Research Article

Wheat Gluten-Laminated Paperboard with Improved Moisture Barrier Properties: A New Concept Using a Plasticizer (Glycerol) Containing a Hydrophobic Component (Oleic Acid)

Sung-Woo Cho,1 Thomas O. J. Blomfeldt,1 Helena Halonen,2 Mikael Gällstedt,2 and Mikael S. Hedenqvist1

1 Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden
2 Innventia, P.O. Box 5604, 114 86 Stockholm, Sweden

Correspondence should be addressed to Mikael S. Hedenqvist, mikaelhe@kth.se

Received 15 October 2011; Revised 27 March 2012; Accepted 30 March 2012

Academic Editor: Wen Fu Lee

Copyright © 2012 Sung-Woo Cho et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This paper presents a novel approach to reduce the water vapor transmission rate (WVTR) and water absorbance of wheat gluten/paperboard laminates by introducing a hydrophobic component (oleic acid (OA)) into the hydrophilic plasticizer (glycerol). Whereas the paperboard showed immeasurably high WVTR, the laminate with gluten/glycerol yielded finite values. More importantly, by incorporating 75 wt.% OA into the plasticizer, the WVTR and water absorbance were reduced by, respectively, a factor of three and 1.5–2. Of particular interest was that the mechanical properties were not changing dramatically between 0 and 50 wt.% OA. The results showed clear benefits of combining a gluten film with paperboard. Whereas the paperboard provided toughness, the WG layer contributed with improved moisture barrier properties. In addition, WVTR indicated that the paperboard reduced the swelling of the outer gluten/glycerol layer in moist conditions; a free standing gluten/glycerol film would yield infinite, rather than finite, WVTR values.

1. Introduction

Wheat gluten (WG) is an interesting alternative to petroleum-based polymeric materials [1] and is available in large quantities as a byproduct from the wheat starch industry [2]. WG films are, however, brittle, and a plasticizer is therefore needed. Using, for example, glycerol, it is possible to make WG-based films and 3D objects using conventional polymer-processing techniques including compression molding, extrusion, and injection molding [3–6]. The resulting material has good gas barrier properties under dry conditions [7], and in its plasticized state it resembles PVC with a high content of plasticizer.

Paperboard coatings for food packaging applications are commonly made from petroleum-based polymers. These coatings are essential for the lifetime of the food products as they act as oxygen and/or water/water vapor barriers [8]. Since wheat gluten is able to form films [1] and has a low oxygen permeability (OP) under dry conditions [9], it is interesting as an alternative in environment-friendly edible and nonedible films for paperboards in food packaging [8]. However, the fact that wheat gluten is hydrophilic and has a high water permeability limits its uses; an effective control of moisture transfer is essential for most foods [10].

Previous studies have shown that the water vapor permeability (WVP) can be reduced when a lipid, such as oleic acid (OA), is incorporated into edible films where the main component is whey [11], chitosan [10], and wheat gluten [12, 13]. However, lipids tend to negatively influence the mechanical properties. In [11] the oleic acid was added after the protein/glycerol emulsion had been prepared and in [10] it was mixed directly with the polymer. In [12] the lipids were coated onto the WG matrix, and in [13] cast films were made from WG, glycerol, and lipids in water and ethanol.

In the work presented in this paper, a new concept of incorporating a lipid, oleic acid, into a wheat gluten material
intended for thermoforming was investigated in order to achieve a more water-resistant material and a higher water vapor barrier without any loss in mechanical properties. The concept was applied to wheat gluten-coated paperboard. The more hydrophobic component (oleic acid) was mixed with the plasticizer (glycerol) prior to adding these to the WG. The oleic acid/glycerol/WG mixture was subsequently applied to the paperboard by compression-molding to mimic extrusion-coating/lamination.

A possible future packaging material for dry foods is a 100% renewable wheat gluten laminate on the outside of the paperboard where the outer layer (consisting of WG with oleic acid/glycerol) is a sufficient water vapor barrier to protect the inner oxygen barrier layer (WG with a small amount of glycerol [14]).

## 2. Materials and Methods

### 2.1. Materials

Commercial WG powder was kindly supplied by Reppe AB, Lidköping, Sweden. According to the supplier, the gluten protein content was 77.7% (according to a modified NMKL nr6 method, Kjeltec, Nx5.7; [http://www.nmkl.com/](http://www.nmkl.com/)). Glycerol with a concentration of ≥99.5 wt.% and a moisture content of ≤0.5 wt.% was supplied by Karlshamns Tefac AB, Karlshamn, Sweden. Oleic acid (OA, C_{18:1}) was purchased from Sigma-Aldrich Co., St. Louis, MO, USA. The paperboard, Korsnäs Duplex 260, was provided by Korsnäs AB, Gäve, Sweden. The grammage was 242 g/m² and the thickness was 0.4 mm. The bottom layer of the paperboard, which was used as a substrate for the lamination, consisted of unbleached softwood sulphite pulp. The middle layer consisted of unbleached chemi-thermomechanical pulp (CTMP), and the top layer consisted of a blend of bleached softwood and hardwood. The hydrophobization was obtained using a dual sizing agent with alkyl ketene dimer (AKD) and rosin. The paperboard was not surface coated on the bottom side.

### 2.2. Sample Preparation

The WG-coated paperboards were prepared by compression molding using a Table-Top Press, Polystat 200T (Servitec MaschinenService GmbH, Wustermark, Germany). A homogeneous dough was first prepared by mixing WG powder with plasticizer (glycerol with or without oleic acid) in a mortar. For simplicity, in the remainder of the study, the glycerol/oleic acid mixture is referred to as the plasticizer. The plasticizer content was 20 or 30 wt.%, based on the total mass of WG films, and the relative contents (wt.%) of oleic acid and glycerol were 0:100, 25:75, 50:50, and 75:25. Ten grams of the dough was spread evenly inside a frame (14 × 14 mm²) between
Figure 2: SEM images showing the surfaces of the WG layer with 30 wt.% of plasticizer containing glycerol and oleic acid in the mass proportions: (a) 100 : 0, (b) 75 : 25, (c) 50 : 50, and (d) 25 : 75.

Table 1: Water vapor transmission rate and surface water absorption.

| Plasticizer content (wt.%) | Paperboard | Specific water vapor transmission rate (g·mm/(m²·day)) | Cobb60 water absorbency (g/m²) |
|---------------------------|------------|--------------------------------------------------------|--------------------------------|
|                           |            | 0 wt.% OA | 25 wt.% OA | 50 wt.% OA | 75 wt.% OA |
| 20                        | UH*        | 400 ± 41 ab | 260 ± 5 de | 199 ± 11 def | 123 ± 6 f |
| 30                        |            | 477 ± 41 a | 370 ± 16 bc | 275 ± 44 cd | 164 ± 8 ef |

Cobb₆₀ water absorbency (g/m²)

|       |            | 24.3 ± 0.3 e** | 42.5 ± 1.1 b | 32.1 ± 0.5 c | 28.0 ± 0.4 d | 28.4 ± 0.7 d |
|-------|------------|----------------|--------------|--------------|--------------|--------------|
| 20    |            | 48.4 ± 1.0 a   | 33.6 ± 1.2 c | 28.9 ± 0.6 d | 24.3 ± 0.1 e |
| 30    |            |                |              |              |              |              |

The results are given with the average value, standard deviation, and significance letter.

*UH: immeasurably high.

**The values having the same letters are not significantly different. Statistics were carried out using the Tukey-Kramer HSD test at a significance level of 0.05.

two Mylar films and two metal plates. The compression molding was performed at 110°C for 30 s, and the molding pressure was set to 200 bar on the machine gauge. The plate assembly was removed from the press after the pressure had been released, and the WG films were separated from the frame using a scalpel. The paperboards were subsequently coated with the prepared films using the same procedure, but without the frame. The WG films were placed on the bottom side of the paperboard, and the molding was carried out at 110°C under a set pressure of 200 bar for 10 min. The WG-laminated paperboards were taken from the press and stored at 23°C and 50% RH prior to characterization and measurements.

2.3. Water Vapor Transmission Rate Measurements. The water vapor transmission rate was measured using a Mocon Permatran-W 3/31 at 38°C and 90% RH (MOCON Inc., Minneapolis, MN, USA) according to ASTM F 1249-90. The specimens (two replicates of each sample) were tightly sandwiched between two aluminum foils, providing a 5 cm² exposure area. The steady-state flow rate through the specimen was then determined and normalized with respect to
Figure 3: Cross-sections of the samples containing 20 wt.% plasticizer with (a) 0 wt.%, (b) 25 wt.%, (c) 50 wt.%, and (d) 75 wt.% OA. The top denser part is the gluten layer, and the bottom porous part is the paperboard.

Table 2: Mechanical properties of the uncoated and laminated paperboard.

| Sample      | E-modulus (GPa) | Strain at break (%) | Stress at break (MPa) | Energy at break (mJ/mm²) | Thickness (mm) |
|-------------|-----------------|---------------------|-----------------------|--------------------------|----------------|
| Paperboard  | 2.50 ± 0.10 de  | 4.1 ± 0.4 a         | 26.5 ± 1.8 bc         | 30.6 ± 4.0 a             | 0.40 ± 0.01    |
| 20-OA0      | 3.24 ± 0.15 c   | 1.5 ± 0.1 d         | 25.2 ± 2.6 c          | 9.5 ± 1.4 cd             | 0.59 ± 0.02    |
| 20-OA25     | 3.64 ± 0.16 b   | 1.5 ± 0.1 d         | 29.2 ± 2.6 ab         | 10.6 ± 1.5 cd            | 0.55 ± 0.01    |
| 20-OA50     | 4.00 ± 0.19 a   | 1.4 ± 0.1 d         | 32.3 ± 2.4 a          | 11.1 ± 1.6 cd            | 0.54 ± 0.03    |
| 20-OA75     | 2.61 ± 0.09 d   | 2.9 ± 0.3 c         | 9.1 ± 1.5 f           | 11.9 ± 1.8 c             | 0.63 ± 0.02    |
| 30-OA0      | 3.11 ± 0.12 c   | 1.4 ± 0.1 d         | 21.8 ± 1.8 d          | 7.7 ± 1.2 d              | 0.57 ± 0.01    |
| 30-OA25     | 3.51 ± 0.19 b   | 1.4 ± 0.1 d         | 26.0 ± 2.6 c          | 8.8 ± 1.0 cd             | 0.51 ± 0.02    |
| 30-OA50     | 3.94 ± 0.23 a   | 1.3 ± 0.1 d         | 27.2 ± 2.7 bc         | 7.1 ± 2.8 d              | 0.49 ± 0.01    |
| 30-OA75     | 2.32 ± 0.06 e   | 3.7 ± 0.4 b         | 18.0 ± 1.5 e          | 20.8 ± 3.9 b             | 0.50 ± 0.01    |

Sample notation: wt.% plasticizer-OA (wt.% oleic acid in the plasticizer mixture).

*The values connected with the same letters are not significantly different. Statistics was carried out using the Tukey-Kramer HSD test at a significance level of 0.05.

the thickness of the coated paperboards to yield the specific water vapor transmission rate (sWVTR).

2.4. Water Absorbency by the Cobb60 Method. The water absorption was determined by Cobb60 in accordance with SCAN-P 12:64. The measurements were performed using an L&W Cobb Sizing Tester (Lorentzen & Wettre, AB, Kista, Sweden) at 23 ± 1°C and 50 ± 2% RH in a controlled climate room. Samples were cut into dimensions of 13 × 13 cm² and conditioned in the climate-controlled room. The apparatus used consisted of a rubber-mat baseboard and a 5 cm high metal cylinder with an inner area of 100 cm². The tester is provided with a clamping device to fasten the cylinder onto the baseboard, having the sample on top. 100 mL of distilled water was then poured into the cylinder. Cobb60 indicates that the absorption is measured after 60 s. The water was poured out after 45 s, the test piece was removed from
the instrument after an additional 15 s, and the residual water on the surface was removed by first laying a blotting paper on the sample and then rolling twice with a brass roller over it. After removal of the blotting paper, the film was weighed on the sample and then rolling twice with a brass roller over the surface was removed by first laying a blotting paper. Before insertion in the microscope, the specimens were coated with gold to a thickness of ca. 6 nm using an agar high-resolution sputter coater (model 208RH) (Agar Scientific, Stansted, UK), equipped with a gold target/agar thickness monitor controller.

2.5. Field Emission Scanning Electron Microscopy (FE-SEM). The WG layer surfaces, cross-sections, and tensile-fractured surfaces were examined in a Hitachi S-4800 FE-SEM (Hitachi High-Technologies Corporation, Tokyo, Japan). Before insertion in the microscope, the specimens were coated with gold to a thickness of ca. 6 nm using an agar high-resolution sputter coater (model 208RH) (Agar Scientific, Stansted, UK), equipped with a gold target/agar thickness monitor controller.

2.6. Infrared Spectroscopy (IR). Infrared spectra were recorded with a Perkin-Elmer Spectrum 2000 FTIR spectrometer, Perkin-Elmer Inc., Waltham, MA, USA, equipped with a single-reflection ATR accessory (Golden Gate from Specac Ltd., Orpington, UK) and controlled by the program Spectrum version 2.00, from Graseby Specac Ltd, Orpington, UK. The sample was tightly sandwiched between a sapphire anvil and the ATR germanium crystal with the WG-coated sample surface against the latter. The spectra were taken as an average of 16 scans between 4000 and 600 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

2.7. Tensile Testing. The tensile tests were performed with an Instron 5566 Universal Testing machine (Instron, Norwood, MA, USA) according to ISO 527-3. Dumbbell-shaped specimens, having a width of 4 mm in the narrow section and a length of 6.5 cm, were punched out to a standard ISO 37-3 shape, using a specimen cutting press from Elastocon AB, Borås, Sweden. The specimens were tested in a climate-controlled room at 23 ± 1°C and 50 ± 2% RH. A load cell

| Pc\(^{+}/Ga^{+} \) | 0 wt.% OA | 25 wt.% OA | 50 wt.% OA | 75 wt.% OA |
|------------------|-----------|-----------|-----------|-----------|
| 20/G\(^{20} \) | 8.3 ± 0.5 | 5.3 ± 0.4 | 8.9 ± 1.6 | 14.4 ± 1.9 |
| 20/G\(^{40} \) | 44.6 ± 1.8 | 32.0 ± 1.3 | 35.3 ± 2.2 | 41.2 ± 2.7 |
| 20/Haze index\(^{***} \) | 34.4 ± 1.3 | 26.6 ± 0.9 | 26.4 ± 1.2 | 26.8 ± 1.9 |
| 30/G\(^{20} \) | 7.2 ± 2.0 | 3.0 ± 0.2 | 8.0 ± 3.8 | 11.4 ± 1.7 |
| 30/G\(^{40} \) | 40.4 ± 7.2 | 21.2 ± 1.2 | 32.2 ± 6.7 | 39.0 ± 2.6 |
| 30/Haze index | 33.2 ± 5.2 | 18.2 ± 1.1 | 24.2 ± 3.4 | 27.6 ± 1.0 |

*The total plasticizer content in the coated paperboard (wt.%).

**Gloss\(^{\text{angle}}(\circ)\): the reflectance measured at angles of 20° and 60°.

***Haze index defined as difference in gloss values measured at angles of 60° and 20° (\( H = G^{60} - G^{20} \)).
of 500 N was used with an extension rate of 10 mm/min and an initial grip-to-grip distance of 40 mm. A preload of 0.1 N (extension rate 10 mm/min) was applied on the samples before measurement to ensure measurements of straight samples. The stress was obtained as the force divided by the initial cross-sectional area of the narrow section, and the strain was determined as the actual grip-to-grip distance relative to the initial grip-to-grip distance. The elastic ($E$) modulus was estimated as the initial slope of the stress-strain curve. A sample series consisted of 10–13 specimens, which were conditioned in the climate room for 120 h before being tested.

2.8. Gloss Test. Gloss was measured using a Zehntner Gloss Instrument ZLR 1050-M supplied by Zehntner GmbH Testing Instruments, Sissach, Switzerland, at an angle of 60° according to ISO 2813. Reflectance, measured at angles of 20° and 60° from the normal to the WG layer surface in accordance with TAPPI T480, is reported as the gloss units $G_{20}$ and $G_{60}$ (GU; percentage multiple of standard). The lamp, lenses, and photodetector were spectrally corrected to give a spectral response corresponding to the CIE luminous efficiency function ($\psi(\lambda)$), which has an effective wavelength of 572 nm. Reflection haze of the coated films was calculated according to ASTM standard method D4039. The haze index ($H$) was defined as the difference in gloss values measured at angles of 60° and 20° ($H = G_{60} - G_{20}$) [16]. A higher $H$ value represents a higher haze.

2.9. Statistical Analysis. Statistical analyses were carried out with a statistical software program JMP version 5 (SAS Institute Inc., Cary, NC, USA). A Tukey-Kramer's HSD (honestly significant difference) test, which performs a statistical means comparison for all pairs, was used at a significance level of 0.05.

### 3. Results and Discussion

#### 3.1. Water Vapor Transmission Rate. It was clear that, while the paperboard had an immeasurably high $sWVTR$, the wheat gluten layer yielded a paperboard laminate with a finite $sWVTR$ (Table 1). In previous work, plasticized standalone wheat gluten films also had immeasurably high $sWVTR$ values [14]. The reason for the difference is probably that the paperboard acted as a support providing mechanical integrity and reducing moisture-induced swelling of the wheat gluten layer.

The specific water vapor transmission rate decreased with increasing amount of oleic acid in the glycerol/oleic acid mixture (Table 1). The value was 3.3 (20 wt.% plasticizer) and 2.9 (30 wt.% plasticizer) times lower with 75 wt.% oleic acid in the plasticizer mixture. This was interpreted as being due to the greater hydrophobicity of oleic acid than of glycerol [17]. In all cases, the material with 30 wt.% plasticizer was more permeable than the material with 20 wt.% plasticizer. It should be noted that the $sWVTR$ data was calculated based on the total thickness of the laminate. Significantly smaller values would be obtained if the WVTR values were instead normalized with the WG layer thickness, neglecting the paperboard, which did not contribute to the barrier properties. It should also be noted that the $sWVTR$ values were obtained at a severe condition (90% RH, 38°C), which is, at least in northern Europe, not a common environment for dry food packaging.

#### 3.2. Water Absorbency: Cobb$_{60}$. The Cobb$_{60}$ values for the laminated board were much higher than those of the uncoated board, but the value decreased with increasing amount of oleic acid, which was in accordance with the $sWVTR$ data (Table 1). The low Cobb$_{60}$ value and the very high $sWVTR$ value of the paperboard indicated that it was highly sized; water vapor was able to penetrate the pores of
the board, but the absorption of liquid water was limited. The greatest difference was found for the samples with 30 wt.\% plasticizer with a decrease of ca. 24 g/m² between 0 and 75 wt.\% OA. The difference in the water absorbance between the samples with 20 and those with 30 wt.\% plasticizer varied with oleic acid content. With the lowest oleic acid content, the sample with 30 wt.\% plasticizer had a significantly higher water absorption than the sample with 20 wt.\% plasticizer. As with the sWVTR, the effect of oleic acid on the water uptake was considered to be due to the greater hydrophobicity of the oleic acid than that of the glycerol.

3.3. Structural Characterization. The surfaces of the samples containing only glycerol felt somewhat sticky and less smooth than the surfaces of the samples containing oleic acid. The latter surfaces felt more “fat-like.” Nevertheless, SEM revealed that the surface of samples with oleic acid contained cracks and a more heterogeneous structure (Figures 1 and 2). The heterogeneity increased with increasing oleic acid content and was highest for the 75 wt.\% OA samples.

Figure 3 shows that the cracks did not extend through the WG layer, which explains why the sWVTR and Cobb⁶₀ values decreased with increasing oleic acid content. An exception was perhaps the sample containing 20 wt.\% plasticizer with 75 wt.\% OA where the SEM pictures were less conclusive (Figure 3). The increased heterogeneity of this sample might explain why it had an unexpectedly high Cobb⁶₀ value (Table 1). However, if the cracks did extend through the WG layer, the sWVTR and Cobb⁶₀ values would have been significantly higher than the values obtained (Table 1). Figure 3 also indicates good bonding between the paperboard and the WG layer.

3.4. Infrared Spectroscopy. The wheat gluten protein structure was analyzed using infrared spectroscopy. The amide I absorbance between 1600 and 1700 cm⁻¹ in Figure 4 is sensitive to changes in the protein secondary structure and reveals the state of the polymerized/aggregated structure [6]. Interestingly, all the wheat gluten layers were found to have a high degree of polymerized/aggregated structure (prominent peak at ~1625 cm⁻¹, corresponding to amide groups in intermolecular β-sheet networks [6]). The peak/shoulder at ~1650 cm⁻¹, corresponding to amide groups in disordered/alpha-helix chain conformations, was less prominent [18]. Aggregation here includes all events that “aggregate” the protein, involving both noncovalent interactions and disruption and reformation of disulfide bonds. The extent of the aggregated structure seemed to decrease with increasing oleic acid content, although the changes were small (the IR curves of the 30 wt.\% plasticizer samples were similar to those of the 20 wt.\% plasticizer samples shown in Figure 4). Hence the sWVTR and Cobb⁶₀
results were most likely not due to changes in the protein structure.

Peaks associated with glycerol and oleic acid were also studied in order to verify that both components existed at the surface of the WG layer (the IR beam penetration into the sample is of the order of a few μm, depending on the IR wavelength [19]). The IR showed that glycerol was indeed present at the surface, with peaks at 925 cm$^{-1}$ and at 850 cm$^{-1}$ assigned to the vibration of the C–C bond and a peak at 1117 cm$^{-1}$ related to the stretching of the C–O bond (data not shown) [20]. Oleic acid was readily observed by the presence of the characteristic peak at 1710 cm$^{-1}$ (attributed to the asymmetric stretching of the C=O bond [21]). Figure 5 shows data for the 20 wt.% plasticizer samples. The results were similar for the 30 wt.% plasticizer samples. Thus both components in the plasticizer mixture were present at the surface of the WG layer to various degrees depending on the mixing ratio.

3.5. Tensile Testing. The results of the tensile tests are shown in Figure 6 and summarized in Table 2. The presence of the WG layer reduced the elongation and energy at break of the paperboard. This was probably due to that, when the WG layer fractured, the sudden increase in the load carried by the paperboard made it fracture as well. However, the difference in extensibility between the uncoated paperboard and the sample with a WG layer containing 30 wt.% plasticizer with 75 wt.% OA was insignificant (Table 2). The sample with 20 wt.% plasticizer with 75 wt.% OA also had a relatively high extensibility. Both the stress at break and the modulus increased when the OA content increased from 0 to 50 wt.% and decreased thereafter. The strength of a few of the laminated samples and the stiffness of the 75 wt.% OA samples were similar to the corresponding values for the uncoated paperboard. Except for samples containing 75 wt.% OA, the difference in modulus, strain at break, and energy at break, between the 20 and 30 wt.% plasticizer samples, was insignificant. The variations in sample thicknesses could not explain the mechanical results since there were no clear trends among the samples (Table 2). Of particular interest was that the mechanical properties of the laminate did not become poorer when up to 50 wt.% OA was added to the glycerol plasticizer. At 75 wt.% OA, the laminates became weaker but on the other hand tougher (30 wt.% plasticizer) and more extensible. The stiffness also decreased but was still similar to that of the uncoated paperboard.

As a complement to the tensile test results, the fracture surfaces were studied with SEM (Figure 7). The paperboard exhibited a high strain to break through fiber pullout, whereas the board with a WG layer experienced a more brittle fracture. Clearly the lower strain at break of the coated paperboard was due to the gluten layer; a hypothesis is that the deformation of the paperboard was restricted by the gluten coating and that both layers were extended in parallel at the same rate, yielding smooth tensile curves. The higher strain at break for the 75 wt.% OA samples was probably due to poor adhesion between the paperboard and the WG layer and/or a weaker WG layer, fracturing more easily and allowing the paperboard to extend further. For the sample with 20 wt.% plasticizer (75 wt.% OA), the tensile curve showed discontinuities suggesting multiple fractures of the WG layer as the coated paperboard was deformed. This could be observed visually as crack development perpendicular to the tensile direction during the testing.

3.6. Gloss of the Laminated Paperboard. The optical appearance of the coating is often of importance. Gloss is a function of the surface refractive index, the extinction coefficient, the angle of incidence of the light beam, and the nature of the reflecting light. A surface with a gloss unit of 70 or greater at an incidence angle of 60° is considered to be a high gloss surface [22]. In this respect, none of the tested sample surfaces were considered to be highly glossy (Table 3). Since the angle of incidence and the nature of the incident light are constant and the two plasticizer components have similar refractive indices (glycerol: 1.47 [23] and oleic acid: 1.46 [24] at 20°C), differences in the extinction coefficient and/or the absorbed light should be the main parameters responsible for the observed variations in gloss. The haze index is related to, and increases with, the irregularity and heterogeneity of the surface. Interestingly the oleic acid-containing samples, despite the microscopic cracks, had a lower haze index than the sample containing glycerol, which is in agreement with the greater smoothness to the touch of the former samples (Table 3).

4. Conclusions

It is known that wheat gluten is a very good oxygen barrier under low-moisture conditions and with a small amount of plasticizer [14]. The results here show the potential of limiting also the water uptake and water vapor transmission rate by incorporating a more hydrophobic component into the hydrophilic plasticizer. This opens up for an interesting concept to create a fully renewable protein-based multilayer water and oxygen barrier WG layer on the outside of paperboard for dry foods. The outer water vapor barrier layer should have a more hydrophobic component (e.g., oleic acid) in the plasticizer (e.g., glycerol), whereas the inner oxygen barrier layer should contain only a small amount of the hydrophilic plasticizer. This concept would probably work not only for wheat gluten but also for other film-forming proteins such as zein and soy protein. Finally, it is important here to note that the laminate is not a “coated” paperboard in that we are here using thicker protein layers. It should rather be considered as a protein/paperboard laminate packaging concept where each layer contributes with important properties to the total, as well as to the adjacent, layer.

Acknowledgments

Vinnova, the Swedish Governmental Agency for Innovation Systems, and the “RenewFuncBarr” consortium are thanked for financial support.
References

[1] B. Lagrain, B. Goderis, K. Brijs, and J. A. Delcour, “Molecular basis of processing wheat gluten toward biobased materials,” Biomacromolecules, vol. 11, no. 3, pp. 533–541, 2010.

[2] T. O. J. Blomfeldt, R. T. Olsson, M. Menon, D. Plackett, E. Johansson, and M. S. Hedenqvist, “Novel foams based on freeze-dried renewable vital wheat gluten,” Macromolecular Materials and Engineering, vol. 295, no. 9, pp. 796–801, 2010.

[3] I. Olabarrieta, S. W. Cho, M. Gällstedt, J. R. Sarasua, E. Johansson, and M. S. Hedenqvist, “Aging properties of films of plasticized vital wheat gluten cast from acidic and basic solutions,” Biomacromolecules, vol. 7, no. 5, pp. 1657–1664, 2006.

[4] M. Gällstedt, A. Mattozzi, E. Johansson, and M. S. Hedenqvist, “Transport and tensile properties of compression-molded wheat gluten films,” Biomacromolecules, vol. 5, no. 5, pp. 2020–2026, 2004.

[5] N. H. Ullsten, M. Gällstedt, E. Johansson, A. Gräslund, and M. S. Hedenqvist, “Enhanced processing window of plasticized wheat gluten using salicylic acid,” Biomacromolecules, vol. 7, no. 3, pp. 771–776, 2006.

[6] S. W. Cho, M. Gällstedt, E. Johansson, and M. S. Hedenqvist, “Injection-molded nanocomposites and materials based on wheat gluten,” International Journal of Biological Macromolecules, vol. 48, no. 1, pp. 146–152, 2011.

[7] N. H. Ullsten, S. W. Cho, G. Spencer, M. Gällstedt, E. Johansson, and M. S. Hedenqvist, “Properties of extruded vital wheat gluten sheets with sodium hydroxide and salicylic acid,” Biomacromolecules, vol. 10, no. 3, pp. 479–488, 2009.

[8] J. Han, S. Salmieri, C. Le Tien, and M. Lacroix, “Improvement of water barrier property of paperboard by coating application with biodegradable polymers,” Journal of Agricultural and Food Chemistry, vol. 58, no. 5, pp. 3125–3131, 2010.

[9] B. Ş. Kayserilioglu, U. Bakir, L. Yilmaz, and N. Akkas, “Drying temperature and relative humidity effects on wheat gluten film properties,” Journal of Agricultural and Food Chemistry, vol. 51, no. 4, pp. 964–968, 2003.

[10] M. Vargas, A. Albors, A. Chiralt, and C. González-Martínez, “Characterization of chitosan-oleic acid composite films,” Food Hydrocolloids, vol. 23, no. 2, pp. 536–547, 2009.

[11] L. Fernández, E. D. Apodaca, M. Cebrián, M. C. Villarán, and J. I. Maté, “Effect of the unsaturation degree and concentration of fatty acids on the properties of WPI-based edible films,” European Food Research and Technology, vol. 224, no. 4, pp. 415–420, 2007.

[12] N. Gontard, S. Marchesseau, J.-I. Cuq, and S. Guilbert, “Water vapour permeability of edible bilayer films of wheat gluten and lipids,” International Journal of Food Science and Technology, vol. 30, no. 1, pp. 49–56, 1995.

[13] N. Gontard, C. Duchez, J.-I. Cuq, and S. Guilbert, “Edible composite films of wheat gluten and lipids: water vapour permeability and other physical properties,” International Journal of Food Science and Technology, vol. 29, no. 1, pp. 39–50, 1994.

[14] S. W. Cho, M. Gällstedt, and M. S. Hedenqvist, “Properties of wheat gluten/poly(lactic acid) laminates,” Journal of Agricultural and Food Chemistry, vol. 58, no. 12, pp. 7344–7350, 2010.

[15] M. Gällstedt, J. Törnqvist, and M. S. Hedenqvist, “Properties of nitrocellulose-coated and polyethylene-laminated chitosan and whey films,” Journal of Polymer Science, Part B, vol. 39, no. 10, pp. 985–992, 2001.

[16] S. I. Hong and J. M. Krochta, “Whey protein isolate coating on LDPE film as a novel oxygen barrier in the composite structure,” Packaging Technology and Science, vol. 17, no. 1, pp. 13–21, 2004.

[17] C. M. Hansen, Hansen Solubility Parameters: A User’s Handbook, CRC Press, Boca Raton, Fla, USA, 2000.

[18] T. O. J. Blomfeldt, R. Kuktaite, E. Johansson, and M. S. Hedenqvist, “Mechanical properties and network structure of wheat gluten foams,” Biomacromolecules, vol. 12, no. 5, pp. 1707–1715, 2011.

[19] M. S. Hedenqvist, M. Krook, and U. W. Gedde, “Two-stage sorption in rubbery semicrystalline polymers: transport of primary alcohols in polysteramide,” Polymer, vol. 43, no. 10, pp. 3061–3068, 2002.

[20] P. Guerrero, A. Retegi, N. Gabilondo, and K. De La Caba, “Mechanical and thermal properties of soy protein films processed by casting and compression,” Journal of Food Engineering, vol. 100, no. 1, pp. 145–151, 2010.

[21] L. Zhang, R. He, and H. C. Gu, “Oleic acid coating on the monodisperse magnetite nanoparticles,” Applied Surface Science, vol. 253, no. 5, pp. 2611–2617, 2006.

[22] J. W. Lee, S. M. Son, and S. I. Hong, “Characterization of protein-coated polypropylene films as a novel composite structure for active food packaging application,” Journal of Food Engineering, vol. 86, no. 4, pp. 484–493, 2008.

[23] L. F. Hoyt, “New table of the refractive index of pure glycerol at 20°C,” Industrial & Engineering Chemistry Research, vol. 26, no. 3, pp. 329–332, 1934.

[24] F. F. De Sousa, S. G. C. Moreira, S. J. D. S. Da Silva, J. Del Nero, and P. Alcantara, “Dielectric properties of oleic acid in liquid phase,” Journal of Bionanoscience, vol. 3, no. 2, pp. 139–142, 2009.
