteins, carbohydrates, and/or lipids have much potential for increasing food quality and reducing food-packaging requirements (Kester and Fennema, 1986; Gennadios and Weller, 1991; McHugh and Krochta, 1994). Biodegradable and edible protein films or coatings have several advantages in the food processing industry (Donhowe and Fennema, 1994). Edible protein films and coatings can be used as carriers of antioxidants, antimicrobials, or flavorings; as coating materials for nuts, shelled eggs, and fruits; to prevent moisture migration in multicomponent foods such as pizzas, pies, and candies. Edible films with adequate mechanical properties could conceivably also serve as edible packaging for selected foods. From an agricultural industry perspective, wide commercialization of biopolymer film would lead to further utilization of agricultural commodities employed as sources of film-forming materials.

Protein based films have been made from casein (Avena-Bustiilos and Krochta, 1993), whey proteins (McHugh *et al.*, 1994; Fairley *et al.*, 1997), corn zein (Mendoza, 1975), soy proteins (Stuchell and Krochta, 1994; Gennadios et al., 1998), wheat gluten (Herald *et al.*, 1995; Gontard and Ring, 1996), and rice bran (Gnanasambandam *et al.*, 1997). Peanut is one of the alternative substrate sources for biodegradable film formation because of its high protein content, ranging from 22-30% (Ahmed and Young, 1982). The limited research into peanut protein film in food applications is due to the unavailability of commercial peanut protein concentrate and also limited literature on peanut protein film. It is important to have knowledge of suitable film forming method, the effect of film forming parameters, and film characteristics for further research on their food application. In previous studies, the development and formation of peanut protein film by the surface and deposition method, and the effect of film forming parameters such as temperature, pH were investigated (Aboagye and Stanley, 1985; Jangchud and Chinnan, 1999a).

Commercialization of peanut protein films requires improvements of mechanical and barrier properties. Functional properties of proteins are often chemically modified. A variety of methods have been employed to modify soy protein film properties including treatment with alkali (Brandenburg *et al.*, 1993); alkylation with sodium alginate (Shih, 1994); treatment with propylene-

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Corresponding author: Yun Joong Kwon, Department, Food Science and Biotechnology, Kyonggi University, Suwon 442-760, Republic of Korea.
Phone: 031-249-9651, Fax:
E-mail: yjkwon@kyonggi.ac.kr

glycol alginate (PGA) (Shih, 1994; Shih, 1996); acylation with acetic and succinic anhydrides (Ghorpade *et al.*, 1995); and treatment with formaldehyde (Ghorpade *et al.*, 1995). Our particular interest is the macromolecular interaction involving the alginate derivative PGA. In addition to being a good film-forming polysaccharide, PGA can cross-link with amino groups in protein. As a result, the presence of small amounts of PGA could significantly modify and often improve the performance of the protein-polysaccharide films (Shih, 1994).

In this work, edible films were prepared using peanut protein isolate and the effects of cross-linking with aldehydes and propyleneglycol alginate (PGA) on mechanical properties of film were investigated.

Materials and Methods

Materials

Partially defatted peanut flour with 12% fat and 50% protein content was obtained from Golden Peanut Company (Alpharetta, GA) and was stored at 4°C prior to use. PGA (Kelcoid S) was obtained from the Kelco Division of Merck & Co. (Rathway, NJ). All other reagents and chemicals used were of ACS reagent grade.

Preparation of peanut protein isolate (PPI)

Defatted peanut flour was made from partially defatted flour (12% fat) by a hexane extraction method. Partially defatted flour was extracted with n-hexane (1:3 ratio) overnight with moderate stirring. After settling, the supernatant was removed by cautious decantation. The same procedure was repeated on the precipitate. The final precipitate was collected and air-dried to yield defatted peanut meal. Peanut protein isolate was prepared from defatted peanut meal by the method of alkaline extraction and acid precipitation (Kim *et al.*, 1992). Defatted peanut meal was suspended in distilled water with the ratio of 1:10. The suspension was extracted by adjusting the pH to 9 with 1 N NaOH and stirring with a magnetic stirrer at medium speed for 1 hr. After extraction, the suspension was consecutively passed through 60 and 120 mesh standard sieves. The filtrate was then centrifuged at 0°C, 10000 rpm for 30 min. The resulting supernatant pH was adjusted to 4.5 by 1 N HCl to form a precipitate and then centrifuged at 0 °C, 10000 rpm for 10 min. The precipitate was suspended in small amount of distilled water and centrifuged for 10 min. This washing procedure was repeated twice. The isoelctric form of wet protein concentrate was then freeze dried for 24 hr. The dry protein isolate was ground and stored in a plastic bag at -20°C until used.

Film preparation

Film-forming solutions were prepared by dissolving 4.0 g of PPI (88.0% protein) in distilled water to provide a 5% protein content in 70.0 g of final weight. The pH of the solution was adjusted to 9.0 by adding 1 N NaOH during dissolution and stirring. Glycerol was added to the film forming solution as plasticizer and then heated to 70°C on a hot plate with magnetic stirring. The solution was filtered through screen (mesh no. 120) after cooling for 10 min, and then poured and evenly spread on a non-stick glass plate for film formation. Films were formed by drying at 90°C for 16 hr, then peeled from the plates after cooling. Film samples were stored in a plastic bag in a desiccator at ambient temperature for further testing. For chemical modification, film also was prepared in a similar manner after formaldehyde solution (38% w/w) or PGA solution (2% w/w) was added to the film-forming solution. The solutions were stirred for 10-20 min at room temperature to allow for interaction between the reagent and the protein and, subsequently, were adjusted pH to 9.0 before heating.

Tensile strength and elongation

Tensile strength (TS) and elongation at break (E) were both measured with Texture Analyzer (Texture Technologies Corp., NY) following the guidelines of ASTM Standard Method D 882-91 (ASTM, 1993). Five thickness measurements were taken along each specimen with a micrometer and the mean of the five measurements was used in the TS calculation. In an apparent deviation from ASTM Standard Method D-882, tensile testing of film samples was conducted, as quickly as possible, in constant room temperature rather than in the recommended atmosphere of 23 ± 2°C and 50 ± 5% RH. TS was calculated by dividing maximum load by initial specimen cross-sectional area of the film. The percent elongation at break was calculated from the maximum elongation during testing versus the original gauge length of the film.

Results and Discussions

The addition of a plasticizer to edible films is required to overcome film brittleness caused by extensive intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chain, thereby improving flexbility and extensibility of the film (Gontard *et al.*, 1993). Glycerol was found to be the most suitable plasticizer to incorporate into a peanut protein concentrate when compared with sorbitol, propylene glycol and polyethylene glycol (Jangchud and Chinnan, 1999b). Glycerol has a high boiling point, is water soluble, protein miscible and nonvolitile; these characteristics make glycerol suitable for water soluble polymers, such as peanut protein concentrate. Though flexibility of peanut protein films was improved by glycerol, the amount had to be limited due to its adverse effect on film strength, elasticity and water vapor barrier properties. Minimizing the amount of glycerol use was attempted, film with glycerol at 0.5 g/g of protein was still brittle and broke during film removal. Intact film (free-standing film) after drying was obtained when a glycerol concentration of 0.75 g/g of protein was used, however it still needed gentle handling to prevent from breaking. Therefore, films with glycerol at 1.0 g/g of protein were prepared for further testing.

To improve the mechanical properties of peanut protein films, acetic anhydride, glutaldehyde, formaldehyde, and PGA were added to the film-forming solutions and their effects on film tensile strength and elongation were determined. Acetylated and glutaldehyde treated films were not successful for improvement in tensile strength. However treatment with formaldehyde and PGA appeared to have some positive effect on the mechanical properties of films with similar water vapor permeabilities based on preliminary works (data not shown). Therefore, different amounts of formaldehyde and PGA were added to the film-forming solutions and tensile strength of the films were compared. As the concentration of formaldehyde added increased, film strength was increased while % elongation of the film decreased (Table 1). When 1.0 g of 38% formaldehyde solution was added to the film-forming solution (ca. 3.5 g of protein), the tensile strength was increased to 2.62 MPa which was 20% higher than that of control peanut protein films. The increased strength of formaldehyde-treated films was attributed to cross-linking within the film structure. Increase in mechanical strength also have been reported

Table 1. Effect of formaldehyde treatment on tensile strength and elongation of peanut protein films[a]

Formaldehyde (38%, g)	Peanut protein isolate (g)	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)
0.0	4.0	0.16	2.14	195
0.1	4.0	0.18	1.94	179
0.5	4.0	0.17	2.28	143
1.0	4.0	0.13	2.62	105

[a] Thickness was the mean of five measurements. Tensile strength and elongation were the mean of three determinations.

Table 2. Effect of propyleneglycol alginate (PGA) treatment at alkaline pH on tensile strength and elongation of peanut protein films[a]

PGA (g)	Peanut protein isolate (g)	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)
0.0	4.0	0.16	2.14	195
0.1	4.0	0.17	1.91	194
0.3	4.0	0.18	2.62	234
0.5	4.0	0.17	3.38	219

[a] Thickness was the mean of five measurements. Tensile strength and elongation were the mean of three determinations.

for formaldehyde treated films from soy protein (Ghorpade *et al.*, 1995) and pea protein (Gueguen *et al.*, 1998).

Protein-PGA films were prepared by addition of 5.0 to 25.0 g of PGA solution (2% w/w) to a film-forming solution (final weight of 70.0 g) containing 4.0 g of peanut protein isolate. A clear increase of maximum tensile strength of films as a function of PGA concentration was observed, accompanied by a slight increase of elongation at break (Table 2). When a PGA amount of 0.5 g was added to the film-forming solution (ca. 3.5 g protein), the tensile strength was increased to 3.38 MPa which was 60% higher than that of control peanut protein film. Stronger and more tenacious films were formed as the protein and PGA reacted to form covalent bonds under alkaline conditions. The crosslinking was caused mostly by the amidation between ε-amino groups of lysine residues in the protein and manuronic acid esters of the polysaccharide (Shih, 1994).

Conclusions

Treatment with formaldehyde improved the strength of peanut protein films, but showed a decrease in the elongation of the films. Addition of small amount of PGA, which interact with protein to form covalent bonds, enhanced the film's tensile strength significantly with slight increase in % elongation. It should be noted that use of formaldehyde for cross-linking protein films may be impractical due to the toxicity of formaldehyde. On the other hand, PGA is safe for human consumption and no undesirable by-products are generated during the interaction. Therefore, the PGA alkylation process has the potential to be used in the preparation of protein-based edible films.

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