Grease Resistance and Mechanical Properties of Isolated Soy Protein-Coated Paper

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ABSTRACT: Grease-resistant paper has been produced by coating paper with isolated soy protein (ISP). Tensile strength (TS) of ISP-coated paper is 28–30 MPa (between the TS of paper and of ISP film). TS of the ISP-coated paper (2.3 kg/ream) was highest (36.0 MPa) among other ISP-coated papers, but elongation (E) of the papers seemed to decrease (though not statistically significantly) as the thickness of the ISP coating increased. ISP-coated papers were highly impermeable to grease penetration for the first 2 h of the test. The percent stained area of two commercially used polyethylene-laminated papers was higher than those of ISP-coated papers. As the amount of plasticizer (a mixture of glycerol and polyethylene glycol) was increased in ISP-coated paper, the TS decreased and the E increased. When tested, the percent stained areas of the paper containing 0.6 and 1.0 g plasticizer/g protein were lower for the first 2 h than those of the papers containing 0.0 and 0.2 g plasticizer/g protein. Also, percent stained area increased with time. Grease resistance of papers coated with ISP at levels higher than 2.0 kg/ream was equal to or lower than that of polyethylene laminates used for quick-service restaurant sandwich packaging.

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KEY WORDS: Grease resistance, isolated soy protein (ISP), ISP-coated paper, percent stained area.

Protein-based biopolymer films have been studied for potential use as wrapping and coating materials for food products and have been widely utilized as gas, oil, and mechanical barriers in food systems for extending shelf life of processed foods (1–3). Zein has been used as an oxygen barrier coating to prevent oxidation in peanut products (4). Additionally, casein coatings could be used on minimally processed fruits to extend their marketing period (5). Trezza and Vergan (6) found that zein-coated paper has a high potential for use as an oil barrier wrapping material in fast-food restaurants and reported that paper coated with zein at ratios of 4.4 and 6.6 kg/ream would be adequate as a grease barrier for quick-service sandwich packaging for 1 to 2 h. Isolated soy protein (ISP) has an excellent film-forming property (7–9). Soy protein films traditionally have been used as edible wraps for meat and vegetable mixes which are then fried in oil. Examples are "Yuba" in Japan, "Tou-Fu-Pi" in China, and "Fu Chok" in Malaysia (10,11). Films produced from ISP are excellent oxygen barriers and are even better than those made from zein and wheat gluten (9).

A common quick-service sandwich packaging is composed of a polyethylene layer between two paper layers. Grease resistance is important for packaging products containing fats or oils. Polyethylene and most plastics are generally classified as good grease barriers. However, the polyethylene content makes separation, recycling, and composting of the materials difficult (12). For foods with extremely short shelf life such as quick-service restaurant sandwiches, papers coated with natural biopolymers could meet packaging requirements as a grease barrier. Zein has limited commercial use because of its high price (13). However, ISP, which is a major by-product from soybean oil extraction, is a cheap biopolymer that is competitive with polyethylene. Barrier and mechanical properties of protein-based films and coatings are affected by factors such as concentration and selection of plasticizer, pH, solvent, and other additives (8,9,13–19). Flexibility is improved, but puncture strength and water vapor and oxygen barrier properties are decreased as plasticizer concentration is increased in wheat gluten films (14–16). Gennadios *et al.* (8) prepared protein films with a blend of wheat gluten and ISP, and studied the effects of varying the pH of the film formation solutions on mechanical properties and water vapor permeability of films. Brandenburg *et al.* (9) reported that ISP films treated with alkali had improved film appearance and elongation properties. ISP films were not clear in appearance because of the presence of insoluble particles (17). Treatments of ISP at high pH and temperature resulted in hydrolyzed and denatured products that were more soluble (18). Denaturation of protein is known to change the shape of protein from globular to extended chain morphology. Theoretically, more protein–protein interactions would result in decreasing gas permeability and increasing tensile strength. Park *et al.* (19) reported that different mixtures of glycerol (GLY) and polyethylene glycol (PEG) as plasticizers greatly affected the mechanical properties and water vapor permeabilities of protein-based films.

No attempts to develop ISP-coated paper as a grease barrier packaging film have previously been reported. This study

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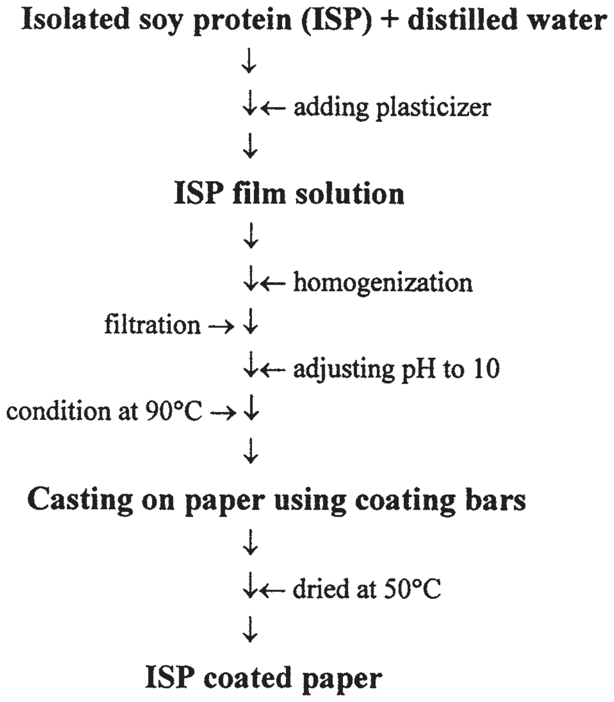
was designed (i) to prepare ISP-coated papers with various coating thicknesses, and (ii) to determine the grease resistance and mechanical properties of the paper.

EXPERIMENTAL PROCEDURES

Materials. The following materials were used to prepare the ISP-coated papers: Supro 500E ISP (Protein Technologies International, St. Louis, MO); glycerol (USP grade), PEG (molecular weight 400, NF grade) (Fisher Scientific, Pittsburgh, PA); paper (8.6 kg/ream) (Kaesung Paper Industrial Co., Kunggi-Do, Korea).

Preparation of ISP coated paper. Film solutions were prepared by dissolving 5 g of ISP in 100 mL of distilled water. A mixture of GLY and PEG was then added as plasticizers. Three different amounts of plasticizer for each film (0.2, 0.6, and 1.0 g plasticizer/g protein) were used, and the GLY/PEG plasticizer ratio was 50:50 (w/w) (19). The film solution was homogenized at 3,000 rpm for 5 min and filtered through cheesecloth to remove insoluble materials. Then pH of the solution then was adjusted to 10 with 0.3 N HCl or 0.3 N NaOH solutions, and the solution was stirred for 5 min. The solution was conditioned at 90°C for 15 min. A volume of 30–50 mL was poured onto the top of a paper-covered glass plate (28 × 28 cm), and then the plate was cast by coating rods (Tester Sanyo Co., Saitama-Ken, Japan) (Scheme 1). Several rods, each with spacers of a different width, were used to provide a cavity of known depth between the rod and the substrate surface, thus allowing the casting of a film of known uniform thickness. The wire size determines the coating thickness (Table 1). The ISP-coated paper was dried at 50°C for 30–60 min and was detached from the glass plates. The coating levels were calculated on the basis of ISP per ream of paper (278 m^2). Samples were prepared for determining water vapor permeability and mechanical properties. A hand-held micrometer (B.C. Ames Co., Waltham, MA) was used to measure film thickness to an accuracy of 0.000127 cm (0.05 mil).



SCHEME 1

Preparation of dyed fat. A loaf of beef fat was placed in a flask, and the flask was heated in an oil bath (120°C). The melted fat was filtered through cheese cloth to remove impurities. The melted beef fat was then dyed red using Oil Red O (Sigma Chemical, St. Louis, MO) for easy detection of grease permeation through the coated paper (6,20).

Grease resistance testing. Grease resistance of coated papers was determined using a modified TAPPI test T-507, "Grease Resistance of Flexible Packaging Material" (20). ISP-coated paper samples, 10 × 10 cm, were cut and then placed above one square of clean sheet (10 × 10 cm) and below one dyed fat-saturated sheet (7.5 × 7.5 cm) of bibulous blotting paper (Scheme 2). A 0.5 mL aliquot of the stained fat was applied to saturate the blotter paper sheet. The saturated sheet was placed in contact with the ISP-coated side of the paper. Stacks of the three-layered system were separated by aluminum foil sheets (12 × 12 cm), and a stainless-steel disk (d = 12 cm) with a mass of 720 g was placed onto stacks of up to 10. The assembly was placed in an oven at 60°C . Samples were removed every hour for 8 h, and the amount of grease that passed through the ISP-coated paper samples to the clean blotters was measured. The percentage area of clean blotters stained with grease was determined by a point-counting method (6,21). This procedure was repeated for two commercially prepared polyethylene-laminated papers used in local quick-service food restaurants.

Mechanical properties. Twelve samples, 2.54 cm wide and 10 cm long, were cut from the ISP-coated paper. Samples were conditioned for 48 h at 25°C and 50% relative humidity (RH) in an environmental chamber before measuring tensile strength (TS) and elongation (E). An Instron (model 4210; Instron Engineering Corp., Canton, MA) was used to measure TS and E at breakage, according to ASTM standard method D 882-88 (22). Initial grip separation and crosshead speed were set at 50 mm and 500 mm/min, respectively. Peak loads and extension at the breakage point were recorded for the tested film samples. TS was calculated by dividing peak loads by specimen cross-sectional areas. The thickness of individual samples, required to calculate cross-sectional area, was determined by averaging five micrometer readings taken on each sample before testing. Extension values were divided by the initial grip separation (50 mm) and multiplied by 100 to yield percentage E at breakage. Units used are Pascal (Pa) and percent (%) for TS and E, respectively.

Data analysis. Ten and three samples were prepared for measuring mechanical properties and grease migration properties, respectively. Duncan's multiple range test was applied to compare the means for mechanical properties. Tables 1 and 2 show the resulting comparisons with a level of significance of $\alpha = 0.05$ (23).

TABLE 1
Mechanical Properties of Papers Coated with Various Levels of ISP

Coating rod		ISP-coated paper properties[a]			
Number	Wet film solution thickness on paper[b] (mil)	ISP film thickness on paper ((m)	Coating levels (kg/ream)	TS (MPa)	E (%)
No coating (paper only)	—	0	0	47.0[a]	4.9[b]
5	0.45	10.9[d]	2.0[c]	30.4[b,c]	5.8[a,b]
7	0.63	11.1[d]	2.0[c]	35.1[b]	6.4[a]
12	1.08	11.9[c]	2.2[c]	35.9[b]	6.7[a]
14	1.26	12.3[c]	2.3[c]	36.0[b]	6.3[a]
28	2.52	17.5[b]	3.1[b]	28.1[c]	6.6[a]
44	3.96	23.0[a]	4.8[a]	28.5[c]	6.9[a]

[a]Films prepared with a glycerol/polyethylene glycol ratio of 50:50; values refer to means of 10 samples; coating level in kilograms of solid [isolated soy protein (ISP) + plasticizer] per ream (278 m^2) of paper. Values in a row with different roman letter superscripts are significantly different as determined by Duncan's multiple range test. TS, tensile strength; E, elongation; mil = 0.001 inch.
[b]Technical data from Tester Sanyo Co. (Saitama-Ken, Japan Co).

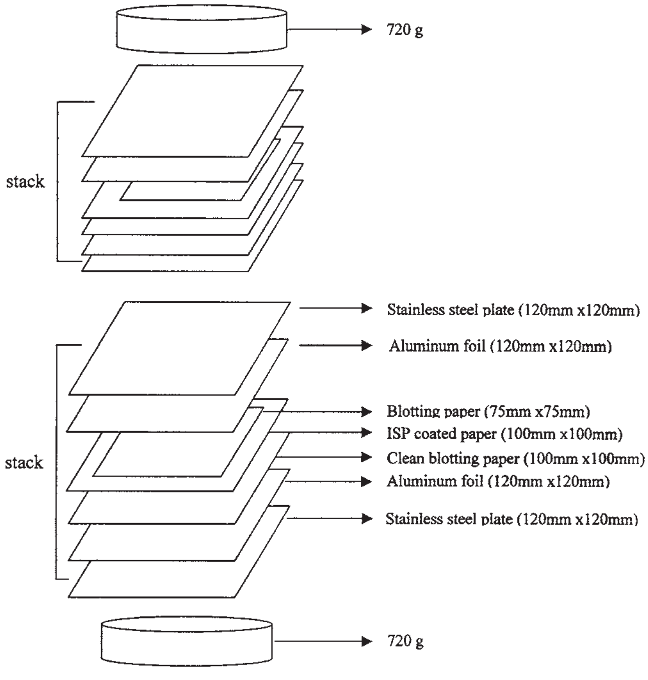
RESULTS AND DISCUSSION

Coating level. The ISP coating level (kg/ream) on paper increased as the wire size increased (Table 1). TS of the paper itself was 47 ± 5 MPa in this study, and TS of ISP film was 5.6 MPa (thickness, 2.61 ± 0.171 mil) (9). TS of ISP-coated papers were 28–36 MPa and, as expected, were between those of the paper and the ISP film. A similar trend was found in TS of a laminated methylcellulose (MC)/corn zein film (24). TS of that laminate was 18–25 MPa, which is between the TS of the MC film (33 MPa) and of the corn zein film (8-13 MPa).

TS of the ISP-coated paper was expected to decrease as the ISP coating thickness on the paper increased. However, the TS of paper coated with ISP at a rate of 2.0 kg/ream was 30.4 MPa and increased as the ISP coating level increased to 2.3 kg/ream (coated with Rod Number 14). When the paper was coated with 3.1 and 4.8 kg/ream, the TS fell below that of the paper coated at 2.0 kg/ream. ISP seemed to be absorbed inside the paper and to strengthen the film properties up to a certain level, but then to weaken the mechanical properties above the critical level. E of the papers seemed to decrease as the level of ISP coating increased, but the E at different coating levels were not significantly different.

Grease barrier properties of the ISP-coated papers were measured and were compared with two commercial polyethylene-laminated papers (Fig. 1). Smaller stained areas per hour indicated greater grease resistance. ISP-coated papers were highly impermeable to grease penetration for the first 2 h. Grease migration was not detectable when papers were coated with ISP at levels of 2.2, 2.3, 3.1, and 4.8 kg/ream, and the percent area stained for the 2.0 kg/ream ISP-coated paper was about 0.6%. The percent stained areas of two commercially used polyethylene-laminated papers were 1.8–2.4% and were higher than those of ISP-coated papers, which may be attributed to the effect of heat sealing on polyethylene-laminated paper. A similar result was found with respect to grease barrier properties of corn zein-coated papers when they were compared with a commercially used polyethylene-laminated paper (6). As expected, the percent stained area increased with time (Fig. 1). Even with uniform coatings, grease would probably permeate through pinholes, cracks, thin portions and other small areas where discontinuities in the coatings occurred. Defects in the coatings may explain why percent stained areas of papers coated at higher level ISP are sometimes higher than those of lower-levels of ISP-coated papers. Grease resistance of papers coated with ISP at higher than 2.0 kg/ream was equal to or lower than polyethylene-laminated papers used for quick-service restaurant sandwich packaging.

Plasticizer concentration. The concentration of plasticizer affected mechanical and grease barrier properties in ISP-coated paper. Increasing concentrations of plasticizer led to higher coating levels (kg/ream) on paper. (i.e., higher solids content in a given coating volume). TS decreased and E increased as the amount of plasticizer was increased in ISP-coated papers (Table 2). For example, TS of the ISP-coated paper containing 0.20 g plasticizer/g protein was 35 MPa and



SCHEME 2

Table 2
Mechanical Properties of ISP-Coated Papers with Various Plasticizer Concentrations

	ISP coated paper propertiesa			
Plasticizer concentration (g plasticizer/g protein)	ISP film thickness on paper (µm)	Coating levels (kg/ream)	TS (MPa)	E (%)
0.0	11.9[a]	1.8[c]	39.5[a]	5.2[b]
0.2	12.1[a]	2.0[b,c]	35.3[b]	5.1[b]
0.6	12.3[a]	2.3[b]	36.0[b]	6.3[a]
1.0	12.4[a]	2.6[a]	27.7[c]	6.2[a]

[a]A #14 coating rod was used for coating ISP solution on paper; films prepared with a glycerol/polyethylene glycol ratio of 50:50. Values refer to means of 10 samples; coating level in kilograms of solid (ISP + plasticizer) per ream (278 m^2) of paper. Values in a row with different roman letter superscripts are significantly different as determined by Duncan's multiple range test. For abbreviations see Table 1.

decreased to 28 MPa as the ratio of plasticizer/protein increased to 1.0 in the films. These results are similar to the results in protein films reported by others. Park *et al.* (19) found that TS decreased and E increased as the amount of plasticizer increased in wheat and corn zein films. Gontard *et al.* (14) reported that puncture strength, one of their mechanical tests, increased as glycerin was decreased in wheat gluten films. Also, the plasticizer mixture ratio affected the mechanical properties of soy protein films, and Jo *et al.* (16) reported that TS of films prepared at pH 10 was the highest (5.6 MPa) for the film prepared with a GLY/PEG ratio of 50:50. In this study, the GLY/PEG plasticizer ratios were 50:50 (w/w), and the films were prepared at pH 10 in ISP-coated paper.

Grease barrier properties in ISP-coated paper were affected by the concentration of plasticizer. In the first 2 h the percent stained area of the paper containing 0.60 and 1.0 g plasticizer/g protein was lower than that of the papers containing 0.00 and 0.20 g plasticizer/g protein. As expected, percent stained area increased with time (Fig. 2). Plasticizer seemed to decrease the grease migration in the ISP-coated paper to a certain level, but increased the grease migration in the ISP coated paper above the critical level. It was observed that the surface of ISP-coated paper, without plasticizer, was very coarse, and the soy protein was easily separated from the paper. Defects on the coating surface might explain why the percent stained area of higher-level ISP-coated papers without plasticizer was higher than that of ISP-coated papers containing plasticizer. The surface of the protein-coated side of the paper becomes smoother as the film content of plasticizer increases. It is very difficult to make ISP film without plasticizer because of its extreme brittleness. But Trezza and Vergano (6) found that the percent stained area of paper coated with corn zein without plasticizer was lower than that of corn zein coated-paper containing 0.25 g GLY/g protein in grease resistance test. This difference is probably due to the difference in molecular interactions among paper, plasticizers, and protein molecules. Corn zein contains large amounts of hydrophobic amino acids such as leucine, proline, alanine, and phenylalanine, and the average hydrophobicity of corn zein is much higher than that of soy protein. Corn zein without plasticizer can be coated easily on paper and have excellent film-forming properties. GLY in corn zein film is well dispersed on the protein film at the beginning, but migrates to the surface of the film matrix (19). This overall situation makes the corn zein-coated paper more permeable to grease, as the corn zein contains more GLY in the film.

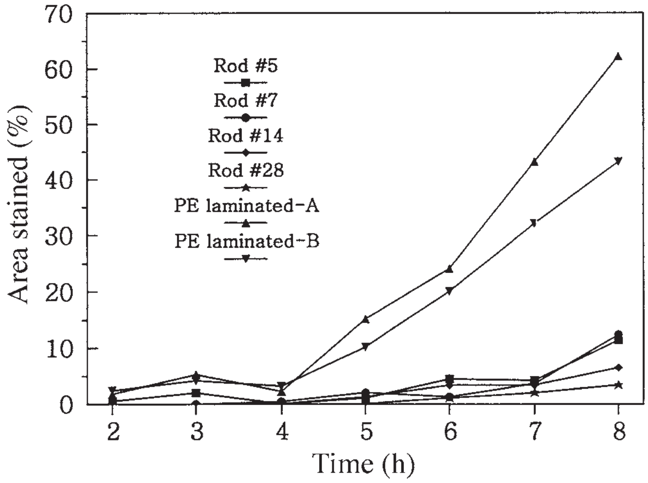


FIG. 1. Grease permeation of isolated soy protein (ISP)-coated papers coated with various coating bars. PE, polyethylene.

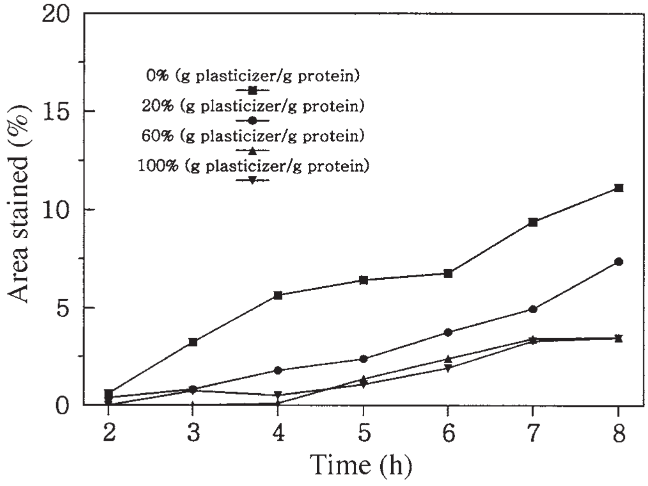


FIG. 2. Grease permeation of ISP-coated papers with various plasticizer concentrations.

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