



Wheat gluten-coated papers for bio-based food packaging: Structure, surface and transfer properties

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ABSTRACT

The objective of the present work was to understand how the structural, surface, water vapour and gas barrier properties of wheat gluten (WG) coated paper could be influenced by the features of paper. For this purpose, a surface treated paper (TP) and an untreated paper (UTP) were compared. Penetration of WG-coating into the bulk of paper was more pronounced in UTP than TP. This led to the formation of a significant junction zone resulting in an interpenetrated structure for WG–UTP, suggesting a composite-like structure, while a bi-layer one was obtained for WG–TP. Differences in WG penetration were related to the hydrophilicity, roughness and porosity of the paper used. Even though the extent of penetration did not greatly affect the surface properties (water and oil resistance), the transfer properties (water vapour, O₂ and CO₂) of WG-coated papers were significantly improved when WG-coating highly penetrated: while the WG–TP behaved as a micro-perforated material, the WG–UTP behaved as WG-film.

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1. Introduction

During the last 20 years, an increasing interest has been expressed towards eco-friendly products leading to consider natural polymers from agricultural origin as raw materials for the design of bio-based materials. Biopolymers such as proteins possess potential film-forming aptitude that make them particularly useful for material development. This is due to the heteropolymeric structure of proteins: the different amino acids forming the polymers offer a large spectrum of chemical functionalities and a wide variety of polymer network structures leading to unique gas barrier properties. For instance, protein-based materials such as wheat gluten (WG) films exhibit RH-dependent gas permeabilities (O₂ and CO₂) and a rather high WVP allowing optimal gas composition for food preservation (Gontard, Thibault, Cuq, & Guilbert, 1996). Moreover, the poor mechanical resistance of protein-based material restricts their utilization for a wide range of applications.

To overcome this drawback, one potential strategy consists in reinforcing the protein matrix by associating it to paper, exploiting the naturally-occurring compatibility due to their hydrophilic nature. Protein can be used as functional coatings for paper, the latter acting as a mechanical support packaging (Chalier, Peyches-Bach, Gastaldi, & Gontard, 2007; Guillaume, Chalier, & Gontard, 2008). Moreover, due to the biodegradable feature of proteins, both recyclability and biodegradability attributes of the paper would be

maintained unlike most of the synthetic coatings currently used for cellulosic substrates.

In literature, several animal and vegetable proteins such as caseinates (Gastaldi, Chalier, Guillemin, & Gontard, 2007), whey protein isolates WPI and concentrates WPC (Gällstedt, Brottman, & Hedenqvist, 2005; Han & Krochta, 1999, 2001; Lin & Krochta, 2003), corn zein (Gastaldi et al., 2007; Trezza & Vergano, 1994; Trezza, Wiles, & Vergano, 1998), WG (Chalier et al., 2007; Gällstedt et al., 2005, 2007) and soy protein isolate SPI (Ben Arfa, Chakrabandhu, Preziosi-Belloy, Chalier, & Gontard, 2007; Ben Arfa, Preziosi-Belloy, Chalier, & Gontard, 2007; Chalier, Ben Arfa, Guillard, & Gontard, 2009; Chalier, Ben Arfa, Preziosi-Belloy, & Gontard, 2007; Park et al., 2000; Rhim, Lee, & Hong, 2006) have already been considered as coatings of paper and paperboard with the goal of improving surface and/or mass transfer properties of the cellulosic substrate. In the case of WPI coating, oil resistance, printability of water-based ink (due to a good water absorption rate), barrier properties against water vapour of coated paper were increased without significant change of optical and mechanical properties (Han & Krochta, 1999, 2001). Soy protein coating made coated paperboard more resistant to water (Rhim et al., 2006) and grease (Park et al., 2000). When paper is coated with corn zein, its grease resistance and water vapour barrier properties were also improved whereas no significant change in oxygen permeability was noticed; this was attributed to a non uniformity of the coating layer onto the paper (Trezza & Vergano, 1994; Trezza et al., 1998). Using WG as coating for paper, (Gällstedt et al., 2005) showed that a reduction of the oxygen permeability was reached with compression-moulded material, underlining the necessity to have a

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continuous and thick enough coating to improve gas barrier properties. Thus, due to interesting gas barrier properties previously demonstrated (Gontard, Guilbert, & Cuq, 1992; Gontard et al., 1996; Mujica Paz & Gontard, 1997; Mujica Paz, Guillard, Reynes, & Gontard, 2005), high availability at low price (≈ 1 €/kg) and remarkable biodegradability and non-ecotoxicity (Domenek, Feuilloley, Gratraud, Morel, & Guilbert, 2004), WG can be considered as an attractive biomacromolecule for paper-coating applications, especially in food packaging systems.

To our knowledge, most of these studies only related the functional properties of coated paper to (i) the chemical structure of protein used as coating (hydrophilic/hydrophobic amino acids content, disulfide bonding potential, combination with polysaccharide etc.) and/or (ii) the processing conditions (coating weight, casting or thermoforming, drying condition, etc.). However to better modulate such properties, it appears essential to investigate as deeply as possible the underlying mechanisms of coating processes of paper with proteins. A deeper understanding on how the protein coating interacts with paper was previously provided through a physico-chemical and microstructural approach in a comparative study (Gastaldi et al., 2007). The main forces acting on this interaction were demonstrated to be surface tension, viscosity, and density of the coating solution as well as its affinity for the paper. Among the three studied proteins stemming from different origins (caseinates, corn gluten meal and WG), WG-coating solutions exhibited the greatest affinity for the paper and the highest level of penetration inside paper. To complete this knowledge, it is necessary to take into consideration also the paper properties. For this purpose, two commercial papers (surface treated and not) were tested for their ability to be coated by a WG solution. Structure, surface and transfer properties of the resulting WG-coated paper were related to the intrinsic properties of each paper.

2. Experimental

2.1. Materials

Two kinds of paper materials made from bleached pulp were provided in sheet form by Smurfit WR (France): a surface treated paper (TP), coated on two sides with calcium carbonate and starch, and an untreated paper (UTP) specially manufactured for this study. Vital wheat gluten (WG) powder, containing 7.2 wt.% of moisture and 76.5 dry wt.% of proteins, was provided by Amylum Aquitaine (France). Acetic acid and sodium bisulfite (Merck) were used to prepare the coating solution, and salts purchased from Merck to condition all materials in expected relative humidity from 0% to 80% (silica gel, $\text{Mg}(\text{NO}_3)_2$, KCl). Amido black, ethanol, and acetic acid (Merck) were used to color samples, then embedded in Epoxy resin (Technovit 7100 historesin, Heraeus K  tler, Germany) for optical microscopy observations.

2.2. Preparation of WG-coated papers

WG-coating solution was prepared at room temperature, according to a two-step procedure (Morel, Bonicel, Micard, & Guilbert, 2000), slightly adapted to obtain free alcohol solutions. Firstly, 20 g of wheat gluten powder was poured into a hermetic box and dispersed, under shaking, in 50 mL of deionised water containing sodium sulfite (0.08 g/100 mL) as a reducing agent of disulfide bonds. Secondly, after 30 min of settling, the solution was adjusted to 100 mL by slowly adding deionised water with acetic acid to reach a pH value of 4, under magnetic stirring.

Prior to coating, all papers were wet and then, flattened under vacuum on levelled aluminium plates to be stuck at the edges using masking tape, to avoid wrinkling during the coating process.

Thereafter, vacuum was stopped and a layer (about 150 μm -thick) was coated onto the surface of treated (TP) and untreated samples (UTP), using a thin-layer chromatography applicator (Braive instruments, Liege, Belgium), to produce either wheat gluten-coated TP, hereinafter referred as WG-TP, or wheat gluten-coated-UTP, hereinafter referred as WG-UTP. Drying was performed at 25 $^\circ\text{C}$ and 50% RH until constant weight. To allow better comparison, uncoated TP and UTP papers were subjected to the same treatment than their respective coated materials, but coating solution was devoid of WG; they were considered as swelled paper.

Before the surface characterization and gas permeation measurements, all samples were stored under thermo-hygrometric conditions by placing each saturated salt solution in a climatic chamber at 25 $^\circ\text{C}$ for one week.

2.3. Evaluation of WG penetration

Average thickness was determined at 25 $^\circ\text{C}$ and 50% RH with a hand-held digital micrometer (Braive instruments) from ten measurements taken randomly over the materials surface. To evaluate the coating weight of coated papers, all samples, including uncoated papers, were previously dried at 103 $^\circ\text{C}$ until constant weight was reached. Coating weight was calculated from three replicates by subtracting the dry basis weight of a defined area of uncoated paper from the dry basis weight of the same area of coated paper.

To evaluate the part of the WG that penetrated the paper in WG-coated paper, the percentage of penetration of the coated layer was defined as follows:

$$\% \text{ penetration} = 100 \times \left(1 - \frac{l_a}{l_s} \right) \quad (1)$$

where l_a (μm) is the apparent thickness of the coated layer and l_s (μm) is the thickness of self-supported wheat gluten film (depositing same coating solution onto a Plexiglas plate).

l_a was calculated from:

$$l_a = l_{cp} - l_p \quad (2)$$

where l_{cp} (μm) is the total thickness of the coated paper and l_p (μm) is the thickness of its respective swelled paper.

l_s was determined according to the following equation previously demonstrated (Gastaldi et al., 2007):

$$l_s = 1.6 \times cw \quad (3)$$

where cw (g m^{-2}) is the coating weight of the self-supported layer per surface unit (same that for coated layer).

2.4. Microstructural observations

Prior to examination in optical microscopy (OM), WG-coated papers were stained for 3 h in a solution containing 1% (w/v) amido black in ethanol:acetic acid (9:1); excess stain was removed by dipping samples in ethanol:acetic acid (9:1) solution several times. Samples were then dried under ambient air and embedded in Epoxy resin (Technovit 7100 historesin, Heraeus K  tler, Germany). Thin sections of 6 μm were sliced with an ultramicrotome (Reichert Jung, France) using a tungsten carbide blade (Leica, France) and mounted on slide. Views of cross-sections were captured on a Kappa camera connected to a Nikon labophot-2 microscope (magnification 10).

Scanning electron microscopy (SEM) observations of material surface were performed on small pieces (10 mm $\times$ 10 mm) directly mounted on a stub with double-sided carbon tape. For cross-sectional views, materials were prior fractured in a frozen state in li-

quid nitrogen. After degassing under vacuum and platinum coating (thickness of 5 nm), samples were observed with a JEOL JSM-6400F FESEM (France). All micrographs were obtained using an accelerating voltage of 15 kV.

2.5. Surface properties

Surface properties of materials were evaluated by contact angle measurements using a contact angle meter (Digidrop, GBX, France), equipped with a diffuse light source, a CDD camera (25 frames per second) and a closed environmental chamber with controlled temperature (20 °C) and relative humidity (50%). Surface energy was calculated using the Owens and Wendt model (Owens & Wendt, 1969) as followed:

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} \quad (4)$$

with γ_s^{LW} the dispersive component (Lifshitz-Van der Waals interactions), γ_s^{AB} the non-dispersive components (polar interactions, Lewis acid-base).

The relation between tension components (S: solid-vapour; L: liquid-vapour) and contact angle is written as:

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_s^{AB}\gamma_L^{AB}} \quad (5)$$

Surface energy was determined by depositing a drop of three reference liquids with known dispersive and non-dispersive components (water, formamide, diiodomethane) on the sample surface and measuring the resulting contact angles at equilibrium.

The sensitivity of papers surface to wetting was investigated by measuring the behaviour of a liquid drop (≈ 3 mL) of the WG-coating solution, water and corn oil, onto papers surface. WG-coating solution was applied onto uncoated papers whereas water and corn oil were applied on both uncoated and WG-coated papers. Contact angle measurements were performed in static conditions (initial contact angle at equilibrium) and then in dynamic (change in contact angle vs. time). Wettability (expressed in s^{-1}) was determined by measuring changes in averaged value of contact angles (measured on both side of the drop) with time. The evolution of volume and width basis of the drop as a function of time allowed evaluating the contribution of the absorption ($mL s^{-1}$) and spreadability ($mm s^{-1}$) phenomena involved in paper wettability. Uncoated and WG-coated paper samples were cut in 10 mm $\times$ 50 mm pieces, stick on glass slide using double side adhesive and conditioned at least 48 h at 20 °C in a dessiccator containing a saturated solution of magnesium nitrate saturated solution (50% HR) before analysis. All measurements were performed at least in triplicate.

2.6. Permeation measurements

Water vapour permeability of each material was determined gravimetrically. Material was sealed on the top of a permeation cell containing distilled water (100% RH), placed in a dessiccator, and maintained at 25 °C and 0% RH with silica gel. The water transferred through the film and absorbed by the desiccant was determined from weight loss of the glass permeation cells. The cups were daily weighed to the nearest 0.1 mg. To prevent the formation of a stagnant air layer on the surface, a minimal 152 mL min^{-1} air speeds outside the test cups was maintained by using a fan inside the dessiccator. The slope of weight line vs. time was obtained by linear regression. At least five replicates were measured for each material. The measured water vapour permeability of the film was determined as following in the international system unit:

$$WVP = \frac{w \times l}{A \times M \times (p_2 - p_1)} \quad (6)$$

where w is the slope of weight vs. time ($kg s^{-1}$), l is the film thickness (m), A is area of exposed film (m^2), M is the molecular mass of water ($kg mole^{-1}$) and $p_2 - p_1$ is the vapour pressure difference across the film (Pa). Water vapour permeability was then expressed in $10^{-12} mol m^{-1} s^{-1} Pa^{-1}$.

Oxygen and carbon dioxide permeation was assessed according to an isostatic and dynamic method on WG-coated materials. Materials were placed in a permeation cell, i.e. between two stainless steel chambers. The inferior and superior chambers were each spread by a 40 mL min^{-1} flux of permeant (O_2 and CO_2) and vector gas (He), respectively. The permeability cell was coupled to a gas chromatograph (GC 3800, VARIAN, Les Ulis, France) which allowed to monitor the evolution with time of the permeant gas concentration in the superior chamber of the cell thanks to an automatic valve. Gas chromatograph was equipped with a filled column (Porapak Q, Chrompak) of 2 m length and 0.32 m diameter for separating O_2 and CO_2 , with a thermal conductivity detector (TCD) and an automatic injector. A minimum of three replicates for each sample and each permeant were measured. The measured gas (O_2 and CO_2) permeability of the film was determined as following in the international system units:

$$P_x = \frac{\Delta Q \times l}{\Delta t \times A \times (p_2 - p_1)} \quad (7)$$

where P subscript x refers to O_2 or CO_2 permeability, ΔQ is the quantity of gas that pass across the film, l is the thickness of material, Δt is the time for which permeation occurs, A is the film area exposed and $(p_2 - p_1)$ is the difference in pressure exerted by the gas on each side of the film. P_x has a constant value for a specific combination of gas and polymer at a given temperature and relative humidity. Gas permeability was then expressed in $10^{-18} mol m^{-1} s^{-1} Pa^{-1}$ unit. To set moisture conditions, both permeant and carrier gas were humidified by bubbling in a wash flask that was containing ultra-pure water and was placed in a cryothermostat regulated at a properly chosen temperature. The differential of temperature imposed between the cryothermostat and the oven (25 °C) permitted the establishment of the desired relative humidity in the permeation cell.

ISO standard procedures were used to characterize air permeation of TP and UTP: ISO 5636-3 for Bendtsen permeability (expressed in $cm^3 m^{-2} Pa^{-1} s^{-1}$), ISO 8791-2 for Bendtsen roughness (expressed in $mL min^{-1}$), and ISO 5627 for Bekk smoothness and porosity (both expressed in s). Roughness and smoothness were related to the topography of papers.

3. Results and discussion

Two kinds of WG-coated papers, WG-TP and WG-UTP, were obtained by coating a wheat gluten solution onto two different papers, TP and UTP, respectively. Structural, surface and transfer properties of WG-coated papers were related to the intrinsic properties of papers.

3.1. Evaluation of the WG penetration related to paper properties

As indicated in Table 1, the deposition of the wheat gluten solution onto the cellulosic substrate led to a thickness increase, regardless the type of paper used. This is due to the formation of a coated layer for which thickness is influenced by the nature of coating polymer, the solid content of coating solution and the applied wet coating thickness (Gastaldi et al., 2007; Gällstedt et al., 2005; Han & Krochta, 1999; Rhim et al., 2006). The increase in apparent thickness (see Eq. (2)) was more important in the WG-TP (22.7 μm more) than in the WG-UTP (13 μm more), with a coating weight of 25.0 and 20.7 $g m^{-2}$, respectively. It was noticeable

Table 1

Thickness and dry basis weight of materials, resulting coating weight of WG-coated papers, and impregnation of WG-coated papers.

Materials	Thickness (μm)	Dry basis weight (g m^{-2})	Coating weight (g m^{-2})	Impregnation ^a (%)
TP	131.3 $\pm$ 1.6	100.8 $\pm$ 1.6	–	–
UTP	60.5 $\pm$ 1.7	36.5 $\pm$ 0.8	–	–
WG-film	40.0 $\pm$ 4.0 ^a	25.0 $\pm$ 2.5 ^a	–	–
WG-film	33.1 $\pm$ 3.5 ^a	20.7 $\pm$ 2.2 ^a	–	–
WG-TP	154.0 $\pm$ 2.7	125.8 $\pm$ 4.1	25.0 $\pm$ 2.5	43.25 $\pm$ 3.5
WG-UTP ^a	73.5 $\pm$ 4.0	57.2 $\pm$ 3.0	20.7 $\pm$ 2.2	61.00 $\pm$ 2.8

^a From the linear equation previously established [4].

that reducing the coating weight of nearly 20% (from 25.0 to 20.7 g m^{-2}) led to a decrease in apparent thickness of the coated layer of almost 60% (from 22.7 to 13 μm). This was related to a higher penetration of wheat gluten proteins into UTP paper than into TP. It was clearly observed on both optical and scanning electron micrographs of the cross-sections of WG-coated papers (Fig. 1). Although the coating layer appeared homogeneous at the surface of both papers, wheat gluten penetrated UTP paper to a higher extent leading to the formation of a significant junction zone corresponding to an interpenetration of fibres and WG, as a composite-like structure, while a simple bi-layer structure was observed for WG-TP. Percentages of penetration were calculated according to equation 1 to assess the amount of proteins that penetrates into the paper structure. This percentage reached 43% when using WG-TP against 61% in WG-UTP (Table 1). The penetration of protein into paper was related to the nature of protein (whey, soy, chitosan, calcium caseinate, corn zein, wheat gluten) and/or the coating weight as reported by previous literature that mentioned (Gällstedt et al., 2005; Han & Krochta, 1999; Rhim et al., 2006) or quantified (Gastaldi et al., 2007) penetration. In the present study,

differences in WG penetration had to be attributed to the intrinsic properties of the two papers i.e. surface chemistry (or its affinity toward WG-coating solution), topography and porosity.

The behaviour of a WG-coating solution droplet deposited at the surface of papers was investigated by static contact angle measurement and compared with water and corn oil. In addition, conventional reference liquids were used to evaluate surface energy of the two papers. All these data are presented in Table 2. UTP paper exhibited a smaller value of the contact angle at equilibrium than TP (15.7° against 76.3°), meaning that its affinity toward the coating solution was greater. Surface energies of the two papers were quite similar but their polar and dispersive components were different. UTP paper displayed a higher polar component ($\gamma_{\text{S}}^{\text{AB}}$ of 13.3 against 4.2 mJ m^{-2}) and a lower dispersive component ($\gamma_{\text{S}}^{\text{LW}}$ of 42.8 against 54.9 mJ m^{-2}) than TP. UTP paper could be thus considered as more hydrophilic than TP with a higher affinity for aqueous coating solutions. This was confirmed by value of contact angle at equilibrium obtained with water and oil droplet (Table 2): TP showed a higher water-contact angle than UTP (109.7° and 43.3°, respectively) and conversely, a lower oil-contact angle (<10° and 38.6°, respectively).

The coated paper topography was then investigated. As observed on scanning electron micrographs of papers surface (Fig. 2), the pre-coating of TP (composed of calcium carbonate and starch) led to a rather smooth surface but with numerous ridges and valleys owing to thick cellulosic fibres. To compare, UTP paper appeared rougher but with a mottled appearance due to entangled thin cellulosic fibres. These observations were in agreement with values obtained for Bendtsen roughness and Bekk smoothness (Table 3): Bekk smoothness value of TP is higher than UTP whereas conversely Bendtsen roughness is lower for TP than for UTP. Roughness is known to emphasize the hydrophilicity of surfaces when contact angle is lower than 90° (Quéré, 2002; Schuman, Wikström, & Rigdahl, 2004). Then, increasing roughness would lead to decreasing contact angle value. As a consequence, the higher roughness of UTP paper could enhance its hydrophilicity in contact angle measurement as compared with TP.

In addition to porosity values (Table 3), the absorption rates of the WG-coating solution were evaluated for both TP and UTP papers through dynamic contact angle measurement (Table 4). Surprisingly, TP exhibited an absorption rate 3-fold lower than UTP paper whereas its porosity was almost 5-fold higher than UTP, also the porosity was expected to favour liquid penetration. Such a contradictory effect between liquid absorption and porosity has been previously obtained (Han & Krochta, 1999) and was attributed to the hydrophobic nature of air-filled voids that may hinder liquid absorption. In our work, the lower absorption rates measured for TP samples should be related to the surface properties (a smooth hydrophobic surface as observed in SEM and contact angle measurements) rather than to the bulk characteristics of the substrate (high porosity). Then, surface properties were considered as the main driving forces involved in penetration of the WG-coating solution into paper.

3.2. Surface properties of WG-coated papers

Surface properties of WG-coated papers were evaluated by contact angle measurements performed in dynamic conditions. Water and oil droplet (Table 4) were chosen to reflect its moisture and grease resistance, which are important criteria for potential use as food packaging material. Water wettability of WG-coated papers was reduced as compared with their respective uncoated papers, but in a higher extend for WG-TP (30-fold less) than for WG-UTP (only 6-fold less). WG-UTP appeared more wettable by water than WG-TP (20-fold more) because of both a higher water absorption rate and spreadability. Such differences could be attrib-

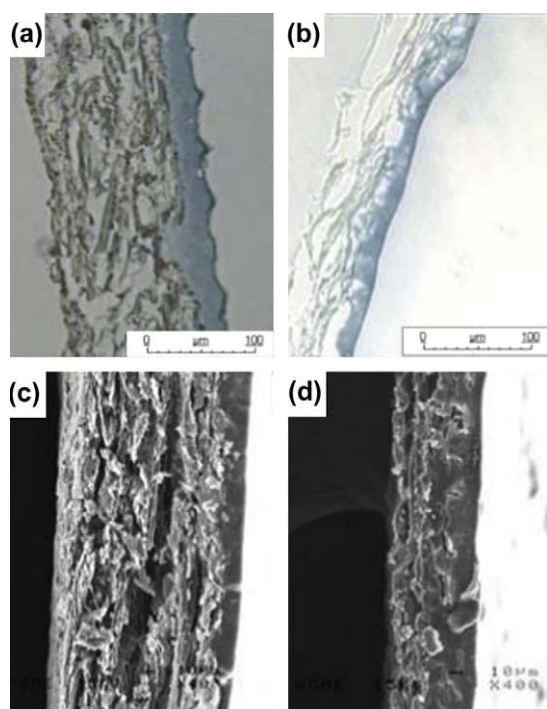
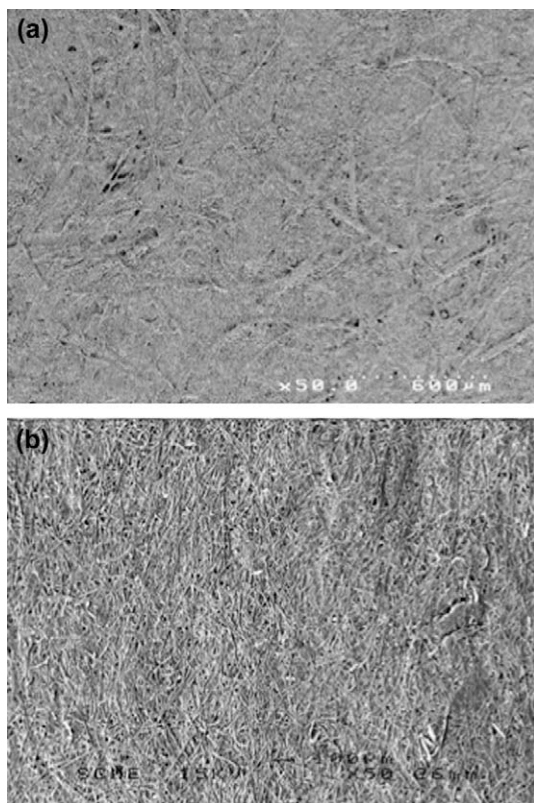


Fig. 1. Cross sectional views of wheat gluten-coated papers obtained by optical microscopy using amido black as protein dyeing: (a) WG-TP; (b) WG-UTP and by scanning electron microscopy: (c) WG-TP, (d) WG-UTP. The WG-coated layer is located at the right of all micrographs.

Table 2

Surface energy and static surface properties of papers determined by contact angle measurements (at 50% RH and 25 °C) using WG-coating solution, water and oil drop.

Papers	Contact angle with WG solution (θ , °)	Surface energy (γ_s , mJ m ⁻²)	Polar component (γ_s^{AB} , mJ m ⁻²)	Dispersive component (γ_s^{LW} , mJ m ⁻²)	Contact angle with water (θ , °)	Contact angle with corn oil (θ , °)
TP	76.3 ± 2.2	59.1 ± 2.5	4.2 ± 0.7	54.9 ± 2.0	109.7 ± 2.7	<10
UTP	15.7 ± 1.5	56.1 ± 2.3	13.3 ± 1.2	42.8 ± 1.8	43.3 ± 1.3	38.6 ± 1.8

**Fig. 2.** Surface view of the two support papers obtained by scanning electron microscopy: (a) TP and (b) UTP.**Table 3**

Air behaviour in papers: surface treated paper (TP) and untreated paper (UTP).

Papers	Bendtsen permeability (10 ⁻⁸ mol m ⁻¹ Pa ⁻¹ s ⁻¹)	Bendtsen roughness (mL min ⁻¹)	Bekk porosity (s)	Bekk smoothness (s)
TP	1405	363	49.0	14.0
UTP	641	620	10.2	4.4

uted to (i) the higher hydrophilicity (polar component) and water wettability of UTP paper, or ii) the lower apparent thickness of the WG-layer in WG-UTP (conversely proportional to the degree of penetration). The latter assumption was not in agreement with

previous report on the concomitant increase in water wettability of WPI-coated papers with the coating thickness (Han & Krochta, 1999). This highlighted the importance of the hydrophilic/hydrophobic nature of proteins on the expected water resistance of coated papers (WPI are known to be more hydrophilic than WG).

Regarding oil sensitivity (Table 4), the coating of paper by WG solution resulted in a significant reduction in oil wettability (more than 400 fold less) whatever the paper used. According to results obtained on SPI (Han & Krochta, 2001; Lin & Krochta, 2003), WPI (Park et al., 2000), and corn zein (Trezza & Vergano, 1994) such an important improvement of grease resistance could only be obtained when:

- the layer is homogenous and thick enough to fill the porous structure of paper,
- the coating weight is higher than a threshold value around 15 g m⁻².

Then, we assumed that the degree of penetration of the coating solution into paper greatly depends on the choice of both the paper and the protein, and allows the tuning of water and grease resistance of the protein coated papers, according to the desired purpose.

3.3. Transfer properties of WG-coated papers

WVP of uncoated and WG-coated papers were evaluated at 25 °C between 0% and 100% RH (Table 5). As expected from previous works (Han & Krochta, 1999; Rhim et al., 2006), coating of paper with protein led to a slight but significant reduction of water vapour permeability WVP; probably because WG filled the porous structure of paper. WVP of WG-UTP and WG-TP (1.27 and 3.27 × 10⁻¹¹ mol m⁻¹ Pa⁻¹ s⁻¹, respectively) were nearly in the same range than that of WG self-supported films previously assessed in the same environmental conditions: from 0.75 (Gontard, Guilbert, & Cuq, 1993) to 6.96 × 10⁻¹¹ mol m⁻¹ Pa⁻¹ s⁻¹ (Aydt, Weller, & Testin, 1991). To compare, WVP of WG-coated papers were greatly lower than that of WPI-coated papers made with 5 and 18 g m⁻²: 9.58 and 6.96 × 10⁻¹¹ mol m⁻¹ Pa⁻¹ s⁻¹, respectively (Han & Krochta, 1999). As shown in Table 5, WVP was decreased by 45% in WG-TP (25 g m⁻² of protein) against 56% in WG-UTP paper (20 g m⁻² of protein) compared to that of their respective uncoated papers (0 g m⁻²). Since the specimen with the lowest coating weight displayed the highest barrier toward water vapour, coating weight cannot be considered as the only parameter affecting WVP of protein coated paper.

Table 4

Dynamic surface properties of papers and WG-coated papers (at 50% RH and 25 °C): wettability (change in contact angle vs. time), absorption (change in drop volume vs. time) and spreadability (change in base width vs. time) of WG solution, water and oil drop.

Material	WG solution absorption (μl s ⁻¹)	Water wettability (° s ⁻¹)	Water absorption (μl s ⁻¹)	Water spreadability (mm s ⁻¹)	Oil wettability (° ss ⁻¹)	Oil absorption (μl s ⁻¹)	Oil spreadability (mm s ⁻¹)
TP	0.12 ± 0.01	0.90 ± 0.12	0.04 ± 0.03	<0.001	17.88 ± 1.52	0.66 ± 0.10	0.83 ± 0.07
UTP	0.33 ± 0.02	4.41 ± 0.50	1.06 ± 0.11	0.8 ± 0.09	16.46 ± 1.67	0.05 ± 0.02	0.79 ± 0.09
WG-TP		0.03 ± 0.01	<0.001	<0.001	<0.001	<0.001	<0.001
WG-UTP		0.70 ± 0.15	0.07 ± 0.02	0.06 ± 0.02	0.04 ± 0.01	<0.001	0.02 ± 0.01

Table 5

Gas and water vapour (WVP) permeability values of paper samples.

Materials	Gas permeability ^a (10^{-18} mol m ⁻¹ s ⁻¹ Pa ⁻¹)		Selectivity ^a	WVP ^b (10^{-11} mol m ⁻¹ s ⁻¹ Pa ⁻¹)
	O ₂	CO ₂		
TP	– ^c	– ^c	≈1	5.91 ± 0.20
UTP	– ^c	– ^c	≈1	3.70 ± 0.10
WG-TP	49689 ± 4963	59000 ± 5367	1.19	3.27 ± 0.80
WG-UTP	8328 ± 989	16927 ± 1989	2.03	1.27 ± 0.06

^a At 25 °C and 80% RH.^b At 25 °C and 0–100% ΔRH.^c Out of range.

At 25 °C and 80% RH, both uncoated papers exhibited too high gas flow, consequently without selectivity, because of their high porosity (Table 5). Then, it was more convenient to refer to air behaviour (Bendtsen permeability) to characterize gas transfer properties of such porous materials as papers that was around 10^{-8} mol m⁻¹ Pa⁻¹ s⁻¹ for both papers (Table 3). As shown in Table 5 and whatever the paper used, WG-coating led to a significant improvement of gas barrier properties of paper by reducing gas permeability of around 30-fold for TP and at least 100-fold for UTP paper. Therefore WG-coated papers cannot be anymore considered as permeable and porous materials. However, but as expected, gas barrier performance and selectivity of WG-coated samples still remained lower than for a WG-film at 25 °C and 80% RH (around 370 and 6000×10^{-18} mol m⁻¹ Pa⁻¹ s⁻¹ for O₂ and CO₂, respectively (Gontard et al., 1996)). Our results confirm the fact that in both cases coating weight was sufficient to allow the WG-coating to partially penetrate into the paper structure and fill voids in the paper surface as previously mentioned. Of the two WG-coated papers studied, the WG-UTP displayed the

lowest O₂ and CO₂ gas permeability and behaved as permselective toward O₂ and CO₂. Conversely, WG-TP behaved almost like a micro-perforated material with a poor selectivity.

To better understand these difference in gas permeability and selectivity, scanning electron microscopy observations were performed. Fracture zones were clearly identified and pointed out a lack in the integrity of the thin coating layer in WG-TP (Fig. 3a). This resulted in local disruptions of the coated layer that lead consequently to permeable zones altering the overall gas barrier performances of the WG-TP. In the case of WG-UTP, no fracture zones were evidenced (Fig. 3b) suggesting that the integrity of the protein layer was maintained. The extent of penetration of the WG layer into paper appeared to significantly influence the subsequent structure of samples. In the composite-like structure (highly penetrated) we assumed that the junction zone enable to react as a tension absorber limiting the formation of fractures in the protein layer. As previously reported for coated papers, the junction zone is known to have greater mechanical properties than the paper and the coating separately (Hagen & Salmen, 1995).

It could be pointed out that gas barrier properties appeared more affected by this discontinuity in the coating layer than WVP which is evaluated between 0% and 100% RH, as previously reported on corn zein coated paper (Trezza et al., 1998). This is due to the plasticizing effect of water vapour on the WG-layer resulting in the swelling of the polymeric matrix and consequently to a decrease in the density of fractures observed in WG-TP.

4. Conclusion

To investigate as deeply as possible the underlying mechanisms of paper-coating by proteins, this study aims to understand how the structural, surface and transfer properties of wheat gluten (WG) coated paper could be influenced by the nature of the paper used. For this purpose, a surface treated paper (TP) and an untreated paper (UTP) were compared. UTP displayed a higher level of protein penetration than TP (61% against 43%) resulting in a better penetration of WG-coating into the depth of paper. This led to the formation of a significant junction zone resulting in an interpenetrated structure for WG-UTP, suggesting a composite-like structure, while a bi-layer one was obtained for WG-TP as clearly evidenced by optical and scanning electron micrographs of the materials cross-section. Through static contact angle and air permeation measurements, both the hydrophilicity and roughness of paper were demonstrated to favour the penetration of the WG-coating solution into paper whereas its air porosity acted against. The level of penetration of the WG layer into paper (and the resulting junction zone) appeared to influence greatly the subsequent gas permeability (toward O₂ and CO₂) of WG-coated papers, and to a minor extent their water vapour permeability (WVP) and surface properties (wettability and grease resistance). Scanning electron microscopy observations performed onto the specimens surface revealed fracture zones in WG-TP but not in WG-UTP. These local disruptions in the coated layer led to permeable zones altering the overall gas barrier performances of the WG-TP without affecting its WVP. Due to the relative humidity gradient set by the WVP measurement, the plasticization of the WG layer would occur resulting in a swelling of the polymeric matrix. As a consequence, the fracture zones would be reduced and the surface integrity of the WG-layer partially restored.

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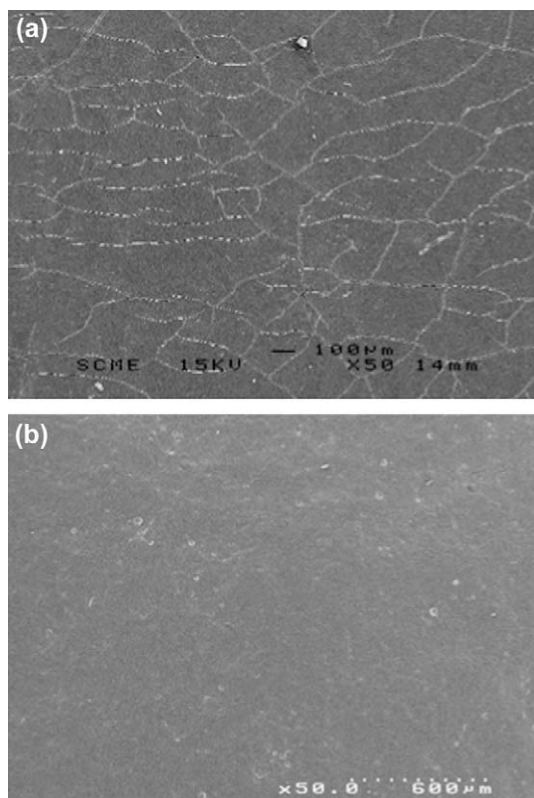


Fig. 3. Surface view of wheat gluten-coated papers obtained by scanning electron microscopy: (a) WG-TP and (b) WG-UTP.

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