Research Article

Effects of carbohydrate/protein ratio on the microstructure and the barrier and sorption properties of wheat starch–whey protein blend edible films

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Abstract

BACKGROUND: Starch and whey protein isolate and their mixtures were used for making edible films. Moisture sorption isotherms, water vapour permeability, sorption of aroma compounds, microstructure, water contact angle and surface properties were investigated.

RESULTS: With increasing protein content, the microstructure changes became more homogeneous. The water vapour permeability increases with both the humidity gradient and the starch content. For all films, the hygroscopicity increases with starch content. Surface properties change according to the starch/whey protein ratio and are mainly related to the polar component of the surface tension. Films composed of 80% starch and 20% whey proteins have more hydrophobic surfaces than the other films due to specific interactions.

CONCLUSIONS: The effect of carbohydrate/protein ratio significantly influences the microstructure, the surface wettability and the barrier properties of wheat starch–whey protein blend films.
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Keywords: edible films; wheat starch; whey protein; interfacial transfers; permeability; aroma and water sorption

INTRODUCTION

Interest in edible films and coatings is still increasing in order to satisfy the rising demand for fresh and minimally processed or non-processed products. For 20 years, a great number of papers dealing with edible and bio-based films for packaging application has been published, displaying huge possibilities of applications for preservation of food and for reducing the use of conventional plastic materials.[1−3] Bio-based packaging materials could offer functional advantages, such as the modification of vegetable tissue metabolism that permits to control the respiration rate. Moreover, bio-based packaging materials can be used as carriers of antimicrobial and antifungal substances, antioxidants, and vitamins to be released to the specific food matrix according to deliberately induced doses.[4] In addition, they protect food products against the loss of valuable components, due to oxidation or to hydrolysis, by controlling permeation of gases and vapours. Coatings and films can contribute to the reduction of food and plastic packaging wastes by increasing the shelf-life of products.[5]

Cellulose, gums, starches and some proteins are the basic materials used for the production of edible films and coatings.[1,6] Films prepared from starch are tasteless and odourless, non-toxic and biodegradable, as well as colourless, or in the case of rice starch, films are more opaque. Therefore, starch materials can be applied to most food products as coatings or wrapping. The main part of the wheat starch production are used for food as

stabilisers, thickeners and gelling, as dietary substances, fat replacers and as substances that modify the structure of the product, but it is also used for making starch-based edible films or coatings.[7−9] Whey protein (WP) was considered as a by-product of the cheese manufacture although it became a key ingredient of the food industry. Whey protein can form transparent coatings and films whose barrier properties to gases and flavours are of key interest but need some additive for mechanical improvement.[10−12]

Compared to other protein films (wheat gluten, soy protein, zein and casein films), whey protein isolate films have poor moisture barrier properties.[13] Janjarasskul and colleagues[14] studied barrier and tensile properties of whey protein isolate–based films obtained from solution-casting and from compressed extruded sheets. Oxygen permeability is 10 times higher for extruded films than for casted films. Basiak et al.[15] also measured wettability

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properties of starch–whey protein films in various ratios. The higher the ratio of protein, the higher is the water vapour permeability. Values of swelling index and water solubility are higher for pure whey protein films than for films made from starch. Water content increases according to the protein content for a given relative humidity.[15] Guckian *et al.*[16] concluded that films prepared from heated whey protein isolate (WPI) solution have much higher mechanical properties (elongation, tensile strength and Young's modulus) than unheated solutions. Strong hydrogen bonding and disulfide bonds are ruptured when proteins are heated. Thus protein denaturation induces more stretchable films. The degree of hydrolysis plays a very important role on the mechanical properties. Sothornvit and Krochta[17] investigated the effect of whey protein hydrolysis and plasticiser content. They showed that the hydrolysed WPI required less glycerol to achieve the same mechanical properties than unhydrolysed WPI. This was attributed to the reduced chain length of hydrolysed proteins which had higher flexibility. Ozdemir and Floros[18] observed that addition of preservatives like potassium sorbate in WPI films allows inhibition of both enzymes and microorganisms and can also improve the optical properties.

Films should also have appropriate mechanical and surface properties in order to satisfy an adequate adherence onto the food surface.[19,20] Parameters such as plasticity and elasticity, hardness, roughness, wettability, lipo-/hydrophilicity and/or hydro-/lipophobicity, solid–liquid properties, as well as surface free energy, surface tension, and contact angle determine the film–food compatibility and performing application.[21] The most basic measure of wettability for a particular liquid–solid combination is the contact angle θ. The lower the contact angle, the more extensively the liquid spreads on the solid. In applications of wetting, the aim is generally to engineer a desirable value or range of values for the contact angle able to favour adhesiveness, cohesiveness and spreading of the coating on a solid surface. The value of contact angle gives overall information about the surface hydrophobicity whereas the droplet volume and angle kinetics refer to spreading and wetting.[22] Ferreira *et al.*[23] characterised chitosan–whey protein films. The water contact angle on the surface of this composite film at 25–50% protein slightly increased, compared with that of pure chitosan film, and then decreased for higher protein contents. All the blended films have a significantly different contact angle compared to pure starch films and pure whey protein films. The contact angle value measurement is also related to roughness of surface, its porosity or 'surface texture'. Thus, the angle measured on the film surface in contact with the support for the casting is mainly influenced by the smoothness/roughness of the support surface. On the contrary, the angle measured on the surface exposed to air during film drying is related to the natural self-organisation of the biopolymer molecules exposed to air when film forming solution was dried.[24] Białopiotrowicz and Janczuk[25] also displayed that the richer in protein content the surface is, the more hydrophobic is the surface, but this depends on the nature of the protein, its composition in hydrophobic amino acids and its solubility in the solvent used for preparing the film-forming solution.

Edible films can be used as carriers of flavour compounds, either for flavouring food surface by coatings, or for providing essential oils having antimicrobial or antioxidant properties.[26] More and more edible films have been developed as active packaging by encapsulation/entrapment of active aroma compounds or plant extracts (essential oils). Whey protein as well as starch has been envisaged for flavour encapsulation. They both allow the retention of organic volatile compounds and protect them against oxidation or temperature.[27–29] Reducing the loss of organoleptic characteristics of food to levels below human sensory detection can be obtained by appropriate use of biodegradable or edible polymers with very low absorption or permeability to aroma compounds.[30] Edible films having high barrier properties for aroma compounds (very low affinity or sorption) could be sought.

Both pure biopolymers often could not form films with satisfactory properties.[26] Interactions between starch and whey proteins are anticipated to greatly affect the rheological properties of food systems, markedly changing the gel network structure and the rheological profile.[31] Combination of two biomaterials (or more) together eliminates each drawback and facilitates obtaining the targeted properties. Polymer combinations can occur as various structures such as emulsions, dispersions or laminates.[14,16,32–36]

The objective of this work was to study the functional properties of edible films based on wheat starch and WPI. The ratio between starch and whey protein was focused and then microstructure, surface and transport (sorption and permeability) properties were assessed. Four ethyl esters (model aroma compounds) having a wide range of hydrophobicity have been used to study the sorption behaviours of both polar and apolar volatile compounds.
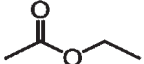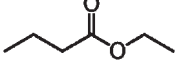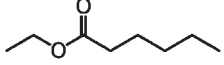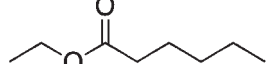
MATERIALS AND METHODS
Materials
Wheat starch was supplied by Hortimex (Konin, Poland). The whey protein isolate (WPI, ~90% protein) BiPRO, was obtained from Davisco Foods International Inc. (Le Sueur, MN, USA). Anhydrous glycerol (99.9% of purity) was purchased from Sigma–Aldrich (St Louis, MO, USA). Ten saturated salt solutions were used for fixing the adequate active relative humidity (RH) from ~3% to 93% (Prolabo, Fontenay-sous-Bois, France). Four ethyl esters (Aldrich Chemical Company, Saint-Quentin Fallavier, France) have been chosen as model of aroma compounds[36] and allowing studying a wide range of volatility and solubility. *n*-Hexane (98% purity; Sigma–Aldrich, Darmstadt, Germany) was used as solvent for the ethyl ester extraction from films after sorption. The physicochemical characteristics of the volatile compounds are given in Table 1. The log P_{part} is the mass partition coefficient of the aroma compound between water and octanol. It represents the polarity/hydrophobicity of the aroma compound. When log P_{part} is higher than 2, it is considered as hydrophobic. Then, ethyl acetate and ethyl butyrate can be considered as hydrophilic compounds, whereas ethyl hexanoate and ethyl octanoate have hydrophobic characters.

Preparation of starch/whey protein edible films
Film-forming aqueous solutions were prepared by mixing by hand and then casting wheat starch and whey protein isolate in the following proportions: 100–0%, 80–20%, 60–40%, 40–60%, 20–80% and 0–100%. Glycerol was used as a plasticiser at 50% w/w of biopolymer dry weight (i.e. 33% of total dry basis). Wheat starch film-forming solutions were prepared by dissolving 5 g of wheat starch powder in 100 mL distilled water. Whey protein film-forming solutions were also prepared by 100 mL dissolving 5 g of WPI in distilled water. The solutions were separately heated in a water bath under a 16 g stirring at 85 °C for 30 min to denature the whey protein and to obtain complete gelatinisation of starch. Then, film

Table 1. Physico-chemical characteristics of aroma compounds used in this study

Aroma compound formula	Chemical structure	Log P_{part} at 25 °C	Molecular weight (Da)	Vapour pressure at 25 °C (mmHg)	Solubility in water at 20 °C (g L^{-1}) *
Ethyl acetate $C_4H_8O_2$		0.71	88.11	111.7 ± 0.1	87.30
Ethyl butyrate $C_6H_{12}O_2$		1.77	116.16	13.9 ± 0.2	4.90
Ethyl hexanate $C_8H_{16}O_2$		2.83	144.21	1.7 ± 0.3	0.63
Ethyl octanoate $C_{10}H_{20}O_2$		3.90	172.26	0.2 ± 0.4	0.07

*From ChemSpider: experimental values or EPI predicted.

forming solutions were cooled down to 40 °C. The plasticiser was added. Thirty millilitres of each film-forming solution was poured onto a Petri plate to obtain a constant film thickness of about 80 µm. Films were dried at 25 °C and 30% relative humidity (RH) for 48 h. Dry films were peeled off and stored at 53 ± 1% RH and 25 ± 1 °C in desiccators containing saturated magnesium nitrate for 7 days prior to testing.

Moisture sorption isotherm

The sorption isotherms of films were determined at 25 °C. Samples of films were cut into small pieces (2×2 cm^2) and weighed to the nearest 0.0001 g into pre-weighed vials. Films were stored up to equilibrium in 10 desiccators, each containing a saturated salt solution which fixed the relative humidity (RH) at 25 °C. A wide range of RHs was selected: lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, magnesium nitrate, sodium nitrite, sodium chloride, ammonium sulfate and ammonium dihydrogenophosphate. Their respective RHs at 25 °C are 11%, 22%, 33%, 43%, 53%, 65%, 75%, 81% and 93%. Film samples were weighed periodically up to equilibrium was reached and checked up to 9 months. The equilibrium water content was determined by drying the films at 105 °C for 24 h. The amount of water absorbed is expressed as kilogram of water per kilogram of dry matter. Measurements were done in triplicate.

Water vapour permeability

Water vapour permeability (WVP) of films was measured gravimetrically according to Debeaufort et al.[37] who adapted the ASTM E96-80 standard method to edible films and coatings. Film thickness was measured with an electronic gauge (Metrison, Mościska, Poland). Precision of the measurement was 1 µm. The average value of five measurements of thickness per type of film was used in all the calculations of WVP. Film samples were placed between two rubber rings on the top of glass cells containing silica gel, sodium chloride or distilled water allowing obtaining internal relative humidities (RHs) of permeation cells at < 0.5%, 75%, and 100%. In addition, these permeation cells were placed in a climatic ventilated chamber (KBF 240; Binder, Tuttlingen, Germany) maintained at a RH of 30% and temperature of 25 °C. The water vapour permeability was calculated using the following equation:

$$WVP = \frac{\Delta m \times e}{A \times \Delta t \times \Delta p} \quad (1)$$

where $\Delta m / \Delta t$ is the weight of moisture loss per unit of time (g s^{-1}), A is the film area exposed to moisture transfer (8.04×10^{-4} m^2), e is the film thickness (m), and Δp is the water vapour pressure difference between two sides of the film (Pa). Measurements were performed at least three times for each RH differential tested.

Measurements of surface properties

Contact angle (θ) is the angle described as a relationship between the surface tension and one of three phases: liquid phase L, solid phase S, or vapour phase V:

$$\gamma_{LV} \times \cos \theta = \gamma_{SV} + \gamma_{SL} \quad (2)$$

where γ_{LV}, γ_{SV} and γ_{SL} are the surface tensions of the liquid–vapour, solid–vapour and solid–liquid, respectively.[38]

The method used to measure the contact angle was the sessile drop method: a droplet of a test liquid was placed on a horizontal film surface. Measurements were done using a DGD-DX goniometer equipped with the DIGIDROP image analysis software (GBX, Romans-sur-Isere, France) according to Karbowiak et al.[39] A droplet of a testing liquid (volume ~1.5 µL) was deposited on the film surface with a precision syringe. The contact angle was measured on both sides of the drop and averaged. The measurement was carried out over 120 s. The effect of evaporation was assessed on a piece of aluminium foil considered as an impermeable reference surface. Then the rate of evaporation was considered in the study of the kinetics of wetting and absorption. Measurements for all samples were done on both sides of the films.

The surface tension of the liquid tested (γ_L) was measured by the sessile drop method and the Laplace–Young approximation.[40] The estimation of the critical surface tension (γ_C) of the starch, protein isolate and starch–protein isolate films was obtained from the Zisman method.[41] The critical surface tension value of film surface was obtained from the extrapolation the linear regression of the cos θ of liquids according their surface tension. Extrapolation at cos $\theta = 1$ yields the value of the critical surface energy of the film surface.

The surface free energy (SFE) and its dispersive (γ_S^D) and polar (γ_S^P) components were calculated by the Owens-Wendt method.[42] Eqn

(3) and Eqn (4) show this method:

$$\gamma_S = \gamma_S^p + \gamma_S^D \qquad (3)$$

$$\gamma_L = (1 + \cos\theta) = 2\left(\sqrt{\gamma_S^p \gamma_L^p} + \sqrt{\gamma_S^D \gamma_L^D}\right) \qquad (4)$$

Using at least two liquids, knowing their surface tension and their dispersive (γ_L^D) and polar (γ_L^p) components, allows determination of the γ_S^D and γ_S^p components of the film surface tension.

Cyclopentanol, diiodomethane, ethylene glycol, glycol, methyl benzoate, n-octane, polyethylene glycol, tetradecane, water and 1-bromonaphtalene were selected as the liquids which the surface tension properties, dispersive and polar components are known.[43] Measurements were replicated at least 10 times.

Film microstructure

Film microstructure was observed using an environmental scanning electron microscope (ESEM XL30, Philips FAI, Hillsboro, USA). A 0.5×1.0 cm^2 film piece was fixed on the support using adhesive, at an angle of 90° to the surface which allowed observation of the cross-section of the film. All the films were cut with a new razor blade to prevent as much as possible any morphological damage. Films were focused up to ×150 000, and magnifications ranging from ×800 to ×8000 were selected, with an intensity of 8 kV and absolute pressure of 230 Pa (RH ∼ 30% at 5 °C). Samples were observed without any preparation or coating.

Aroma compound sorption

Ethyl acetate (99.5% purity), ethyl butyrate (99%), ethyl hexanoate (98%), ethyl octanoate (98%) have been selected to mimic fruit flavour compounds. In order to assess the aroma compound retention by the films or their affinity for the aroma compounds, films were exposed to atmospheres being saturated with the vapour of the aroma compounds. Pieces of dry film were placed in glass vials along with respected aroma compound. All vials were put in sealed jar containing pure aroma compounds. The jars containing vials of films and the aroma were kept for a minimum of 3 weeks at 25 °C. After equilibrium was reached, n-hexane was added in vials for extraction for 24 h at room temperature at a ratio of 500 mg of film in 4 mL solvent. The yield of extraction was previously set up in the lab and ranged between 95% and 97%.[44] The volatile flavour compounds were quantified by injection of the n-hexane extract into a gas chromatograph. The amount of aroma extracted from the films was calculated from an external calibration curve.

The chromatography analyses was done using a Shimadzu GC 2014 gas chromatograph (Shimadzu, Marne La Vallée, France), equipped with a flame ionisation detector (GC-FID) and 30 m length DB-Wax column (J&W, Les Ulis, France) with 0.53 mm i.d. and 1.0 μm film thickness and nitrogen as carrier gas (60 kPa). Hydrogen and air were used as ignition gases. The oven temperature program was set at 210 °C, isothermal. The injector and detector temperatures were at 240 °C, isotherm. For each sample minimum three repetitions were done.

Statistical analysis

Statistical analysis was performed with Statgraphics Plus, version 5.0 (Manugistics Corp., Rockville, MD, USA). The analysis of variance (ANOVA) and Fisher's LSD multiple comparisons were performed to detect significant differences in properties of films. The significance level used was 0.005.

RESULTS AND DISCUSSION

Film microstructure

Differences in the morphology of the pure starch, mixture and whey protein isolate films were investigated by environmental scanning electron microscopy (ESEM). On Fig. 1 are displayed the micrographs of films cross-sections.

Preparing film-forming solutions of starch, WPI and their blends caused changes in the films structure and network mainly due to starch gelatinisation and protein denaturation. Morphology of all samples is significantly different. Structure of starch films (100S-0WP) seems much more heterogenous, fibrillar and less dense than structure of whey protein films (0S-100WP). The framework of blend films seems more complex (80S-20WP, 60S-40WP, 40S-60WP, 20S-80WP). The higher the protein content, the denser and more homogeneous the films are. Sun et al.[45] showed that starch–whey protein films are not completely homogenous but homogeneity increases with the protein content. However, the difference in the colour of the images suggests a differentiation in density of packing the material in the films formed basing on the starch and whey proteins.[46] Films containing more starch are thicker. Elsewhere, the glossy parameter depends on two factors: ratio of ingredients and film's side. Starch films are dull whereas whey protein films are shiny. The more starch in the matrix the less glossy is the matrix. In all cases the air side is matter than the reverse side. Anyway, regardless of the starch–whey protein ratio all films are smooth (smoothing shows the higher homogeneity of the films), without any cracks, holes and damage. No open pores are observed onto the matrix surfaces (not shown in this paper). In previous work, Basiak et al.[15] investigated wheat starch-WPI films in five different ratio ingredients. These authors noticed similar effects of surface and cross-section matrices. According to Fabra et al.[32] and Jiménez et al.,[47] evaporation of solvent causes changes in component concentrations at the surface which thus affects the inner structure of the film surface. These also affect the barrier, mechanical and optical properties.

Moisture sorption isotherm

Moisture sorption isotherms results are given in Fig. 2. The sorption isotherm curves of starch films (100S-0WP), of WPI films (0S-100WP) and their mixture films showed a typical behaviour of water vapour sensitive hydrophilic biopolymers. Curves for all kinds of films did not show a significant difference of the shape. The isotherm displays typical shape for protein or polysaccharide edible film. Such non-linear water sorption isotherm is typical of hydrophilic biopolymers and is related to the swelling of the matrix at RH higher than 70%. Olivas and Barbosa-Canovas[48] obtained similar dependence in whey protein films containing glycerol (50% dry basis). Soazo et al.[12] reported that in WPI films, the moisture isotherm had sigmoidal shape that is typical of product rich in hydrophilic polymers. At $a_w > 0.58$, moisture content of films rapidly increased. Obtained values for films made from starch, whey proteins and their mixtures are weakly lower than observed by other researchers for the same film compositions. This could be attributed to different contents of glycerol concentration and higher content of whey protein isolate. Mali and Grossman,[49] and Al-Hassan and Norziah,[50] observed, in polysaccharides films, relatively weak slopes at low water activity but a significant increase at a_w above 0.75. Starch structure consists of crystalline and amorphous parts. The starch adsorption isotherms are attributable to hydrogen bonding of water molecules to the available hydroxyl groups of the substrate, i.e. those in the amorphous parts and
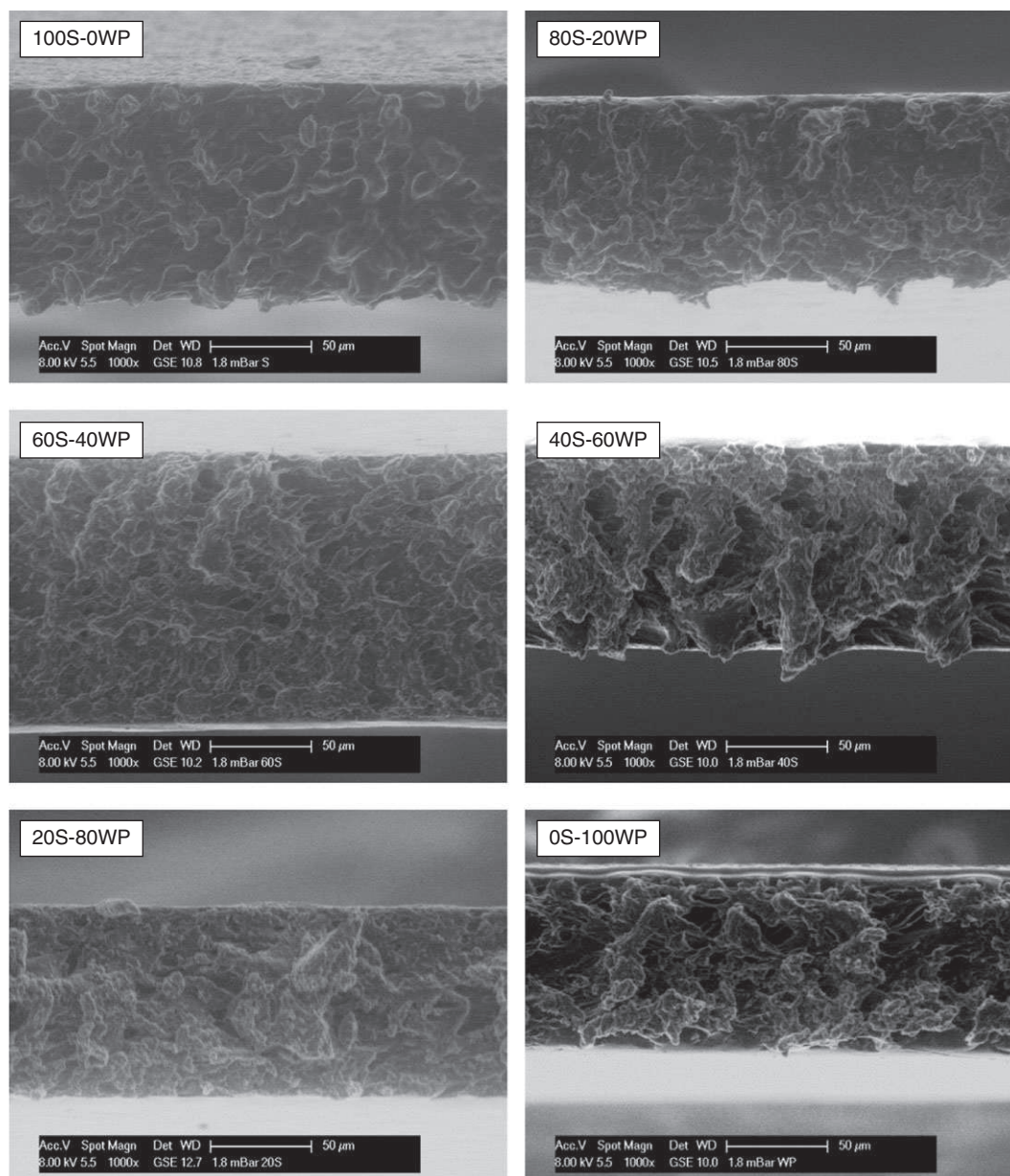
Figure 1. ESEM micrographs of film cross-section as a function of starch/whey protein ratio. Magnification, ×1000.

on the surfaces of the crystallites. The crystalline spheres typically exhibit resistance to solvent penetration, thus water affects the structure acting as a plasticiser of the amorphous surfaces. Plasticising effect is low at low activity of water and the ability of the amorphous parts is restricted. At higher water activity, the sorbed moisture causes a subsequent swelling of the biopolymer, the degree of crystallinity goes down and increasing availability of the polar groups to the water molecules is observable. This explains why moisture content of films increased with the starch content.[51]

Contact angles of water and other liquids

Surface wettability is assessed from the contact angle (θ) and the critical surface tension. These parameters are used to estimate the surface hydrophobicity of films. Table 2 gives the initial water contact angle of films (extrapolated at time = 0 s). The balance between adhesive and cohesive forces (between film area and drop of liquid) determines the contact angle. Thus, a water-wettable surface proves its hydrophilic property. The value of contact angle for water is the lowest for starch films (43°) and the highest for whey protein films (93°). This is in agreement with the higher moisture affinity of moisture for starch as displayed on the sorption isotherms. At the end of the experiment time (2 min), all films displayed a convex lens shape with a section less than the radius of curvature, because the contact angles are higher than 30°. Only whey protein films can be classified to the group of incomplete wetting; it forms a section greater than the radius of curvature, corresponding to an angle higher than 90° (Fig. 3). The higher the protein content, the higher is the contact angle. Starch has more hydrophilic groups than whey protein. Increasing the amount of whey protein in films leads to increasing the hydrophobicity. Basiak et al.[15] observed that the addition of whey protein isolate increased contact angles. This appeared because starch has a higher hydrophilic character than proteins. Usually,
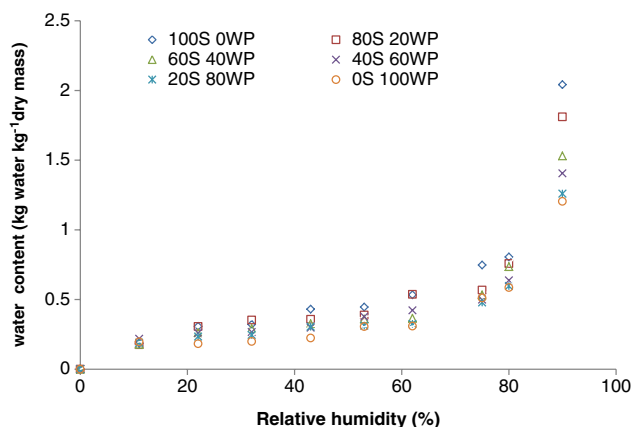
Figure 2. Moisture sorption isotherm of starch, starch–protein isolate and protein isolate films (kg water kg^{-1} dry mass).

another substance added to starch matrix such as oil, proteins or chitosan, caused a rise of the surface hydrophobicity. Results are in good agreement with literature: Heydari et al.,[52] Jiménez et al.,[53] and Wiącek[54] showed the effect of pure starch films on contact angles changes according the incorporation of hydrophobic or hydrophilic substances. The contact angle is directly related to the ratio of the both biopolymers. Shape of the curve (the angle versus the protein or starch content) is linear ($R^2 = 0.93$). In case of other liquids (cyclopentanol, diiodomethane, ethylene glycol, glycol, methyl benzoate, n-octane, polyethylene glycol, tetradecane, water and 1-bromonaphthalene), contact angles are very similar for all films. The contact angle at equilibrium for diiodomethane is 41–48°, for ethylene glycol it is 45–60°, for glycerol it is 59–68°, but for cyclopenthanol, methyl benzoate, n-octane, tetradecane, 1-bromonaphtalene and polyethylene glycol, the contact angle was not measurable as these liquids spread immediately. These results can be related to the polar and dispersive components of the surface tension, detailed in following section.

The contact angle measurements deals with the attraction between the water molecules and on polymer surface.[51] The lower contact angle is, the stronger the attraction value that could be noted.

Surface tension and critical surface tension
The critical surface tension and the surface tension (or surface free energy) with its polar and dispersive components, the cohesion coefficient and the spreading coefficient, were determined for

starch, whey protein and blend films (Table 2). The surface tension of films was estimated from the contact angle measurements of the seven liquids, and then an estimation of the dispersive and polar surface energy components were obtained. Measurements on both film surfaces (air and support sides) did not give significant differences. The pure starch films, pure protein isolate films and films containing of 80% of starch and 20% of whey protein had the lowest value (about 60 mN m^{-1}), the value of the other blend films (40S-60WP, 60S-40WP and 20S-80WP) are of same value and the highest (more than 70 mN m^{-1}). This means they are more polar than other films. A slight difference in surface free energy between pure films and mixtures (except 80S-20WP films) is a result of a different molecular organisation in the network. This behaviour is explained by the polar component of the surface free energy. Indeed, all films, whatever their composition have same dispersive component. The γ_S^D ranges from 35 to 39 and is not significantly different. On the contrary, the γ_S^P value of starch films, whey protein films and 80S-20WP films have significantly reduced value, indicating that they are less polar. Critical surface tension is the highest for the starch films and for the whey protein films. Blends of starch and whey protein at ratios 20:80, 40:60 and 80:20% are very similar slightly above 33 mN m^{-1}. Finally, the 60:40% starch–whey protein film displays the lowest critical surface tension value. This critical surface tension value is obtained from linear extrapolation from contact angle of various liquids. However, it accuracy has to be related to the angle measured at a meta-stable equilibrium (the kinetic of wetting not considered). This value cannot easily be compared to surface free energy value as the condition of angle measurement differs. However, these data seem to confirm that interactions between whey protein and starch induce a network with less hydrophilic groups at the film surface and then films having lower surface tension.

Dealing with the spreading coefficient (W_s) and the critical surface tension (γ_c), significant differences have been observed between all films (Fig. 4a and b). Pure starch films, pure WPI films and films in ratio 80S-20WP have the highest W_s and γ_c. Values for mixtures films in ratio 60S-40WP, 40S-60WP and 20S-80WP are the lowest. In case of pure starch films, pure protein isolate films and mixture films of 80% of starch and 20% of protein isolate, the non-polar energy is predominant on polar energy. It means pure starch films, pure protein isolate films and their mixtures have more ability to participate in dispersive interactions. Ghanbarzadeh et al.[33] obtained similar results for the polar part of zein films. Polar interactions were much stronger than apolar interactions. The disperse part was three times lower than polar part. They also admitted that critical surface tension values are

Table 2. Comparison of surface tension and the dispersive (γ_S^D) and polar (γ_S^P) components of starch, starch–protein isolate and protein isolate films, adhesion (W_A), cohesion (W_C) and spreading coefficient (W_S), contact angles (degrees) for water at 20 °C

Film sample	Contact angle (°)	Surface tension (mN m^{-1})	γ_S^D (mN m^{-1})	γ_S^P (mN m^{-1})	Critical surface tension, γ_c (mN m^{-1})	W_A (mJ m^{-2})	W_C (mJ m^{-2})	W_S (mJ m^{-2})
0S 100WP	93[c]	63.70[a]	38.45[a]	25.25[a]	35.95 ($R^2 = 0.94$)	113.74[a]	129.67[a]	−15.93[a]
20S 80WP	89[c]	71.58[b]	39.11[a]	32.47[b]	33.01 ($R^2 = 0.83$)	133.98[b]	139.79[b]	−5.81[b]
40S 60WP	86[c]	70.21[b]	37.99[a]	32.22[b]	33.85 ($R^2 = 0.88$)	131.66[b]	138.63[b]	−6.97[b]
60S 40WP	65[b]	73.28[b]	37.99[a]	35.29[b]	31.98 ($R^2 = 0.82$)	139.22[b]	142.41[b]	−3.19[b]
80S 20WP	61[b]	60.88[a]	38.01[a]	22.87[a]	33.64 ($R^2 = 0.82$)	106.12[a]	125.86[a]	−19.74[a]
100S 0WP	43[a]	60.28[a]	35.40[a]	24.88[a]	34.31 ($R^2 = 0.88$)	108.08[a]	126.84[a]	−18.76[a]

Measurements were done on the surface exposed to air during film drying.
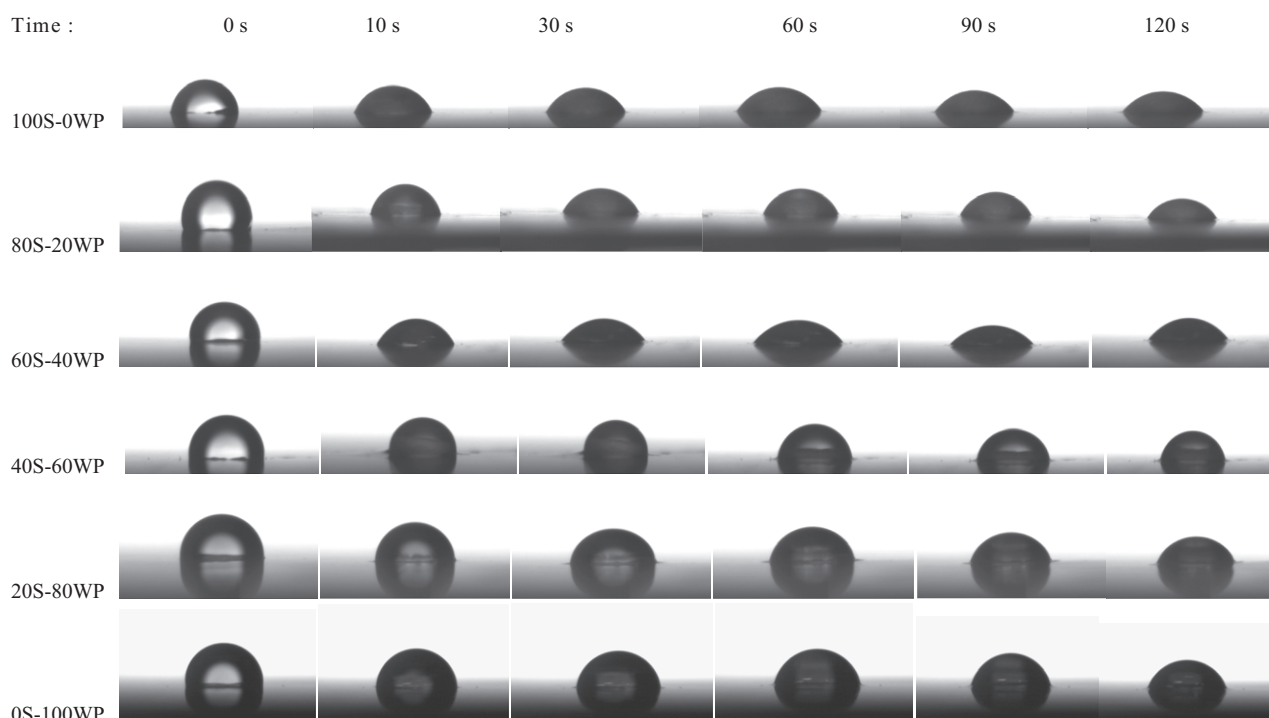Values having the same superscript in a column are not significantly different at a P value = 0.05

Figure 3. Behaviour of water droplets on film surfaces as a function of time.
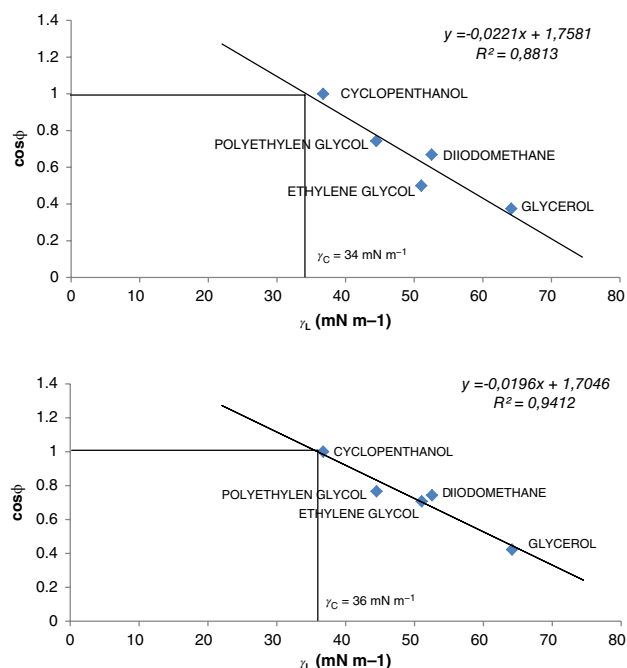

Figure 4. Zisman plots of (a) 100S–0WP and (b) 0S–100WP films determined with five different liquids for the determination of the critical surface tension, γ_c.

mostly lower than the surface tension values of the same tested surfaces.

Interactions between WPI and polysaccharides depend on the colloidal systems and then affect final properties of systems.[55,56] If the interactions in solution at pH 7 between the whey protein molecules with those of the starch were hydrophobic and not electrostatic in origin (as charge is a non-charged polymer), the orientation of the hydrophobic groups of the adsorbed protein molecules might have prevented their interaction with the polysaccharide of the continuous phase.[56,57] Potato starch-WPI complexes in several ratios (from 1: 0.5 to 1: 5 starch–WPI) were studied by Zaleska et al.[58] They displayed the composition of the product was dependent on the composition of solutions. The lower the starch content of the solution, the slower is the rate. Between polysaccharides and proteins exists numerous interactions. These authors also stated that water might take an active part in the construction of the network structure and then affects the final surface properties of films after cast solution have been dried.

Work of adhesion (W_A) and work of cohesion (W_C) fold on wettability (work of spreading W_S). Those parameters are opposite because the first one represents contraction, the second one the spreading of the liquid. Results for starch films, whey protein films and blend films are given in Table 2. As in case of other surface parameters, spreading coefficient (W_S) and work of cohesion (W_C) behave differently for the pure starch films, pure whey protein isolate films and for the 80S-20WP films.

The higher the difference between those two parameters, the lower is the spreading coefficient. Work of spreading is an important process for coating applications to ensure the continuity of the layer and then its barrier efficiency. Liquids deposited on these films have a tendency to spread very easily. Guettler et al.[3] studied soy materials and they obtained very similar values for work of adhesion: 104.3 mJ m^{-2} for soy protein isolate and 120.2 mJ m^{-2} for heated soy protein isolate. All protein materials displayed a hydrophilic character and have relatively similar dispersive surface tension characteristic which influences on parameters as adhesion work. The work of cohesion obtained was insignificantly lower: 88.2 (mJ m^{-2}) for soy protein isolate and 106.4 (mJ m^{-2}) for heat-treated soy protein isolate. Values obtained by Guettler et al.[3]

Table 3. Water vapour permeability (1×10^{-10} g m^{-1} s^{-1} Pa^{-1}) of films at 25 °C at three relative humidity differentials

Film sample	33–0% RH	75–30% RH	100–30% RH
0S 100WP	3.94 ± 0.61^a	$6.11 \pm 0.21^{d,e}$	$7.45 \pm 0.91^{g,h,i}$
20S 80WP	$3.97 \pm 0.08^{a,b}$	$6.15 \pm 0.39^{d,e,f}$	$7.11 \pm 0.75^{e,f,g,h}$
40S 60WP	$4.27 \pm 0.34^{a,b,c}$	$6.69 \pm 0.93^{e,f,g,h}$	$7.08 \pm 0.21^{e,f,g,h}$
60S 40WP	$4.86 \pm 0.29^{a,b,c}$	$6.17 \pm 0.70^{d,e,f}$	$6.58 \pm 0.68^{e,f,g}$
80S 20WP	$4.99 \pm 0.14^{b,c}$	$6.37 \pm 1.03^{e,f}$	$7.16 \pm 0.54^{f,g,h,i}$
100S 0WP	$5.24 \pm 0.26^{c,d}$	$7.70 \pm 0.85^{h,i}$	7.87 ± 0.65^i

Value having the same letter are not significantly different at a P value $= 0.05$

Figure 5. Relationship between log P_{part} and concentration of aroma sorbed by starch–WPI films.

Water vapour permeability

WVP is a measure of the amount of moisture passing through unit area of material per unit of time. For hydrophobic polymer films such as polyethylene or polypropylene, the WVP is proportionally constant whatever the water vapour pressure gradient applied across the films. Natural biopolymers used for making edible films are often hydrophilic. They contain polar groups which interact with permeating water molecules inducing plasticisation during permeation. Indeed, water sorption occurring during permeation process increases the polymer free volume allowing the polymeric chain segments to raise their mobility due to swelling. Higher mobility leads to higher WVP.[58,59]

WVP of films made from starch, WPI and their blends are given in Table 3. The WVP depends on relative humidity gradient as expected (RH). Indeed, the higher the gradient, the higher is the WVP. However, using different gradients allowed obtaining different average moisture contents in films at the stationary state of permeation, and then permitting to discriminate permeation behaviours according the film composition and plasticisation. As expected, the WVP obtained for the 33–0% RH differential were the lowest, for 75–30% values were higher and the highest were for the ones stored in 100–30% (RH). Regardless of RH, WVP values are always of the same dependency according the starch/protein ratio. When starch content increases, the WVP increases too. As WVP is the result of both sorption and diffusivity of moisture in solid matter, probable is that starch either increases the affinity of the film for water or induces a local viscosity decreases and then increases of the diffusivity. Sorption isotherms confirm that starch favours moisture absorption compared to whey protein which contributes to WVP increases with the starch content. So the increase of WVP observed for starch film is also attributed to the increases of moisture affinity. In that way, it is also suggested that less swelling occurs in the presence of lower content of starch.

The WVP could be related to the polar component of the surface tension, and then is directly related to the film surface polarity and work of spreading. At 30–75% RH differential and then higher, water content is high enough (according the moisture sorption isotherm) to induce water plasticisation significantly.

Aroma compound sorption

Vapour sorption coefficients of ethyl acetate, ethyl butyrate, ethyl hexanoate and ethyl octanoate in films are presented in Table 4. The sorption coefficients were determined at equilibrium (after
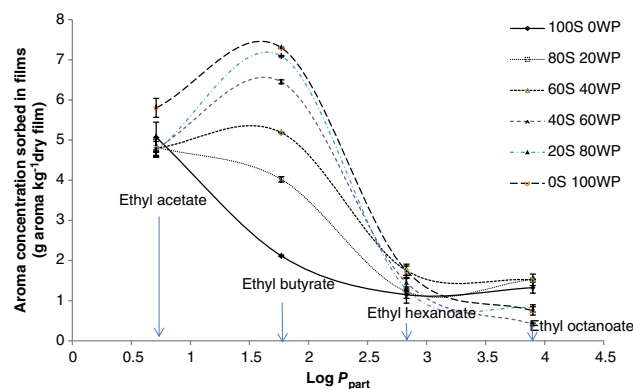
21 days of storage). Ethyl acetate sorption seems not to depend on the starch content, and is slightly higher in whey protein film. Ethyl acetate is a polar substance in which log P_{part} is the lowest (0.71) among aroma compounds studied (Fig. 5). This may explain its peculiar behaviour that seems not to be related to film composition. As it is highly soluble in glycerol, it is probable that sorption of ethyl acetate is dominated by its solubility in the glycerol. The ethyl butyrate has an average hydrophobicity, probably closer to that of protein which explains its sorption increases with whey protein content. It is probably also more sensitive to the polarity of the film as estimated from contact angle measurement. Increasing the hydrophobicity and decreasing the volatility of the aroma compound induce a reduced sorption as observed for ethyl hexanoate and ethyl octanoate. This means that whey protein films could be better barrier to more hydrophobic aroma compound of less volatile. However, the nature of the chemical group of the aroma compound could also play and important role on sorption and transport through protein film, through interaction with amino acids.

Thanh et al.[61] demonstrated that the caseinates substrates sorb higher quantities of volatile compounds than carbohydrates. Błaszczak et al.[62] demonstrated the sorption capacity stronger depends on hydrophobicity and molecular structure of odorant volatiles rather than starch origin. In contrast, Boutboul et al.[63] showed that interactions involving hydrogen bounds and dipole–dipole interactions between aroma compounds and starch exist. Chalier et al.[64] reported that the permeability of 2-heptanone was decreased by coatings made from casein or gluten.

Mauricio-Iglesias et al.[65] investigated concentration of aroma compounds (ethyl butanoate and ethyl hexanoate) through polylactide films (PLA). The results obtained are on the level 0.3–0.6 g of ethyl butanoate per kg of PLA films and 0.7–1.6 g of ethyl hexanoate per kg of PLA film. Terta et al.[66] used polysaccharide matrices for investigation of aroma compounds concentration (limonene and trans-2-hexanal). The data obtained show the aroma concentration sorbed in films is around 0.6–1.6 g aroma compounds per kg of biodegradable film.

As well as starch, starch–whey protein and whey protein films, PLA films and polysaccharide films have polar character and thus have less affinity for apolar volatile compounds like aromas. These films have amounts of aroma sorbed comparable with data obtained in this study. On the contrary, the quantity of aroma sorbed by plastic films like polyesters with high crystallinity or polyolefins[65,67] is at least two magnitudes higher.

Table 4. Concentration of four aroma compounds (ethyl acetate. ethyl butyrate. ethyl hexanoate. ethyl octanoate) sorbed in films (g aroma kg^{-1} dry film) according the ratio between starch and whey protein isolate

Aroma compound	100S 0WP	80S 20WP	60S 40WP	40S 60WP	20S 80WP	0S 100WP
Ethyl acetate	5.07 ± 0.37[h,i]	4.82 ± 0.24[h,i]	4.80 ± 0.22[h]	4.79 ± 0.17[h]	4.73 ± 0.02[h]	5.80 ± 0.24[j]
Ethyl butyrate	2.11 ± 0.02[f]	4.02 ± 0.07[g]	5.19 ± 0.01[i]	6.45 ± 0.05[k]	7.09 ± 0.01[l]	7.30 ± 0.02[l]
Ethyl hexanate	1.15 ± 0.09[c,d]	1.22 ± 0.07[d]	1.75 ± 0.11[e]	1.45 ± 0.11[d,e]	1.28 ± 0.34[d]	1.74 ± 0.17[e]
Ethyl octanoate	1.32 ± 0.14[d]	1.53 ± 0.01[d,e]	1.52 ± 0.14[d,e]	0.41 ± 0.03[a]	0.81 ± 0.09[b,c]	0.74 ± 0.10[a,b]

Value having the same letter are not significantly different at a P value = 0.05.

CONCLUSIONS

The effect of transport properties at the starch–whey protein-based films was studied. The microstructure, surface and wettability properties of wheat starch films, whey protein films and their mixtures were investigated. Starch films are more heterogeneous and less dense than protein films. The lower the starch content, the more homogenous and dense are the films are. Starch films, whey protein films and 80S-20WP mixture films have a higher dispersive component of the surface energy than other blends. Also, surface tension, work of adhesion, work of cohesion and spreading coefficient are lower for mono-component films and 80S-20WP films than for other mixtures. The contact angle and the sorption of ethyl butyrate decrease with the starch concentration whereas the WVP and the water content increased. Increasing the hydrophobicity and decreasing the volatility of the aroma compound induced a reduced sorption as observed for ethyl hexanoate and ethyl octanoate. This means that wheat starch films will be poorer barriers to aroma compounds that are less hydrophobic.

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