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Effect of Polyethylene-Wax/Soy Protein Based Dispersion Barrier Coating on the Physical, Mechanical, and Barrier Characteristics of Paperboards

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ABSTRACT

Application of barrier dispersion coatings on the paperboards, which must have proper moisture and grease resistance for food applications, has always been an interesting subject for the packaging industry. In this study, paperboards were coated with a novel dispersion barrier coating prepared through mixing soy protein isolate (SPI) and polyethylene wax (PE-wax). Different characterization methods were used to study the effects of coating and its composition on the physical, mechanical, and barrier characteristics of paperboards. The results indicated that the incorporation of PE-wax into the coating formulation caused significant reduction of the viscosity of coating slurries. It had no effect on the coating weight of the samples but increased the thickness of the coated paperboards as compared with those coated with SPI only. The increase of the wax content led to a reduction of 5 to 16% in the tensile strength values in comparison with the uncoated paperboards. Barrier characteristics, i.e. water vapor permeability (WVP), surface wettability, and water resistance improved by adding PE-wax. In addition, it was found that there was a critical level for the addition of PE-wax, 50% of SPI, as no oil migration was detected when the paperboards coated with SPI coatings contained less than 50% PE-wax.

Keywords: *Paperboard; Dispersion coating; Soy protein isolate; Polyethylene wax; Barrier characteristics.*

1. Introduction

Packaging, which is one of the major strategic marketing tools at the national and international levels, has a key role in protecting the product quality and increasing sales, reducing inventory and maximizing the profits of manufacturing companies and increasing exports. [1,2] Cellulosic substrates such as paper or paperboard play a vital role in the evolving global packaging market due to their good mechanical properties while being lightweight, low price, easy to print, biodegradable, recyclable, and usable in various industries. The growing consumer awareness about sustainable packaging, along with the strict environmental regulations concerning the utilization of environment-friendly packaging products, has convinced the market to allocate a

larger share to paper and paperboard than to other materials in packaging applications. As such, the share of paper packaging from the global packaging market with a total value of USD 851 billion, was USD 64.4 billion in 2017 and is predicted to reach USD 82.4 billion until 2023. [3,4]

Since the interaction between the food components and its continuous contact with the packaging material may cause changes in its nutritional value that occur over time, the food contacting materials must have good barrier characteristics in addition to high performance, low cost, causing no environmental concerns, and being recyclable. Moisture, gas, and grease resistance are the major needs for paperboard packages in food and food service industries. [5,6] Since the cellulose fibers are naturally hydrophilic given the hydroxyl groups in the glucose units, water (whether from the environment or from food) can easily be absorbed by paper packages, and cause a reduction in physical and mechanical characteristics. The porous structure of the network of cellulosic fibers weakens water vapor barrier characteristics of paper materials and facilitates the transmission of moisture through the paper structure. It can be well–defined by two diffusion mechanisms i.e. water vapor diffusion through the pores and condensed water diffusion through the fiber cell walls. [7,8] Several technologies have been employed to provide paperboard packaging resistance against moisture, gas, and grease including specialty chemical treatment, polymer extrusion coating, and lamination. [9–16] These functional coatings cannot be applied to paper and paperboard by conventional papermaking machines and mostly require specialized converting machines, which can apply the coatings using a hot melt, solvent or extrusion techniques, and then print and cut the paper and paperboard into the finished package. Thus, the application of aqueous barrier coatings to paper and paperboard using conventional paper coating machinery can lead to great savings in time and money.

Naturally renewable biopolymers can act as gas and soluble barriers and provide environmental benefits such as recyclability and reusability in contrast to synthetic polymers. Thus, the attentions of the researchers have been focused on this issue in recent years. [17] Soy protein isolate (SPI) is a commercially available form of soy protein powder with the utmost purity, which contains at least 90% protein regardless of moisture. Similar to other proteins, SPI is a unique sequence of amino acids in each polypeptide. It consists of three major components: 46% of glycinin with a molecular weight of 340–375 kDa, 23% of β-conglycinin with a molecular weight of 140–170 kDa, and 31% of lipophilic proteins containing very little lipid whose composition is not obvious. The combination and interaction of these individual proteins determine the functional properties of SPI. [18] It has some desirable functionalities including emulsifying, gelation, and water holding abilities, making it an important ingredient with an excellent processing ability in food production. [19–21] As an emulsifier, when SPI is applied into the emulsion system, it is adsorbed at oil–water interface, where the protein's lipophilic and hydrophilic groups will be exposed to lipid and aqueous phases, respectively. This molecular orientation reduces the interfacial tension between oil and water, which forms a layer to prevent the oil globules from flocculation or coalescence via electrostatic repulsion. [22–25] SPI is known to have desirable film formation ability, great oxygen, water vapor, and grease barrier characteristics but unpleasant mechanical and surface hydrophobicity characteristics.[26–29] Surface hydrophobicity is a structure-related factor influencing the functional characteristics of proteins, which is modifiable by pH and thermal treatments, [30–33] incorporation of hydrophobic compounds [34–37] or by chemical or enzymatic cross-linking treatments. [38–42]

Waxes are saturated hydrocarbons with good barrier characteristics making them valuable chemicals in the food industry for coating the food and food contact packaging materials such as paper and paperboard from immemorial times. [43,44] There are several well-established groups of

waxes including paraffin wax, macro- and micro-crystalline waxes, soft waxes (isoparaffinic and naphthenic waxes), etc.[45] They can be especially mixed with hydrocarbon polymers such as polyethylene to modify the melting point temperature. Coatings made of polyethylene and macro- and micro-crystalline waxes are glossy and impermeable, which do not tend to block. At least 3 to 5 wt. % of polyethylene is required to obtain the desirable gloss, melting point, and flexibility. [46] Unfortunately, wax coating as melt complicates recycling cellulose products because of its hydrophobic nature which hampers the penetration of water into the paper during repulping process. The use of dispersion coating helps resolve this problem by decreasing and replacing the share of wax with the hydrophilic compounds (like SPI) along with maintaining hydrophobic properties, which is a great advantage of this method. [47]

Since water-based polyethylene wax emulsion is not able to form a uniform film, [48] in the present study, an aqueous dispersion barrier coating composed of a mixture of soy protein and oxidized polyethylene wax was prepared whose effects were evaluated on physical, mechanical, and barrier characteristics of coated paperboards. To the best of the authors' knowledge, the effect of emulsified PE-wax and soy protein blend as a barrier dispersion coating on paperboard substrates has not been scrutinized by any researchers so far.

2. Experimental

2.1. Materials

All compounds were used as received. Soy protein isolate (SPI) 90% was purchased from Bulk Powders® (Colchester, United Kingdom); sodium hydroxide (NaOH) and sodium carboxymethyl cellulose (CMC) (M_W=250,000 Da) from Merck (Missouri, United States). Glycerol anhydrous was bought from Honeywell Fluka™ (Seelze, Germany), Sudan III (oil-soluble red dye) from MP Biomedicals (Ohio, United States) and oxidized PE-wax emulsion with a solid content of 20% containing 5% of ultra-low molecular weight polyethylene (Rockawax MUPE-100) was purchased from Rock chemistry Co. (Tehran, Iran). Deionized water was provided by a Milli–Q ultrapure water purification system (Millipore, Massachusetts, United States) and uncoated solid bleached sulfate (SBS) paperboard (PankaTray, 250 gsm) from Pankaboard (Helsinki, Finland).

2.2. Methods

2.2.1. Coating formulation

Initially, 10 g of SPI powder (based on dry weight) was dissolved by constantly stirring in 100 ml of Milli–Q water and 4 g of plasticizer, glycerol, and then poured. After pH adjustment to 10 by 1N NaOH, the solution was heated and stirred for 30 min at 90 ℃ in a constant temperature oil bath until completely denatured. The final polyethylene-wax/soy protein-based barrier coating formulations were prepared at a constant solid content of 14 wt% and protein to PE-wax ratios of 9:1, 7:3, 1:1, and 3:7, of which PE-wax content was determined as the share of protein content. For this purpose, a certain volume of PE-wax emulsion was added dropwise to the hot denatured SPI solution and the homogenization was done at 10000 rpm for 2 min and then at 20000 rpm for 3 min using an ULTRA-TURRAX® high-performance homogenizer (T25, IKA®-Werke GmbH & Co. KG, Staufen, Germany). During the homogenization, 0.5% CMC solution was added dropwise as a thickener. Finally, the mixture was filtered twice by a fine mesh cheesecloth to remove the

bubbles and then, cooled at ambient temperature before paperboard coating. In reporting the results, the notations of SPI, RSA, RSB, RSC, and RSD are used to show the coatings with PE-wax contents of 0, 10, 30, 50, and 70%, respectively.

2.2.2. Paperboard coating procedure

The final coatings were applied onto SBS paperboard (20×30 cm) using a manual four–sided frame applicator (FA–1 Frame Applicator, Mirnezam Machinary Co., Iran). After mounting the paperboard on a flat laminated board using the masking tape, 10 ml of the coating was poured in the middle of the applicator and spread over the paperboard using the 120µ side of the applicator. The coated paperboards were then dried and conditioned at 23 ℃ and 50% RH for at least 72 h prior to testing.

2.2.3. Characterization Methods

2.2.3.1. Rheological characteristics of coatings

In order to measure the solid content of the coatings, 2g of each coating was poured into separate petri dishes and then, placed in the oven at 103 ± 2 °C for 24 h. Afterwards, solid content values were calculated using Eq. 1:

$$Solid\ content\ (\%) = \frac{Avg.\ weight\ of coating\ after\ drying\ (g)}{Avg.\ weight\ of\ coating\ before\ drying\ (g)} \times 100 \quad (1)$$

The viscosity of the coatings was measured using Anton-Paar rheometer (model Paar Physica MCR 300, Filderstadt, Germany) using the cone-plate system with diameter of 75 mm and cone angle of 1°. A Peltier temperature control unit was used to maintain a constant temperature of 24 ± 0.1 °C during the measurements and prevent evaporation of the samples. Rotational tests (flow curves and viscosity curves) were done by controlling the shear rate from 0.01 to 100 s^{-1}, and measuring torque, shear viscosity, and shear stress. Physica RheoPlus was utilized to analyze the data.

To determine flow consistency and behavior indices, flow curves resulting from the shear stress changes against the shear rate were fitted to the power law model (Eq. 2):

$$\tau = K\gamma^n, \quad (2)$$

Where:
τ: shear stress,
K: flow consistency index,
n: flow behaviour index (n=1 Newtonian fluid; n<1 Pseudoplastic; n>1 Dilatant)

2.2.3.2. Physical characteristics of paperboards

After conditioning, the uncoated and coated paperboards were weighed, and the grammage was calculated using TAPPI standard T410 om-02. [49] The thickness of the 10 × 10 cm^2 specimens was measured using a micrometer thickness gauge (model HEBIKA, Lorentzen & Wettre, Kista, Sweden) in accordance with TAPPI standard T411 om-05. [50] Five random measurements were done for each specimen and averaged. The apparent density was determined using Eq. 3 in accordance with TAPPI standard T220 sp-01. [51] The average coating thickness of each treatment

was obtained from the difference between the average thickness of the coated and uncoated samples (Eq. 4). The uncoated and coated samples were placed in the oven at 103 ± 2 °C for 24h, and thereafter, the average coating weight was calculated for each treatment using Eq. 5:

$$Density\ (g/cm^3) = \frac{Grammage\ (\frac{g}{m^2})}{Thickness\ (\mu m)} \quad (3)$$

$$Avg.Coating\ Thickness = Avg.thickness\ of\ coated\ samples - Avg.thickness\ of\ uncoated\ samples \quad (4)$$

$$Avg.Coating\ Weight\ (g/m^2) = \frac{Avg.\ dry\ weight\ of\ coated\ samples\ (g) - Avg.\ dry\ weight\ of\ uncoated\ samples\ (g)}{Sample\ length\ (m) \times Sample\ width\ (m)} \quad (5)$$

2.2.3.3. Mechanical characteristics of paperboards

The tensile strength of a material is expressed as the maximum amount of tensile stress it can take before failure or breakdown. An Instron testing machine (Model 33R4465, Bucks, United Kingdom) was used to evaluate the mechanical characteristics (tensile strength and elongation at break) of specimens in accordance with TAPPI standard T494 om-01. [52] Defect-free testing specimen strips with a width of 15 mm and a length of 150 mm were prepared. The load cell force, strain rate, and clamp distance were 5 KN, 25 ± 5 mm/min, and 100 mm, respectively.

2.2.3.4. Barrier characteristics of paperboards

Water vapor permeability (WVP) of the paperboards was determined at 25 °C and 75% RH in accordance with ASTM standard E96/E96M−10.[53] Circular specimens (70 mm in diameter) were mounted on the WVP cups filled with 43 g of dry $CaCl_2$ granules (particle size 1-2 mm) and sealed by a rubber O-ring and six screws. They were then placed in an acrylic desiccator cabinet (Nalgene® 5317-0070, Thermo Fisher Scientific, Massachusetts, United States) containing three petri glass dishes filled with saturated sodium chloride solution (relative humidity of 75%). The air was circulated inside the chamber by a fan at a rate of 0.15 m/s over the saturation solutions. The weight of the cups with an exposed area of 31.65 cm^2 was measured every 12 hours until two consecutive constant weights were obtained. The linear regression analysis of weight changes as a function of time was used to measure the WVTR, which is the slope of the linear portion of the curve. The WVP was calculated by Eq. 6:

$$WVP = \frac{WVTR \times L}{\Delta p}, \quad (6)$$

Where:
WVP: Water vapor permeability (g.mm/kPa.h.m^2),
WVTR: Water vapor transmission rate (g/m^2.h),
L: Average thickness (mm) of the specimens,
Δp: Partial water vapor pressure difference (KPa) across the two sides of the specimen.

The wettability of the paperboard surface was determined as the average of contact angles on two sides of a water drop in air on the sample surface using a KSV CAM 200 Optical Tensiometer (KSV Instruments Ltd., Helsinki, Finland) according to TAPPI standard $T558\ om-06$.[54] The program used to analyze the results was KSV CAM Optical Contact Angle and Pendant Drop Surface Tension Software, version 4.01. For this purpose, a micro-syringe was used to place

a ~4 µl of distilled water drop on the surface of coated or uncoated paperboard glued on the movable sample stage. Dynamic changes in the contact angles were tracked by recording them for 300 s.

Water absorptiveness (Cobb value) is defined as the mass of water absorbed by one side of 1 m^2 of paper placed under 1 cm of water during a given time. The 60 s Cobb test was performed in accordance with ISO standard 535:2014(E).[55]

Grease resistance of the paperboard samples was evaluated in accordance with the TAPPI standard $T507\ cm-99$.[56] The paperboard specimen with a size of 10×10 cm was placed above a 10 × 10 cm clean sheet, such that its coated side was in contact with a 7.5 × 7.5 cm dyed oil-saturated sheet of blotting paper prepared by applying a 1 mL of Sudan Ш stained olive oil. About 10 series of these arrangements were piled on top of each other so that each stack separated by 12 × 12 cm aluminum foil sheets, and a 720 g square stainless-steel plate (12 × 12 cm) was placed on the top of the pile. The assemblies were immediately put in an oven for 4 h at 60 ± 3 °C. Trezza and vergano point-counting method[57] with five replicates was used to evaluate the oil-stained area on the originally clean blotters with the counting repeated three times for each sample to ensure the reliability of the point values.

2.2.3.5. Morphological characteristics of paperboards

The surface morphology of the uncoated and coated paperboards was evaluated by a Hitachi S–4800 field emission scanning electron microscope (FE-SEM). Before imaging, sputtering a ~4 nm layer of Au/Pd onto the specimens was done to improve the image quality.

2.2.4. Statistical Analysis

All statistical analyses were done through the analysis of variance (ANOVA) at least in triplicate ($n \geq 3$) using IBM SPSS Statistics (Version 21, IBM Corporation, New York, United States). The significant differences of data were evaluated by One-way ANOVA and Duncan's post-hoc tests at the accuracy of 95%. All results were reported as means ± standard deviations.

3. Results and discussion

3.1. Solid content and viscosity of coatings

The solid content of coating slurry and frame applicator gap depth are two major factors affecting the thickness of the coating layer and the structural uniformity. [58] Since the applicator gap depth was a constant factor in this study, any changes in the solid content of the coatings can result in altered coating weight. As shown in Table 1, there was no significant difference in the solid content of the samples even when PE-wax was added into the coating formulation. This may show the proper distribution of PE-wax particles inside the protein coating slurry.

The rheological characteristics of the coatings have been summarized in Table 1. The results showed that SPI coating slurry had the greatest viscosity which diminished significantly with increasing the PE-wax share in the coating formulation, after which the consistency index dropped. This may be due to the reduction of the denatured protein content in the coating formulation together with increase of the PE-wax share, which cannot participate in the chemical reaction with protein molecules.

The study of flow behavior index of the coating slurries indicated that all coatings showed pseudoplastic flow behavior (n<1) and the addition of PE-wax had no significant effect on the flow behavior. In addition, the regression analysis of shear stress changes as a function of shear rate confirmed that Power-Law model was successfully fitted on the data of each treatment with a high R-squared score (>0.97).

Table 1. Rheological characteristics of the coatings.

Treatment	PE-wax concentration (%)	Measured Solid Content (%)	Viscosity (mPa.s)	*K*	*n*	R^2
SPI	0	13.6 ± 0.3^{a}	52 ± 5^{a}	0.079 ± 0.001^{a}	0.58 ± 0.01^{a}	0.97 ± 0.03^{e}
RSA	10	13.7 ± 0.1^{a}	37 ± 1^{b}	0.050 ± 0.010^{b}	0.61 ± 0.02^{a}	0.98 ± 0.03^{a}
RSB	30	13.5 ± 0.4^{a}	34 ± 1^{bc}	0.046 ± 0.007^{b}	0.61 ± 0.01^{a}	0.97 ± 0.01^{a}
RSC	50	13.6 ± 0.6^{a}	30 ± 3^{c}	0.038 ± 0.006^{b}	0.58 ± 0.02^{a}	0.98 ± 0.01^{a}
RSD	70	13.7 ± 0.5^{a}	22 ± 4^{d}	0.025 ± 0.005^{c}	0.61 ± 0.01^{a}	0.99 ± 0.01^{a}

3.2. Physical characteristics

Apparent density, which is obtained through dividing the grammage by thickness, is considered as one of the quality indices of paper-based packaging materials. [59] Table 2 reports the thickness and apparent density of the paperboard samples. The physical characteristics of the paperboards with SPI/PE-wax coating were significantly different from those of the uncoated paperboards as well as those coated with SPI only (p-value ≤ 0.05). The addition of the PE-wax enhanced the paperboard thickness and decreased its density significantly. By increasing the PE-wax share, the feasibility of contact between the protein and wax molecules improved, resulting in diminished aggregation forces of the protein structure thereby causing a bulky coating matrix and an intense increase in the thickness of coating layer. A similar behavior has been reported regarding the incorporation of waxes into some polymeric solutions. [60–62] Increasing PE-wax content to 70% of the protein induced a greater increase in the thickness (1.5 times higher than that of 50% PE-wax) indicating the loss of homogeneity in the coating layer.

Since there was no significant difference in the solid content of coating slurries, and the same applicator gap depth was also used for all treatments, the coating weight of the coated paperboards represented no significant change by adding PE-wax into the coating formulations.

3.3. Mechanical characteristics

A tensile strength (TS) evaluation was performed on packaging materials to determine the maximum load a material can withstand before it ruptures or tears. Different factors such as fiber strength, length, surface area, and interfacial bonding strength affect the tensile strength of paper materials. [63] As reported in Table 2, uncoated paperboards had a significantly greater tensile strength than coated paperboards did, while the extensibility of the paperboards increased significantly in response to the coating. These results indicate that the extensibility of coated paperboards is greater than that of uncoated ones. The penetration of the coating solution into the fiber network leading to fiber swelling and interfering with fiber-to-fiber bonding may explain the

decrease in TS. [63–65] While the reduction of TS value varied from 5 to 16% with the increase of the PE-wax content, no significant differences were recognized in the TS values of SPI-coated paperboards and coated paperboards containing up to 30% PE-wax. The decline of the protein content in the coating formulation and thus the increase in the solvent contribution led to increased penetration of the coating materials into the fiber network and greater reduction in TS especially in the samples where the PE-wax content was more than 50% of the SPI content.

Table 2. Physical and mechanical characteristics of the paperboard samples.

Treatment	PE-wax concentration (%)	Paperboard thickness (µm)	Coating thickness (µm)	Coating Weight (g/m^2)	Paperboard density (g/cm^3)	TS (MPa)	*E* (%)
Uncoated	-	118.3 ± 2.5^{f}	-	-	2.09 ± 0.02^{a}	80.3 ± 1.2^{a}	5.7 ± 0.2^{f}
SPI	0	134.3 ± 1.8^{e}	16 ± 1.2^{e}	7 ± 0.2^{a}	1.86 ± 0.02^{b}	77.2 ± 1.5^{b}	6.1 ± 0.1^{e}
RSA	10	137.3 ± 1.6^{d}	19 ± 0.6^{d}	7 ± 0.3^{a}	1.83 ± 0.01^{c}	76.4 ± 2.0^{b}	6.4 ± 0.1^{d}
RSB	30	140.3 ± 1.4^{c}	22 ± 0.6^{c}	7 ± 0.2^{a}	1.80 ± 0.01^{d}	74.2 ± 1.0^{bc}	6.7 ± 0.1^{c}
RSC	50	143.0 ± 1.8^{b}	24.7 ± 1.0^{b}	7 ± 0.1^{a}	1.77 ± 0.01^{e}	72.7 ± 1.6^{c}	6.9 ± 0.1^{b}
RSD	70	147.7 ± 2.1^{a}	29.4 ± 1.5^{a}	7 ± 0.2^{a}	1.72 ± 0.02^{f}	67.8 ± 2.4^{d}	7.2 ± 0.1^{a}

3.4. Barrier characteristics

A major requirement food packaging materials have to fulfil is the ability to minimize the moisture transfer from the environment to the packaged food. Thus, they should have the minimum WVP possible. [66,67] As expected, uncoated paperboards had the highest WVP due to the porous structure of cellulose fibers (Table 3). The SPI coating reduced the WVP of the paperboards by 36%, representing its ability to cover the cavities between the fibers on the paperboard surface thus preventing the transmission of water vapor molecules. The research performed by Rhim et al. [63] found a 14% decrease in WVP of paperboard in response to the coating (thickness: 236.7 ± 6.0 µm; coating thickness: 27.5 µm), which is lower compared to the results of the current study. SPI-coated paperboards had a higher WVP than the paperboards coated with SPI containing PE-wax, suggesting that the hydrophilic nature of soy protein facilitates greater passage of water vapor. [62] On the other hand, Hagenmaier and Shaw [68] expressed that since emulsified PE-wax was not able to form a uniform film on the surface, use of the coating for fruit protection against weight loss was not as efficient as using PE films, where the addition of only 10% of PE-wax to SPI coating solution resulted in higher water vapor resistance with a reduction of 44% compared to the uncoated samples. SPI coating containing 50% of PE-wax had the best WVP reduction (by 88%), demonstrating that the hydrophobic nature of the PE-wax substantially reduced the hydrophilicity of the SPI coating layer. Chao et al [36] and li et al. [69] reported a similar behavior regarding SPI and beeswax. In another study by Kim et al. [34] with SPI and Sorghum wax, a 60% reduction of WVP was achieved by adding 20% Sorghum wax to the protein solution.

A different behavior was observed for the paperboards with a coating containing 70% PE-wax. It showed lower water vapor resistance than samples with 50% PE-wax in the coating. Adding solid polar compounds over a certain content may cause further disturbances in the coating

matrix, resulting in loss of homogeneity and formation of numerous small cavities at the protein-wax interface, which allows easier transfer of vapor molecules within the coating layer. [70,71]

Table 3. Barrier characteristics of the paperboard samples

Treatment	PE-wax concentration (%)	WVP (g.mm/h.KPa.m^2)	Initial WCA (deg)	WCA decreasing rate (deg/s)	COBB (g water/m^2)	Area stained (%)
Uncoated	-	3.74 ± 0.05^{a}	80.7 ± 0.2^{d}	0.06 ± 0.01	30.9 ± 1.4^{d}	39.7 ± 6.3^{a}
SPI	0	2.39 ± 0.05^{b}	66.7 ± 1.0^{f}	0.11 ± 0.02	74.4 ± 1.6^{a}	0^{c}
RSA	10	2.08 ± 0.01^{c}	78.6 ± 1.2^{e}	0.08 ± 0.01	62.2 ± 2.0^{b}	0^{c}
RSB	30	1.03 ± 0.01^{d}	95.3 ± 0.2^{c}	0.07 ± 0.01	40.4 ± 1.3^{c}	0^{c}
RSC	50	0.45 ± 0.02^{f}	114.0 ± 0.7^{b}	0.05 ± 0.01	23.5 ± 2.2^{e}	0^{c}
RSD	70	0.83 ± 0.05^{e}	121.5 ± 2.1^{a}	0.04 ± 0.01	10.8 ± 1.7^{f}	3.7 ± 1.8^{b}

Contact angle measurement is a prevalent technique for determining the surface or material wettability. Fig. 1 a_1-a_6 displays the geometrically determined contact angles of the uncoated and coated paperboards, which were calculated by applying a tangent line from the contact point along with the gas/liquid interface on an enlarged photograph. The results of the contact angle measurements are summarized in Table 3. Due to the hydrophilic nature of cellulose fibers, the uncoated paperboards had a contact angle of 80.7 ± 0.2°. SPI coating considerably reduced the contact angle of water, indicating that the paperboard surface became more hydrophilic. Furthermore, SPI-coated samples had the greatest WCA descending rate. Since SPI coating covered the pores in the fiber network, roughening the surface, with a layer of hydrophilic biopolymer, the paperboard surfaces became smoother, as well as more homogeneous and hydrophilic, thereby increasing the surface tendency to absorb water. [63] The addition of the PE-wax to the coating significantly increased the WCA on the paperboard surface. In particular, the samples with coatings containing a minimum of 30% PE-wax showed WCAs higher than 90°. In addition, when the PE-wax content increased, the WCA decreasing rate of the coated samples was strikingly reduced. These results reflect the change in the surface nature of the coated paperboards from the hydrophilic to relatively hydrophobic. The linear regression analysis of dynamic change of WCAs proposed that a linear model for each sample successfully fitted to the data with a great R-squared score (Fig. 1b).

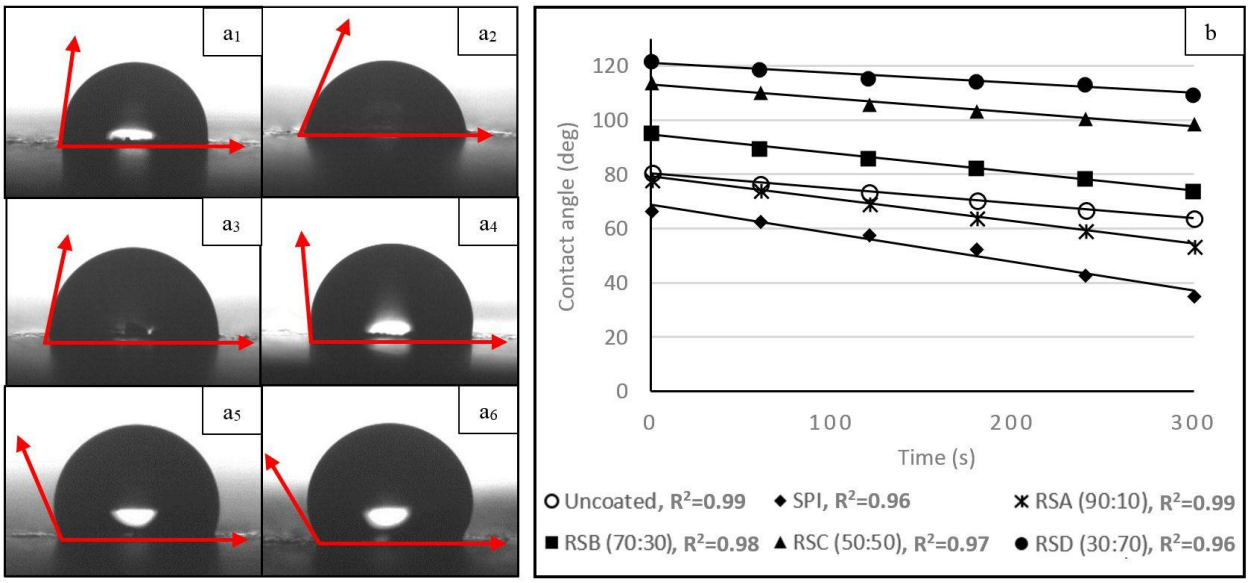

Fig 1. Initial contact angle of uncoated (a_1), SPI-coated (a_2) and coated paperboards containing 10 (a_3), 30 (a_4), 50 (a_5) and 70% (a_6) PE-wax; and dynamic changes of contact angle (b) of the uncoated and coated paperboards recorded for 300s.

The water absorptiveness test (COBB test) is an important means of testing the water resistance of materials used in food packaging and printing industries. Indeed, it represents the amount of water that can be absorbed by the packaging material in direct contact with the food. [72] The results of COBB tests are presented in Table 3. The COBB value of uncoated paperboard was 30.90 g water/m^2. The COBB value increased dramatically, by 2.4 times, through coating with SPI. This confirms that the coatings based on the hydrophilic biopolymers (e.g. SPI) accelerate the water absorption, resulting in a considerable enhancement of the total capacity of the material to absorb water. This result is consistent with the findings of previous research by Rhim et al., [63] in which the alginate-coated paperboard had greater water absorption than SPI-coated uncoated paperboards. They concluded that the coating compounds absorbed far more water and significantly swelled compared to the paperboard samples.

Increasing the PE-wax share in the coating formulation considerably reduced the COBB value of the coated paperboards, demonstrating enhanced resistance to water absorption in the coated samples affected by the hydrophobic nature of PE-wax. Specifically, the paperboards coated with coatings containing 50 and 70% PE-wax showed 24 and 65% reductions in the COBB value compared to the uncoated paperboard, respectively.

One of the main requirements for paper-based food packaging materials especially for fatty foods packaging (e.g. foodservice packaging bags, food wrapping, etc.) is high resistance against staining by fat/oil of the food products. [17] The uncoated paperboards were highly impermeable to oil penetration, as outlined in Table 3. No oil migration was detectable when the paperboards were coated with SPI, suggesting the high grease resistance of the SPI coating due to its substantial hydrophilicity. The same behavior has been reported for Zein and whey protein coatings. [57,64,73] The findings of a research carried out by Park et al. [74] regarding the effect of coating weight and plasticizer concentration on the grease resistance of paper samples revealed that complete grease barrier characteristics were obtained for the first 2 hours in all SPI-coated papers. However, the percentage of the stained area increased over time due to the defects in the coating layer. In

addition, the grease migration diminished with increasing the plasticizer share up to a specified content, where elevation of the plasticizer content over the critical value weakened the grease barrier characteristic of the coated samples.

The addition of PE-wax up to 50% of the SPI content to the coating had no effect on the grease resistance of the coated paperboards and there was no oil migration to the specimen surfaces. It seemed that 50% is the critical content of PE-wax in the coating formulation, as oil stains were observed in the originally clean blotters which were under the paperboards coated with SPI containing 70% PE-wax. Reducing the protein content in the coating formulation led to defects in the coating layer such as very small voids, which may be a possible reason for the oil penetration through the coating layer.

3.5. Morphological characteristics

The morphological characteristics of the uncoated and coated paperboards were evaluated using a field emission scanning electron microscope (FE-SEM) (Fig. 2). The FE-SEM images indicated that the SPI coating covered and filled the porous fibrous structure and led to a very smooth surface on the SPI-coated paperboard. Han and Krochta, [75] also reported that coating of paper with whey protein isolate(WPI) resulted in a more level and flat surface compared to the uncoated one. At the concentrations of less than 50% PE-wax, the particles covered the surface of the coated paperboards uniformly. This can explain the reduced wettability of the coated paperboards containing PE-wax compared to the SPI-coated one. Increasing the PE-wax content in the coating formulation to 70% of SPI resulted in a loss of homogeneity and appearance of very small voids on the surface of the coating, as displayed in Fig. 2 a'_6. This explains why its WVP value increased significantly compared to the case where the coating contained 50% PE-wax.

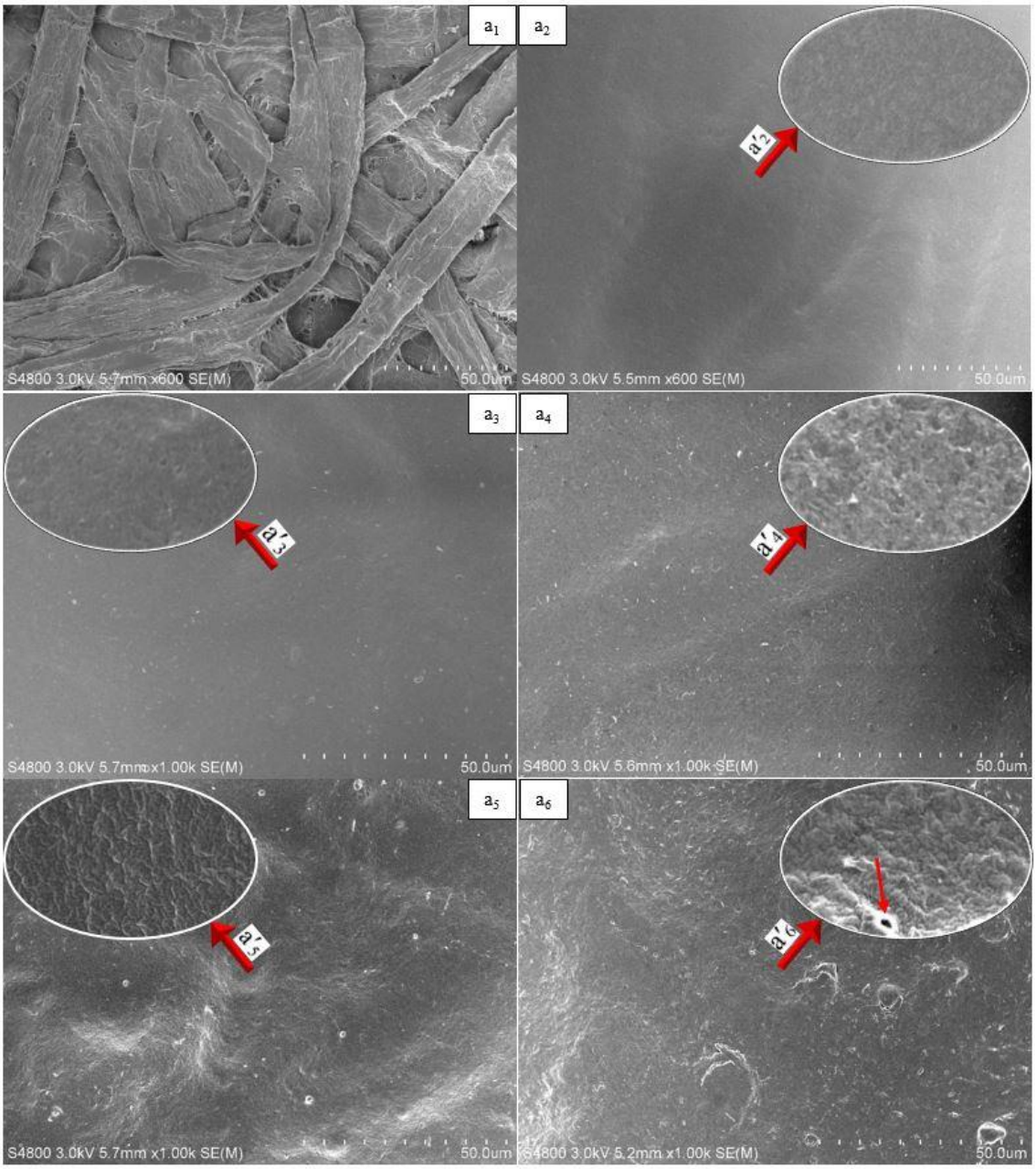

Fig. 2. FE-SEM images of the uncoated (a_1), SPI-coated (a_2) and coated paperboards containing 10 (a_3&a'_3), 30 (a_4&a'_4), 50 (a_5&a'_5) and 70% (a_6&a'_6) PE-wax. Magnification values are 1.00k and 3.0k for a_1-a_6 and a'_2-a'_6, respectively.

4. Conclusion

A novel dispersion coating based on soy protein solution and the polyethylene-wax emulsion was developed. The applied coatings remarkably affected the physical, mechanical, and barrier characteristics of paperboards. The density of SPI coatings was reduced by incorporating PE-wax. While elevating the PE-wax content in the coating weakened the tensile strength of the coated samples, their extensibility increased. In addition, WVP decreased and water barrier

characteristics improved upon adding PE-wax into the SPI coating formulation, while no oil migration was observed in the coated papers when the PE-wax content was 50% of the SPI content. These results indicate that a new food packaging material with improved characteristics was achieved by applying the dispersion barrier coating containing 50% PE-wax.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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