

Optical and Surface Properties of Whey Protein Isolate Coatings on Plastic Films as Influenced by Substrate, Protein Concentration, and Plasticizer Type

Seok-In Hong,¹ Jung H. Han,² John M. Krochta³

¹Korea Food Research Institute, Kyonggi 463-746, Korea

²Department of Food Science, The University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

³Department of Food Science and Technology, University of California, Davis, California 95616

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ABSTRACT: Composite film structures of common plastic polymers including polypropylene (PP) or poly(vinyl chloride) (PVC) with whey protein isolate (WPI) coatings may be obtained by a casting method. Optical and surface properties of the resulting WPI-coated plastic films, as affected by protein concentration and plasticizer type, were investigated to examine the biopolymer coating effects on surface modification with polymeric substrates of opposite polarity. The measured properties involved specular gloss, color, contact angle, and critical surface energy. Regardless of the substrates, WPI-coated films possessed excellent gloss and no color, as well as good adhesion between the coating and the substrate when an appropriate plasticizer was added to the coating formulations. The protein concentration did not sig-

nificantly affect gloss of WPI-coated plastic films. Among five plasticizers applied, sucrose conferred the most highly reflective and homogeneous surfaces to the coated films. The WPI coatings were very transparent and the coated films with various protein concentrations and plasticizers showed no noticeable changes in color. Experimental results suggest that WPI coatings formulated with a proper plasticizer can improve the visual characteristics of the polymeric substrate and enhance water wettability of the coated plastic films.
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Key words: biopolymer coatings and films; oxygen barrier; optical properties; water wettability; critical surface energy

INTRODUCTION

Transparent gas-barrier films are available as competitive products for food and medical packaging.¹ Typical oxygen-barrier layers in polymeric packaging materials consist of expensive synthetic barrier polymers including poly(vinylidene chloride) (PVDC) and ethylene vinyl alcohol (EVOH) copolymers that are commonly used in the form of coatings or coextruded films. Recently, excellent barrier properties have been obtained by vacuum evaporation or sputtering of inorganic substances or by plasma-enhanced chemical (such as silicon oxide) vapor deposition on common polymer films.^{2,3} These films are of commercial interest for those packaging applications requiring microwaveability and/or product visibility.⁴ However, such transparent coating processes require very high technology processes (e.g., coextrusion, vacuum, or

plasma deposition) and expensive materials (e.g., PVDC, EVOH). Furthermore, the resulting multilayer films cannot be recycled.

Naturally renewable biopolymers have been the focus of much research in recent years because of interest in their potential use as edible and biodegradable films and coatings for food packaging. Biopolymers derived from various natural sources can reportedly be formed into either coatings or stand-alone films. Properties and potential uses of biopolymer films and coatings based on polysaccharides, proteins, and lipids have been reviewed.^{5–9} Among them, low oxygen permeability whey protein films as a biopolymer packaging material have been developed.¹⁰ Such whey protein films can be formed as a transparent coating material for improving the oxygen-barrier property of packaging. It has been shown possible to obtain a high oxygen-barrier property on common plastic films such as LDPE and PP by using whey protein as a new barrier coating material to produce a composite structure.^{11,12} In addition, the whey protein coatings can be separated chemically or enzymatically from the substrates, enhancing recyclability and reutilization of the plastic layer.

Important factors that must be considered in designing for whey protein coatings, with the intention of conferring high oxygen-barrier functionality on

Correspondence to: J. M. Krochta (jmkrochta@ucdavis.edu).

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TABLE I
Plasticizers Used for Study and Their Properties

Plasticizer type	M_w	Formula and Shape	Refractive index (n_{20})
Propylene glycol	76	$C_3H_8O_2$, straight chain	1.4324 ^a
Glycerol	92	$C_3H_8O_3$, straight chain	1.4746 ^a
Sorbitol	182	$C_6H_{14}O_6$, straight chain	1.5105 ^{a,b}
Polyethylene glycol	200	$H(OCH_2-CH_2)_4OH$, straight chain	1.4590 ^c
Sucrose	342	$C_{12}H_{22}O_{11}$, ring structure	1.5376 ^a

^a Data from literature.¹⁹

^b Extrapolated from the data on the aqueous solutions of various concentrations.

^c Data from the chemical manufacturer (Aldrich Co.).

polymer substrates, include mechanical properties and appearance. Mechanical properties of the coated polymer as a packaging material generally tend to rely strongly on the substrate rather than the coating. Appearance is also important, affecting the saleability of the coated polymer for a package. Gloss is a highly desirable appearance attribute in packaging applications. From a physical point of view, gloss is reduced by the amount of light scattered by a material. Light scattering is usually associated with the material surface roughness, because in many cases the bulk contribution is small.¹³ Another aspect of appearance is haze, a term that refers to the tendency of light-transmitting plastics to scatter light, producing a cloudy appearance as a result. The effect of haze is largely aesthetic, although in extreme cases haziness may interfere with one's ability to distinguish details of contents in packages that are important to consumers.¹⁴ Biopolymer coatings made from whey proteins have the potential to improve the visual quality of foods, especially appearance, because of their high gloss and transparency.¹⁵

The surface energy or surface tension is a controlling factor in the processes involving wetting and coating of substrates with coating formulations, including the coating process, coating adhesion, and printing operations. The surface energy of solid polymers is found to be generally anisotropic, dependent on the spatial variations in surface structure and composition, surface roughness, and orientation of crystal-growth faces.¹⁶ Because the surface energy of solid polymers cannot be measured directly, several indirect methods have been proposed. For convenience in commercial practice, the surface energy of plastic surfaces can be measured using a calibrated set of solutions (modified Visking analytical technique).¹⁷ A more sophisticated method is to measure the contact angles that several probe liquids make with the surface. The surface energy of the solid polymer is then related to the surface tensions of the liquids and the contact angles. This method invokes various restrictive assumptions¹⁸ and requires extrapolation of the probe liquid contact-angle results. The intercept of the

plot (Zisman plot) at $\cos \theta = 1$ gives the critical surface energy, γ_c . In practice, γ_c varies with testing fluids, and Zisman plots are often complicated by scatter and curvature. However, little is known about the optical and surface properties of whey protein coatings on plastic films. A greater understanding of these properties will allow packaging technologists to optimize the visual and printing characteristics of the coated films.

The objectives of this study were to form plasticized whey protein isolate (WPI) coatings on common polymer films made from polypropylene (PP) and poly(vinyl chloride) (PVC), and then to determine the optical and surface properties of the WPI-coated films in terms of gloss, color, contact angle, and critical surface energy as influenced by substrate, protein concentration, and plasticizer type. Of particular interest was characterizing the WPI coatings on synthetic polymeric substrates (PP and PVC) of opposite surface polarity.

EXPERIMENTAL

Materials

WPI [97.7% dry basis (db) protein] used to form coatings was provided by Davisco Foods International (BiPro WPI, Le Sueur, MN). The plasticizers, glycerol, sorbitol, and sucrose, were obtained from Fisher Scientific (Fair Lawn, NJ). The plasticizers propylene glycol (PG) and polyethylene glycol 200 (PEG) were purchased from Aldrich (Milwaukee, WI). These plasticizers represent different chemical compositions, sizes, and shapes (Table I). Oriented polypropylene (PP) film of $50.8 \pm 0.5 \mu\text{m}$ thickness (Plastic Suppliers Co., Fullerton, CA) and PVC film of $107.8 \pm 1.1 \mu\text{m}$ thickness (C-Line Products, Inc., Sacramento, CA) were used as polymeric substrates for whey protein coatings.

Surface modification

PP and PVC films were cut into sizes of $20 \times 25 \text{ cm}$, and the sample films were washed with acetone and

distilled water, and finally dried. Corona discharge treatment (25–30 kV/cm, 4–5 MHz) was performed only on the surfaces of PP films by using a laboratory corona treater (Model BD-20AC, Electro-Technic Products Inc., Chicago, IL) to increase the surface energy of the films. The surface dimensions of the electrode and the gap distance were 1.4×7.0 cm and about 0.5 cm, respectively.

Coating formation

WPI solutions of different protein concentration [5, 7.5, and 10% w/w on wet basis (wb)] were prepared by mixing WPI powder in distilled water and heating at 90°C for 30 min in a water bath to denature the protein.²⁰ Solutions were cooled in an ice bath to room temperature and degassed by applying vacuum to remove dissolved air, followed by adding a given amount of each plasticizer and then degassing again. The plasticizer concentration in WPI solutions was 0.60M (PG: 29.1%, glycerol: 33.3%, sorbitol: 50.0%, PEG: 52.2%, sucrose: 65.0% w/w db). For the coating solutions containing 5 and 7.5% WPI, glycerol as a plasticizer was added on the weight basis of 33.3% (WPI : glycerol = 2 : 1). Standard amounts (~ 2.5 mL) of coating solutions were applied on corona discharge-treated PP films, as well as on untreated PVC films, and then spread evenly using a Bird-type applicator (Paul Gardner Co., Pompano Beach, FL) to achieve a wet coating thickness of 0.25 mm. Coatings were then dried at ambient temperature (23–25°C and 40 ± 5% RH) for 18 h. Four replications, at least, were used to determine optical and surface properties.

Thickness

Coated film thickness was measured with a micrometer (Model No. 2804-10, Mitutoyo Manufacturing Co., Tokyo, Japan) to the nearest 0.1 mil (2.54 μm) around the film testing area at 10 random positions. WPI coating thickness was calculated by subtracting the substrate (PP or PVC) thickness from the coated film thickness. Thicknesses of the films were measured at room temperature (23°C and 40% RH) and expressed as the average and standard deviation (SD) values.

Gloss

Specular gloss of WPI-coated plastic films was measured with a reflectance meter (micro-TRI-gloss, BYK Gardner Inc., Silver Spring, MD). Reflectance measured at angles of 20 and 60° from the normal to the coating surface, in accordance with standard ASTM method D523,²¹ is reported as a gloss unit (G.U.; % of standard) based on six readings each, for at least four replications. A highly polished plane surface of black glass with a refractive index of 1.567 served as the

primary gloss standard and was arbitrarily assigned a gloss value of 100, which differed according to the angle used. Gloss measurements were carried out on the coated films placed on the matte surface of black acrylic plates (3.2 mm thick sheet, TAP Plastics, Sacramento, CA), which have 0.2 and 3.0 gloss units for the 20 and 60° angles, respectively, at room temperature (23°C and 40% RH).

Color

A Hunter LabScan colorimeter (Hunterlab, Reston, VA) was used to assess the color of WPI-coated plastic films. The instrumental parameters applied were a Mode of 0/45, a 2° Observer, a D65 (sodium) illuminant, a port size of 0.25 in. (0.635 cm), and an area view of 0.635 cm. A white standard color plate ($L = 93.24$, $a = -0.85$, $b = 0.16$) for the instrument calibration was used as a background for color measurements of the coated films. In this system, color is represented as a position in a three-dimensional sphere, where the vertical axis L indicates the lightness (ranging from black to white), and the horizontal axes, indicated by a and b , are the chromatic coordinates (ranging from $-a$: greenness, $-b$: blueness to $+a$: redness, $+b$: yellowness). The values of a and b approach zero for neutral colors and increase as the color becomes more chromatic and more saturated. Hunter L , a , and b values were averaged from three readings across for each coating replicate. The total color difference (ΔE) can be calculated by the following equation²²:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

The results were also expressed as ΔE values with the substrates having no WPI coatings as reference ($n \geq 4$).

Contact angle and critical surface energy

As probe liquid materials, dimethyl sulfoxide (DMSO), ethylene glycol (EG), formamide (FA), glycerol (Gly), and water (HPLC grade) were selected and purchased from Sigma Chemicals (St. Louis, MO). Their surface tensions are 44.0, 48.0, 58.2, 63.4, and 72.8 mJ/m², respectively. Using a microsyringe, 10-μL samples of the probe liquids were placed on the coated film surface that was glued on a well-leveled plastic platform. A digital microscope (Intel QX3, Mat-tel Inc., El Segundo, CA) was positioned horizontally next to the film to capture the side-view image of the probe liquid following the Choi and Han procedure.²³ At the lens position of $\times 10$, the side-view image was acquired and converted into a binomial edge-enhancing picture using conventional photo-editing software (CorelDRAW 9, Corel Corp. Ltd., Ottawa, Ontario, Canada) to measure the contact angles. The surface

energy was calculated from the regression analysis for a Fox-Zisman plot (cosine contact angle versus surface energy).

Statistical analysis

Statistical analyses were performed using SAS software.²⁴ The general linear models (GLM) procedure was used for analysis of variance (ANOVA). The Duncan's multiple-range test was used to determine any significant difference between specific means at a 95% confidence interval. For the critical surface energy calculation to obtain surface energy when the cosine contact angle was zero, the linear regression procedure of data analysis tool of Excel 2000 (Microsoft Corp., Redmond, WA) was used at the confidence level of 95%.

RESULTS AND DISCUSSION

Coating formation

Polypropylene, one of major polyolefins, is very prominent in flexible food packaging as films and laminae in composites and multilayers. However, PP exhibits poor adhesion to polar materials because of its nonpolar nature as a low surface energy plastic. This poor adhesion results in poor physical properties of the laminated forms. Surface modification of PP is, therefore, necessary to impart good adhesion with polar materials and better resulting strength of the prepared laminates. Thus it was very difficult to coat the surface of untreated nonpolar PP films evenly with the polar aqueous WPI solutions. The nonpolar nature of the PP surface was not likely to offer binding sites for WPI coatings. Several methods have been used to modify the nonpolar plastic surfaces, including corona discharge, flame treatment, plasma treatment, and chemical etching.²⁵⁻²⁷ Corona discharge is the process of impinging an electrical discharge of high energy on a surface. In this study, corona discharge as a surface pretreatment was applied to improve the ability of PP films to adhere to whey proteins in a coating operation. This treatment appeared to work successfully by imparting some degree of oxidation to the surface of the polymer, resulting in an increase of the surface energy of the film. In this process, electric energy flows from a high-voltage conductor through ionized air and through the film. In the ionization, some of the oxygen in the air is converted to ozone, which can oxidize the surface of the film, and the film surface is slightly ionized.²⁵ After the PP surfaces were treated with corona discharge, thin and transparent WPI coatings could be uniformly formed on the PP films. Contrary to PP, PVC could have uniform WPI coatings formed on its surface without any pretreatment, probably because of the polar nature of the polymer. As is

well known, PVC is the high molecular weight compound formed by the structure $\text{CH}_2=\text{CHR}$, where R represents a chlorine atom. This molecular structure apparently provides enough binding sites for whey proteins to adhere well onto the surfaces of PVC.

WPI is generally heated to denature the protein and expose the internal sulfhydryl groups to allow formation of intermolecular disulfide bonds, which affect the coating and film structure.^{20,28} However, proteins by themselves, including whey protein, form brittle films, so that they require proper plasticizer addition to overcome film brittleness by reducing protein chain-to-chain interaction. The result is an increase in the mobility of polymer chains and more flexible films.²⁹ Thus, the amount of each plasticizer added in the coating formulations was determined on an equivalent molar basis (0.60M) to give a sufficient plasticizing effect on WPI coatings. The resulting WPI-coated films possessed excellent gloss and flexibility, as well as good adhesion between the coating and the base film, when an appropriate amount of plasticizer was added to the coating formulations. It was also observed that when such plasticizers as sorbitol and sucrose were added on the dry weight basis of 33.3% (WPI : plasticizer = 2 : 1) to coating solutions, the coatings obtained were more brittle and susceptible to partial detachment from the substrate films. In the case of insufficient plasticizer content, the dried WPI-coated films also tended to show some cracks on the surface and curl up, with the coated layer inward as dried out, probably attributable to strong interaction of the protein molecules with each other rather than between the protein and the polymer substrates.

WPI concentration exerted no effect on coating formation on the polymeric substrates. In the limited range of 5 to 10% protein concentrations, WPI coatings plasticized with glycerol showed good adhesion as well as clear and smooth appearance regardless of substrate type. On the other hand, the coating thickness of WPI-coated films increased linearly with whey protein concentration applied (data not shown). Generally, a linear relationship can be expected between film thickness and solids content of coating solutions, when Bird-type applicators are used for coating works. The values of coating thickness for corona discharge-treated PP films were relatively larger than those for PVC films, which is presumably attributable to the surface energy difference between both substrates. Without any pretreatment to the plastic, PVC typically has the greater critical surface energy of 33–38 mJ/m^2 , compared to about 29–31 mJ/m^2 for PP. However, use of corona treatment generally raised the surface energy level of PP to values in excess of 42 mJ/m^2 .³⁰ Thus, PP films treated with corona discharge can have higher surface energy than that of PVC, producing more binding sites to which whey proteins can adhere. WPI-coated plastic films also exhibited

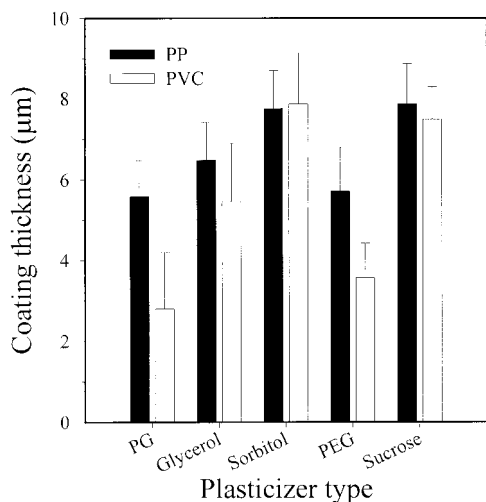


Figure 1 Effect of plasticizer type on coating thickness of WPI-coated PP and PVC films. The concentration of plasticizer added in 10% (w/w wb) WPI solutions was 0.60M. Each data point is presented with the average and standard deviation (SD) values. Error bar shows SD.

differences in coating thickness depending on the plasticizer added (Fig. 1). Among five different plasticizers used, sucrose and sorbitol, which are solids at ambient conditions, gave relatively thicker WPI coatings than the liquid-phase plasticizers. This might be caused partly by the molecular size effect of plasticizers and largely by the characteristic bulky molecular size of sucrose and the crystallization tendency of sorbitol.³¹ Sorbitol-plasticized WPI coatings on plastic films indeed tended to crystallize after storage for 2 months at ambient temperature (23–25°C) and low relative humidity (40 ± 5% RH). No significant difference in coating thickness between PP and PVC was also observed for sucrose-, sorbitol-, and glucose-plasticized WPI coatings, but a statistically significant difference for PG- and PEG-plasticized WPI coatings was observed.

Gloss and color

Gloss values of the coated films measured at an angle of 60° were higher than 130 gloss units, regardless of the substrates (data not shown). According to the manual for the gloss meter used in this study, measurements are recommended to range between 10 and 70 gloss units for best accuracy and differentiation among films. A surface with a gloss of 70 or greater at 60° is considered a high gloss surface.³² Thus, to obtain a better differentiation of the gloss values, all the measurements were also carried out at 20°. However, gloss values at 20° for all the coated films (>125 gloss units) were still much greater than the suggested range. Very high gloss even at an angle of 20° meant that double reflection effects, which may interfere

with coating gloss measurement, occurred with our coated film. Considering that WPI coatings plasticized with glycerol had gloss values of 90.8 ± 1.4 unit at 60° and 72 ± 17 unit at 20°,^{15,33} high gloss of the coated films would be likely to come from the substrate films rather than the coatings. Gloss of the substrate films without coating showed 133.4 ± 2.2 units for PP and 128.1 ± 1.4 units for PVC at 20°. Accordingly, the protein concentration did not affect the gloss of WPI-coated plastic films, although the gloss values for WPI-coated PP were slightly higher than those for the coated PVC (Fig. 2). With respect to gloss durability, it was found that WPI coatings had stable gloss values at various RH conditions and maintained a high gloss after over 7 months of storage at 23°C and 75% RH.³³

The coating gloss on plastic films was influenced to some extent by the type of plasticizer used (Fig. 3). Among the plasticizers applied, sucrose conferred more highly reflective surfaces to the coated PP films than did the other plasticizers, probably because of its high refractive index (Table I). Specular reflectance, gloss, is known to be a function of refractive index of the surface, the extinction index, the angle of incidence of the beam of light, and the nature of the reflecting light.^{15,34} The gloss value of the coated films with sucrose was even greater (although not significantly) than that of normal PP films without WPI coatings. Lee et al.³⁵ also observed that WPI coatings plasticized with sucrose provided chocolate with the highest and most stable gloss among the four plasticizers studied. Significant modification of physical properties of the whey protein coatings and films was reportedly attributed to the ring structure and size of sucrose.^{12,31} The

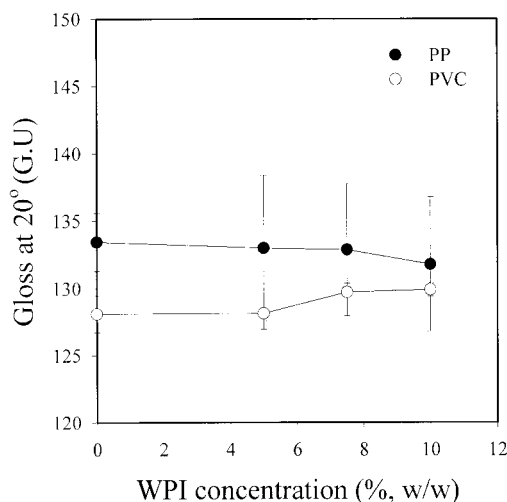


Figure 2 Effect of whey protein concentration on gloss of WPI-coated PP and PVC films at 20°. Coatings based on WPI plasticized with 33.3% (w/w db) of glycerol were used for gloss measurements. Each data point is presented with the average and SD values. Error bar shows SD.

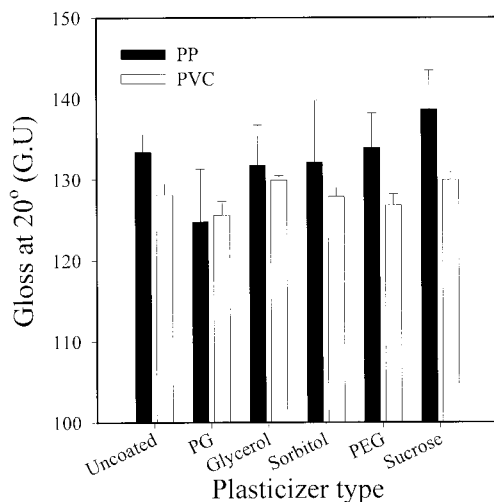


Figure 3 Effect of plasticizer type on gloss of WPI-coated PP and PVC films at 20°. The concentration of plasticizer added in 10% (w/w wb) WPI solutions was 0.60M. Each data point is presented with the average and SD values. Error bar shows SD.

plasticizer effect on the gloss of coated PVC films did not differ noticeably from the results with PP. Overall, however, the gloss values for the coatings on PVC substrate were relatively lower than the gloss values for the coatings on PP, except for PG-plasticized samples. This difference in the coating gloss on PP and PVC was probably caused by the significant intrinsic gloss difference between the substrates themselves without coating (Fig. 3), as mentioned above.

Color of the coated films with varied protein concentrations and plasticizers showed no remarkable differences among the samples (Table II). To obtain a better differentiation of the color measurements,

Hunter L , a , and b values measured were converted to total color difference (ΔE) values with the substrates as reference. Although ΔE of the coated films increased with WPI content, those values (≤ 0.30 for PP and ≤ 0.11 for PVC) were too small to differentiate the film samples from each other. Similarly to the protein concentration effect, the plasticizer type also did not affect color of the resulting WPI-coated films, regardless of the substrates (Table II). The coated PP films had ΔE values of 0.26 to 0.31, and the PVC films showed ΔE values ranging from 0.04 to 0.11, depending on the plasticizer type used. However, it is generally known that ΔE values less than 3.0 cannot be easily detected by the naked human eye.²² In fact, no color differences between the films with and without WPI coatings could be visually observed.

Contact angle and critical surface energy

The effect of WPI concentration and therefore coating thickness on the wettability of the WPI-coated PP and PVC films was examined (Fig. 4). All the coating solutions contained a WPI : glycerol mass ratio of 2 : 1. Uncoated films showed very different contact angles compared to that of the coated films, particularly at the surface energy of 44.0 and 48.0 mJ/m² (DMSO and ethylene glycol, respectively). Uncoated PP and PVC films produced lower cosine contact angle values, which represent high contact angles, than the WPI-coated films (Table III). Among the coated films, WPI concentration (i.e., coating thickness) appears not to significantly affect the contact angles or the critical surface energies of the films (Fig. 5). The effect of plasticizers on the wettability of the WPI-coated films was also determined (Table IV). The coated films were produced from coating formulations consisting of 10%

TABLE II
Color of WPI-Coated PP and PVC
Films with Various Protein Concentrations and Plasticizers^a

WPI content ^b Plasticizer ^c	PP				PVC			
	L	a	b	ΔE	L	a	b	ΔE
Substrate ^d	89.88 ± 0.03	-0.93 ± 0.01	0.41 ± 0.02	—	88.23 ± 0.01	-0.96 ± 0.01	0.59 ± 0.01	—
5.0/Gly	89.64 ± 0.02	-0.90 ± 0.06	0.50 ± 0.04	0.28* ± 0.02	88.26 ± 0.04	-0.97 ± 0.01	0.61 ± 0.01	0.04** ± 0.03
7.5/Gly	89.61 ± 0.01	-0.94 ± 0.01	0.51 ± 0.03	0.30* ± 0.02	88.20 ± 0.01	-0.96 ± 0.01	0.62 ± 0.02	0.05** ± 0.02
10.0/Gly	89.61 ± 0.01	-0.95 ± 0.01	0.52 ± 0.01	0.30* ± 0.01	88.18 ± 0.02	-0.97 ± 0.01	0.68 ± 0.02	0.11* ± 0.01
10.0/PG	89.59 ± 0.01	-0.94 ± 0.01	0.51 ± 0.01	0.31* ± 0.01	88.24 ± 0.02	-0.96 ± 0.01	0.63 ± 0.01	0.04** ± 0.01
10.0/Sor	89.63 ± 0.01	-0.96 ± 0.01	0.49 ± 0.01	0.27** ± 0.01	88.23 ± 0.01	-0.96 ± 0.01	0.61 ± 0.01	0.03** ± 0.01
10.0/PEG	89.66 ± 0.01	-0.97 ± 0.01	0.52 ± 0.01	0.26** ± 0.01	88.28 ± 0.02	-0.98 ± 0.01	0.02 ± 0.65	0.08* ± 0.03
10.0/Suc	89.60 ± 0.01	-0.96 ± 0.01	0.47 ± 0.01	0.30* ± 0.01	88.25 ± 0.02	-0.97 ± 0.01	0.62 ± 0.01	0.04** ± 0.02

^a Values are represented as the average and standard deviation. Means with the same superscript within the same column are not different at $p < 0.05$.

^b Whey protein concentration is on wet weight basis of percentage (% w/w wb).

^c Plasticizers used for study include glycerol (Gly), propylene glycol (PG), sorbitol (Sor), polyethylene glycol (PEG), and sucrose (Suc).

^d Each substrate without WPI coatings serves as reference for determination of the total color difference (ΔE).

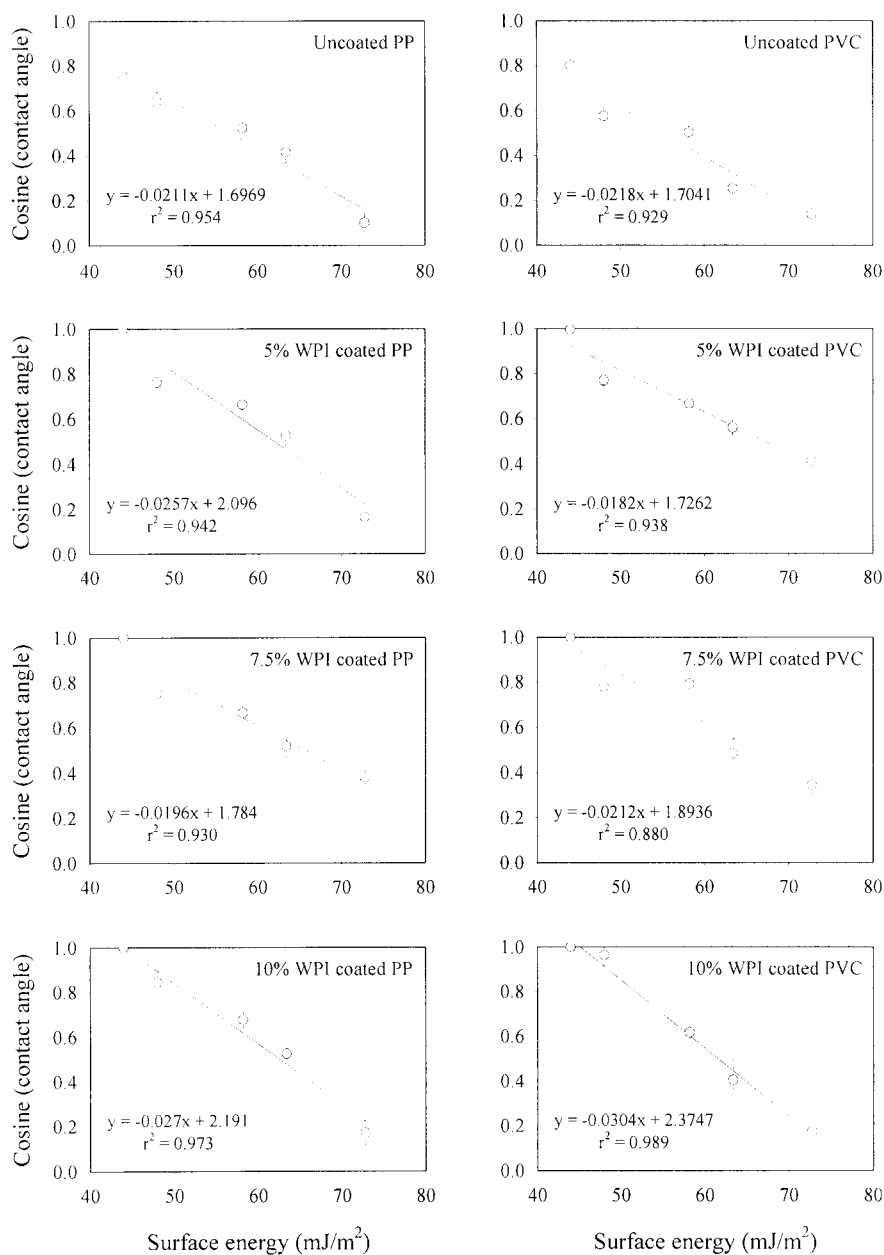


Figure 4 Effect of whey protein concentration on wettability of WPI-coated PP and PVC films. Coatings based on WPI plasticized with 33.3% (w/w db) of glycerol were used for wettability determination. Each data point is presented with the average and SD values. Error bar shows SD.

TABLE III
Regression Analysis for Fox–Zisman Plot of WPI-Coated PP and PVC Films with Various Protein Concentrations

Film	Linear regression model	r^2	Calculated critical surface energy (mJ/m ²)
PP			
Uncoated	$Y = -0.0211X + 1.697$	0.954	33.04 (±7.00) ^a
5% WPI coated	$Y = -0.0257X + 2.096$	0.942	42.62 (±6.30)
7.5% WPI coated	$Y = -0.0196X + 1.784$	0.930	40.08 (±8.12)
10% WPI coated	$Y = -0.0270X + 2.191$	0.973	44.08 (±4.98)
PVC			
Uncoated	$Y = -0.0218X + 1.704$	0.929	32.30 (±7.18)
5% WPI coated	$Y = -0.0182X + 1.726$	0.938	39.80 (±7.48)
7.5% WPI coated	$Y = -0.0212X + 1.894$	0.880	42.17 (±9.81)
10% WPI coated	$Y = -0.0304X + 2.375$	0.989	45.18 (±4.57)

^a Values in parentheses are 95% intervals of the critical surface energy.

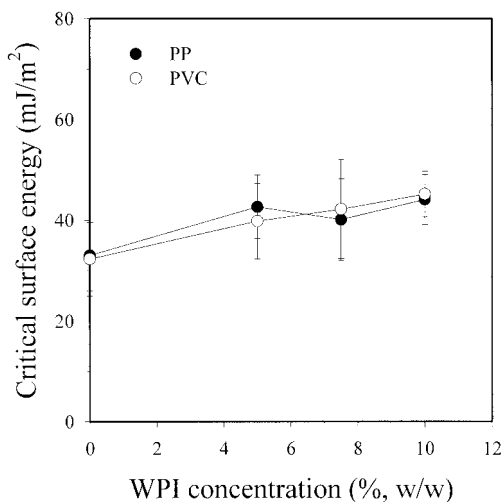


Figure 5 Effect of whey protein concentration on critical surface energy of WPI-coated PP and PVC films. Coatings based on WPI plasticized with 33.3% (w/w db) of glycerol were used. Error bar shows standard estimation error.

(w/w) WPI and 0.6M plasticizers. Regression analysis for the WPI-coatings plasticized with PG and glycerol on PP and PVC films show good linear profile with high r^2 values above 0.97. Compared to PG- and glycerol-plasticized WPI coatings on PP and PVC, the WPI coatings with the other plasticizers showed different linear profiles of wettability. Sorbitol-, PEG-, and sucrose-plasticized WPI coatings have: (1) lower value for the Y-intercept, (2) lower slope, and (3) lower r^2 values than those of the coatings with PG and glycerol. With the increase of molecular weight of the plasticizers (PG < glycerol < sorbitol < PEG < sucrose), the Y-intercept values became smaller, the slopes became lower, and the r^2 values decreased. As the molecular weight of plas-

ticizer increased, the cosine contact angle of water increased. The increase in cosine contact angle of water reflects a decrease in the contact angle of water. This phenomenon was caused by the hydrophilic interaction between water and hydrophilic film components. Because the WPI concentration and the molar concentration of the plasticizers were fixed as 10% (w/w) and 0.6M, respectively, this phenomenon of increase in hydrophilic interaction with increasing molecular weight of plasticizers resulted from the increase in the interaction between the water and plasticizers. The higher molecular weight plasticizers interact more strongly with water and interfere with the wettability measurement.

The critical surface energy results are summarized in Figures 5 and 6. It is shown that glycerol-plasticized WPI coatings on PP and PVC increased the surface energy from 32–33 to 40–45 mJ/m². WPI coatings altered the surfaces of PP and PVC films to be more hydrophilic. Varying the WPI content from 5 to 10% (modified coating thickness and weight) did not significantly change the critical surface energy (Fig. 5). However, uncoated PP and PVC films had significantly different critical energies compared to those of WPI-coated PP or PVC films. The effect of plasticizers on the critical surface energy was also determined (Fig. 6). The sorbitol-, PEG-, and sucrose-plasticized WPI coatings on PP and PVC films had lower critical surface energies and larger standard deviations that were significantly different from the glycerol- and PG-plasticized WPI coatings. Glycerol and PG are more hydrophilic plasticizers. A surface tension ≥ 40 mJ/m² has been generally found to indicate a degree of treatment normally regarded as acceptable to polyolefin films and intended for commercial flexographic printing.¹⁶ Hydrophilic WPI coatings increased the surface

TABLE IV
Regression Analysis for Fox–Zisman Plot of WPI-Coated PP and PVC Films with Various Plasticizers

Plasticizer	Linear regression model	r^2	Calculated critical surface energy (mJ/m ²)
PP			
Uncoated	$Y = -0.0211X + 1.697$	0.954	33.04 (± 7.00) ^a
PG-WPI coated	$Y = -0.0212X + 1.917$	0.972	43.26 (± 6.08)
Glycerol-WPI coated	$Y = -0.0270X + 2.191$	0.973	44.08 (± 4.98)
Sorbitol-WPI coated	$Y = -0.0145X + 1.392$	0.702	27.09 (± 17.19)
PEG-WPI coated	$Y = -0.0710X + 1.639$	0.692	37.63 (± 15.26)
Sucrose-WPI coated	$Y = -0.0079X + 1.177$	0.568	22.39 (± 21.64)
PVC			
Uncoated	$Y = -0.0218X + 1.704$	0.929	32.30 (± 7.18)
PG-WPI coated	$Y = -0.0253X + 2.090$	0.979	43.12 (± 4.86)
Glycerol-WPI coated	$Y = -0.0304X + 2.375$	0.989	45.18 (± 4.57)
Sorbitol-WPI coated	$Y = -0.0129X + 1.396$	0.794	30.72 (± 13.82)
PEG-WPI coated	$Y = -0.0091X + 1.199$	0.762	21.80 (± 16.64)
Sucrose-WPI coated	$Y = -0.0084X + 1.158$	0.713	18.82 (± 18.40)

^a Values in parentheses are 95% intervals of the critical surface energy.

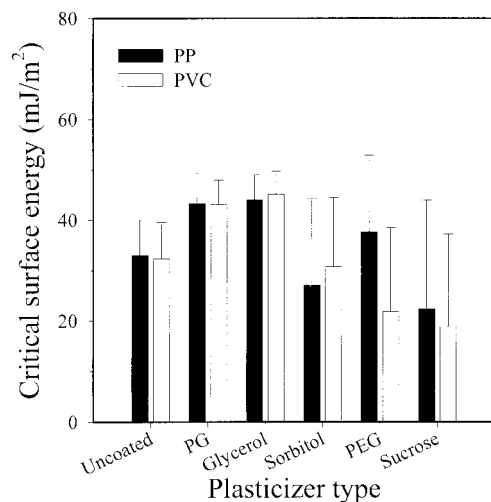


Figure 6 Effect of plasticizer type on critical surface energy of WPI-coated PP and PVC films. The concentration of plasticizer added in 10% (w/w wb) WPI solutions was 0.60M. Error bar shows standard estimation error.

energy of the coated plastic films, along with increasing water affinity to reduce the water contact angle.

CONCLUSIONS

Transparent and smooth WPI coatings with various plasticizers on common PP and PVC films can be obtained. The nonpolar nature of PP films requires a surface treatment such as corona discharge to modify their surfaces to accomplish better adhesion between WPI coatings and the substrate. The resulting WPI-coated films have very high gloss, as well as no color, comparable to that of the synthetic polymer substrates. In addition, hydrophilic WPI coatings confer increased surface energy on the substrate films, along with increased water affinity. As a replacement for existing synthetic oxygen-barrier polymers, WPI coatings with a proper plasticizer have great potential for improving the visual characteristics of the polymeric substrate and for enhancing water wettability of the coated plastic films.

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