Physical Properties and Oil Absorption of Whey-Protein-Coated Paper

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ABSTRACT: Whey-protein-isolate coating on paper produced a smooth surface, which was observed by scanning electron microscopy. Increasing coating weight decreased the breaking stress and the Young’s modulus. However, the maximum breaking strain was not affected by coating weight. Tearing strength was not changed by WPI coating. The coated paper was slightly darkened with a small reduction of L value, but the a and b values were not changed significantly. WPI coating made the coated paper slightly shiny with increased gloss. Thus, with the exception of about 12% reduction in breaking stress for 10 g/m² coated paper, WPI coating did not change the mechanical and optical properties of the paper markedly. WPI coating significantly reduced the rate of oil contact angle decrease on paper associated with oil absorption by paper. Therefore, WPI coating improves packaging material performance of paper by increasing oil resistance without significant change of optical and mechanical properties.

Key Words: whey protein isolate, paper, mechanical strength, optical property, contact angle, oil absorption

INTRODUCTION

Paper is the most widely used packaging material. The surface of paper is treated to improve paper properties, including physical strength, oil/grease resistance, wettability, smoothness, and optical properties. The surface sizing treatment uses pigments and adhesives such as polystyrene particles, clay, starch, modified starches, carboxymethyl cellulose, poly (vinyl alcohol), casein, soy protein, rubber latex, and acrylic-based emulsions (Casey 1960; Robertson 1993; Han and Krochta 1999).

Whey protein isolate (WPI) has been used for edible coating and film materials to extend the shelf life of foods, such as fresh produce, dried nuts, and meats (Krochta and De Mulder-Johnston 1997). Our previous research showed that WPI coating on pulp paper increased ink printability and reduced water-vapor permeability of the paper (Han and Krochta 1999). To further explore the practical usability of the WPI-coated paper for food packaging, the general requirements as a food packaging material must be studied. General properties beyond those already studied include mechanical properties (tensile properties, tearing strength, and burst strength), optical properties (color and gloss), and grease resistance. This paper reports the tensile properties, tearing strength, color, gloss, and grease resistance of WPI-coated paper.

Tensile testing measures the characteristic ultimate tensile stress (strength), strain (elongation), and elastic modulus (Young’s modulus) of materials. These 3 values are intrinsic properties of a material, independent of specimen dimensions (Black 1992). The change of paper color after coating can affect the use of the coated paper. The Hunter Lab L, a, and b color scale is widely used to quantify color. This scale also can be easily converted to R-B-G (red-blue-green) scale and H-L-c (hue-lightness-chroma) scale. The a value measures greenness to redness, b measures blueness to yellowness, and L measures lightness (Hunter and Harold 1987). Gloss is the ratio of light flux reflected in specular direction to incident flux. This specular gloss is defined in ASTM E284 (ASTM 2000).

Grease resistance is one of the important properties of food wraps and bags. Oil-soluble dye penetration is a common method for measuring the grease resistance of paper (TAPPI 1994). To quantify grease resistance, oil absorption can also provide data for comparison among papers. However, oil weight gain by paper was found to have experimental difficulties in our preliminary work. This method produces varying results because wiping the excess oil from the paper surface leaves residual surface oil, with resulting incorrect data with large deviation for oil absorption.

The contact angle of a liquid drop on a solid surface is a characteristic constant reflecting the surface energies of the solid surface, liquid, and air (Zisman 1973). This characteristic contact angle changes because of change of the mass of liquid drop, caused by evaporation of the liquid, and/or absorption of the liquid by the solid (Toussaint and Luner 1993). Ignoring the evaporation of an oil drop, the dynamic change of the contact angle of an oil drop on a paper surface is only related to the oil absorption of the paper. In this case, the rate of contact angle decrease is assumed to be related to the liquid-absorption rate (Han and Krochta 1999). Faster absorption shows as faster decrease of the contact angle with time, which can be measured by the slope of the contact angle against time plot (Han and Krochta 1999).

The study reported in this paper determined common mechanical and optical properties of WPI-coated paper and contact angle changes of oil drops on the coated paper. The intent was to examine the potential of practical use of WPI-coated packaging paper related to the physical strength and oil-resistance properties after coating.

MATERIALS AND METHODS

Whey Protein Isolate Coating on Paper

The same materials and coating methods were used as in a previous study of wetting properties and water-vapor permeability (Han and Krochta 1999). WPI (Davisco Foods International, Le Sueur, Minn., U.S.A.), glycerol (Sigma Chemicals...
Co., St. Louis, Mo., U.S.A.), and pulp paper (Strathmore Paper Co., Westfield, Mass., U.S.A.) were used. Paper was trimmed and placed on an acrylic plate, and the coating solution was applied by a thin layer chromatography (TLC) applicator with a slit size of 0.127mm or 0.254mm. WPI solution was formulated to 10% and 11.5% (w/w) in distilled water. Glycerol was added to the WPI solution to obtain 60:40 ratio (by weight) of WPI:glycerol in the solution. The coating solution was degassed by a rotary vacuum pump and denatured in a 90 °C water bath for 30 min. Three combinations of WPI concentration and TLC applicator slit size (10%, 0.127mm; 11.5%, 0.127mm; and 10%, 0.254mm) were selected to coat the solutions on 10 sheets of pulp paper for each treatment. After coating, the papers on the acrylic plates were dried in a 50 °C oven for 2 h.

After drying, the coated papers and uncoated paper were trimmed to discard edges, weighed, and measured by area. The coating weight was calculated by the weight of coating materials (g) per unit paper area (m²). Among 10 sheets of coated papers for each treatment, 5 to 6 sheets of paper were selected for the experiments after discarding wrinkled paper samples.

Coated papers were placed in a desiccator overnight, then cut by blade for a cross-sectional view. The coating surface and the cross-sectional views were taken by a scanning electron microscope (SEM), which is located in the Facility for Advanced Instrumentation at the Univ. of California, Davis.

Tensile Test and Tearing Test

An Instron universal testing instrument (model 1122, Instron Engineering Corp., Canton, Mass., U.S.A.) was used for the tensile and tearing tests. The test machine has 500kgf and 2kgf load cells for the tensile test and the tearing test, respectively. The gauge length was 10 cm for both tests. The cross-head with clamp jaw was moved up at 5 cm/min speed, and the data was collected automatically by a data-acquisition system. The tensile-test paper and tearing-test specimens are shown in Fig. 1A and 1B, respectively. Specimens for tensile and tearing tests were obtained from the 5 to 6 paper samples that were selected for the coating weight measurements. Each paper sample provided 1 specimen for tensile testing and 1 for the tearing test. Thickness was determined as an average of measurements at 4 different places on each sample using a caliper micrometer (Mitutoyo Mfg. Co., Ltd., Japan). Breaking stress (in MPa) and strain (in % elongation), ultimate stress (in MPa) and strain (in % elongation), and Young’s modulus (elastic modulus) (in MPa) were measured and calculated according to ASTM standard method D882 (ASTM 1991). For the tearing-test specimen (Fig. 1B), only breaking stress and ultimate stress were measured and divided by the thickness of the specimen to calculate tearing force in N/m. The temperature and relative humidity of the testing atmospheric conditions were approximately 26 °C and 40%, respectively. The tearing test involves precutting a tear over 7.4 cm of a 9-cm-long sample then determining the force to tear the remaining 1.6 cm of length.

Color and Gloss

A Hunter Lab colorimeter (Labscan II, Hunter Lab, Reston, Va., U.S.A.) with HunterLab Universal software (version 3.1.2) was used to quantify the surface color of the WPI-coated paper. Gloss of the WPI-coated paper was measured by a Micro-TRI-gloss reflectometer (BYK-Gardner Inc., Silver Spring, Md., U.S.A.) with light angle geometries of 20° and 60°. A minimum of 5 samples was used for measuring the color and gloss of the WPI-coated paper for each coating treatment.

Contact Angle and Oil Absorption

Contact angles of oil drops in air on the WPI-coated paper surface were measured using a Wild M5A horizontal micro-
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scope (Wild Heerbugg, Switzerland) equipped with a goniometer. For each coating treatment, a drop of corn oil (Mazola Corn Oil, Best Foods Division, CPC International Inc., Englewood Cliffs, N.J., U.S.A.) was placed on each of the 5 to 6 WPI-coated surface samples, which were selected from coating-weight experiments. The contact angles (θ) on both sides of the drop were measured with time (t) to assure symmetry and horizontal level. All contact angle measurements

Figure 3—SEM images of cross-section (A, B, and C) and surface (D, E, and F) of coated and uncoated papers
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were performed at room temperature and 50% RH. Oil-absorption rate was assumed related to the rate of contact angle change, which was the slope of the contact angle against time (θ against t) plot. To calculate the slope, the contact angle data, which showed above $R^2 > 0.9$ for linearity, were collected and used for linear regression analysis. The initial contact angle was calculated from the intercept of Y-axis ($t = 0$) of the linear regression line on the $θ$ against $t$ plot.

Results and Discussion

Whey-Protein Coating on Paper

Three different WPI-coating conditions and 1 uncoated paper generated 4 sample paper groups. The uncoated paper had 0 g/m² coating weight and was used as a reference. The 10% (WPI content), 0.127mm (slit size) sample had a 10.2 g/m²; the 11.5% WPI, 0.127mm sample had a 8.8 g/m², and the 10% WPI, 0.254mm sample had a 17.9 g/m² WPI-coating weight (Fig. 2). The 0 g/m², 10.2 g/m², 8.8 g/m², and 17.9 g/m² coating weights are simply noted as 0 g/m², 10 g/m², 9 g/m², and 18 g/m², respectively, in this paper. An important point is that the coating weight from 11.5% WPI, 0.127mm was slightly smaller than that of 10%, 0.127mm, although the difference is not significant because of large standard deviation for both groups (Fig. 2). These 2 sample groups were found to be in the same group statistically, however, the data of these 2 groups were not combined together as the same treatment in this paper. Synthetic surface-sizing agents are commonly coated on paper at about 4.9 to 6.5 g/m² (3 to 4 lb/ream) of coating weight. Thus, WPI coating was 1.5 to 3 times conventional synthetic coating weight.

SEM images showed very smooth surfaces for WPI-coated papers (Fig. 3). Upper sides of the cross-sectional views (Fig. 3-A, B, C) are the WPI-coating sides. The coating surface became smoother with increasing coating weight. The 18 g/m² sample shows an extremely smooth coating surface. Comparison of the surface images (Fig. 3-D, E, F) of uncoated and coated papers shows that the porous fibrous structure of paper was covered and filled by WPI coating. Figure 3 verifies that WPI coating produces a homogeneous, smooth coating surface and fills the pores to increase water-vapor resistance and decrease roughness of paper (Han and Krochta 1999).

Tensile and Tearing Strength

Figure 4 shows the results of tensile testing. The breaking force (breaking stress in MPa) was decreased with increasing coating weight, while the breaking strain (in % elongation) was not changed. The breaking stress and ultimate stress were found to be the same value for all specimens. The breaking force of the 10 g/m² WPI paper was 20% less (0.63 MPa) than that of 0 g/m² (0.79 MPa). The 18 g/m² WPI-paper breaking force was measured at 25% less (0.59 MPa) than that of 0 g/m² (0.79 MPa). The elastic modulus (Young's modulus) decreased 14% and 26% for 10 g/m² and 18 g/m², respectively, which theoretically means that WPI coating increased flexibility of the paper. With 95% confidence, the least significant difference (LSD) test showed a significant difference in Young's Modulus and breaking force with 0, 10, and 18 g/m² coatings. But breaking strain was not changed.

Figure 4—Results of tensile testing with different coating weights

Figure 5—Changes in color and gloss of WPI-coated paper with different coating weights

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Statistically. However, paper ductility was not increased because the breaking strain was not changed by WPI coating. During the coating process, WPI solution swells the cellulose fiber structure and penetrates into spaces between fibers. After drying, WPI remains in the cellulose structure and interferes with fiber-to-fiber interaction. Because the coated paper structure has smaller interaction force between fibers because of WPI interference, the tensile strength is decreased after coating. Internal sizing agents, which are added during the pulping and beating process of papermaking, usually decrease the paper strength for the same reason suggested in this paper (Casey 1960).

Tearing forces of 0 g/m², 8.8 g/m², 10.2 g/m², and 18 g/m² WPI-coated paper were 3680 N/cm (± 184.8 N/cm), 4093 N/cm (± 534.9 N/cm), 3962 N/cm (± 675.6 N/cm), and 3263 N/cm (± 869.0 N/cm), respectively. WPI coating does not change the tearing strength significantly. However, increasing coating weight increased standard deviations of tearing force. This may suggest that increasing the portion of WPI in paper fiber by WPI coating affects the consistency of tearing resistance of the coated paper. The increasing trend of deviation may also be caused by increasing deviation of thickness of papers after coating, which was shown in Fig. 2. Overall, it is concluded that the WPI coating did not change the tearing strength of paper.

Color and gloss of WPI-coated paper

The L value of paper decreased slightly but significantly with increasing coating weight, although the a and b values did not change (Fig. 5). The L value was reduced from 92.2 to 90.5 as coating weight increased from 0 g/m² to 18 g/m². The difference may not be noticeable with the human eye. We could observe only very slight difference in the lightness of papers after coating. For all practical purposes, the WPI coating did not change the color of papers significantly and thus still provides the same background color as uncoated paper, which is very important in the case of the printing process.

Gloss of the coated paper at high angle (60°) was slightly increased with increasing WPI-coating weight. At 20°, the gloss was not changed (Fig. 5). Although the gloss at the 60° angle was increased with increasing coating weight, it was still only 9.3% at 18 g/m² compared to 3.4% at 0 g/m². With a large standard deviation (2.58% at 18 g/m²), the increased gloss of paper after coating may not be critical for practical purposes. Gloss difference was barely noticeable, even though gloss data showed some difference before and after coating. The increased gloss may be caused by the paper surface being more homogeneous and smoother after WPI coating. Compared to the fibrous paper structure, WPI-coating materials (mainly WPI and glycerol) are very small molecules. They are much smoother materials than the paper fibers after drying. Because of coating with smoother materials, the paper becomes smoother, resulting in a slightly glossier surface after coating. The increase of surface smoothness and homogeneity were also suggested by the previous research of Han and Krochta (1999). They found increasing linearity between surface energy and contact angle of polar liquids on the WPI-coated paper with increasing coating weight. They also suggested that the pore spaces of fibrous paper structure are filled with WPI-coating material, with resulting increased homogeneity and hydrophilic affinity of the paper.

Contact Angle of Corn Oil on WPI-Coated Paper

The contact angle decrease of a water drop on paper with time was used to measure the water-absorption rate of paper in previous research (Han and Krochta 1999). This method more easily quantifies the liquid-absorption rate than any other method, including the oil-soluble dye method for grease resistance. The rate of contact angle decrease of corn oil on the WPI-coated paper was decreased significantly.
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Conclusions

Whey-protein coating on paper did not change the tearing strength of papers or their optical properties. However, the tensile strength and elastic modulus were slightly decreased by WPI coating, while the elongation was not changed. The oil-absorption rate was decreased by WPI coating, and 18 g/m² WPI coating on the paper showed an extremely high oil resistance. Therefore, WPI coating could be practically useful as an oil barrier on paper wraps and bags for hamburgers, fried foods (that is, potato chips, fried fish, vegetables, and so on), and other greasy foods. The WPI-coated paper is biodegradable, consisting of cellulose and whey protein. It is an environmentally friendly material compared to any other grease-resistant materials, including plastic laminated materials or aluminum foil.

References


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