Properties of Whey-Protein-Coated Films and Laminates as Novel Recyclable Food Packaging Materials with Excellent Barrier Properties

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In case of food packaging applications, high oxygen and water vapour barriers are the prerequisite conditions for preserving the quality of the products throughout their whole lifecycle. Currently available polymers and/or biopolymer films are mostly used in combination with barrier materials derived from oil based plastics or aluminium to enhance their low barrier properties. In order to replace these non-renewable materials, current research efforts are focused on the development of sustainable coatings, while maintaining the functional properties of the resulting packaging materials. This article provides an introduction to food packaging requirements, highlights prior art on the use of whey-based coatings for their barriers properties, and describes the key properties of an innovative packaging multilayer material that includes a whey-based layer. The developed whey protein formulations had excellent barrier properties almost comparable to the ethylene vinyl alcohol copolymers (EVOH) barrier layer conventionally used in food packaging composites, with an oxygen barrier (OTR) of <2 cm³(STP)/(m²d bar) when normalized to a thickness of 100 μm. Further requirements of the barrier layer are good adhesion to the substrate and sufficient flexibility to withstand mechanical load while preventing delamination and/or brittle fracture. Whey-protein-based coatings have successfully met these functional and mechanical requirements.

1. Introduction

High demands are put on packaging material, especially in the food industry, in order to preserve the quality of the packed good throughout its lifecycle. Protection against oxygen is one determining factor that guarantees the maximum shelf life of food products [1].

The requirements of packaging material are specific to the type of food to be packed; materials need to fulfil different needs in terms of light, moisture, water vapour, and gas barriers. Appropriate levels of oxygen and carbon dioxide, packing atmosphere, and respiration rate have to be taken into account to optimally preserve the packed food, avoid colour or taste deviation, oxidation of grease, formation of microorganisms, damaging of nutrients, and so forth [2, 3]. Figure 1 summarizes and quantifies the barrier requirements of selected food and pharmaceuticals [4].

To achieve these requirements, expensive multilayer coextruded or laminated plastic films are widely used in the packaging industry in order to combine the respective technofunctional properties the polymers [2, 5–7]. These films often make use of ethylene vinyl alcohol copolymers (EVOH) to create a sufficient oxygen barrier. Polymers used for those applications are petroleum based and their combination
in various layers hampers recyclability as monomaterials of high purity are needed for reprocessing [8]. Thus, research into sustainable packaging materials that maintain the performance of composite structures has recently intensified. The current study (WHEYLAYER project, http://www.wheylayer.eu/) is a research project targeted at developing sustainable packaging solutions. As the whey-protein-coatings are biodegradable, the resulting multilayer films can offer greatly improved recyclability. Furthermore, as opposed to many renewable materials, which normally do not provide sufficient barriers, the whey protein coating has the potential to extend the shelf life of food by virtue of its intrinsic barrier properties against gases like oxygen [9–12].

Among proteins that could be used in the field of packaging, especially for food sensitive to water and gas permeation, whey is one of the most promising. Whey is a byproduct of cheese manufacturing that contains approximately 7% dry matter. In general the dry matter includes 13% proteins, 75% lactose, 8% minerals, about 3% organic acids, and less than 1% fat. Whey protein can be separated and purified from the liquid whey in an efficient membrane filtration process and subsequent spray drying to obtain either Whey Protein Concentrate (WPC, average protein concentration 65–80% in dry matter) or Whey Protein Isolate (WPI, highly pure grade with concentrations over 90% in dry matter). In general these whey proteins are used as additives in the agrofood industry, such as the athletic drinks [12]. Nevertheless, whey is in abundant supply; data from the International Whey Conference 2008 shows that 40% of the 50 million tonnes of whey produced annually in Europe are still unprocessed, which makes it an interesting resource in view of its excellent oxygen barrier properties [13].

Whey protein coatings were already tested as edible films on, among others, peanuts, salmon, fruits, or cereals, whereby whey coating offered good aroma, fat, humidity, and oxygen barriers. It could be shown that they helped to improve the shelf life of, for example, peanuts, by retarding the lipid oxidation causing rancidity [14]. In addition, those edible films were reported not to modify the sensory attributes of the coated good or its aspect, while providing some health benefits for the consumer [15].

Numerous authors have reported potential uses for whey protein in the packaging field, emphasizing in particular its good barrier properties, especially for its use as a coating on paper [16, 17], but also on plastic substrates [18–22]. Indeed, whey coatings on polypropylene (PP), polyvinylchloride (PVC), and low-density polyethylene (LDPE) demonstrated excellent visual properties, such as excellent gloss and high transparency, as well as good mechanical properties [17, 23].

Finally, it was also shown that it was possible to process whey-based formulations for packaging applications and edible coatings through extrusion as well as compression molding. Research has shown the importance of suitable conditions to control denaturation and cross-linking as well as the benefits of whey mixed with other plant proteins [15, 24, 25].

However, the incorporation of plasticizing agents was generally reported as necessary to overcome the intrinsic brittleness of whey protein coatings [10, 14]. Glycerol and sorbitol were commonly used plasticizers for this purpose [14, 18, 26]. Plasticizers enhance the mobility of polymer chains through an increase in intermolecular spacing and thus lead to films with enough flexibility to keep their integrity once applied and subsequently formed. However, use of plasticizers has the disadvantage of lowering barrier properties [14, 22, 27].

Whey proteins can be hydrolyzed by different enzymes, such as protease, in specific conditions [15]. Similarly, the present study confirmed, in the case of multilayer configuration, that resulting coatings could be biodegraded using enzymatic detergent [22, 28]. This makes multilayer
films recyclable, since the separation of the layers made up of conventional petroleum-based plastics and associated by the whey-based layer is facilitated, enabling them to be handled separately. As an alternative, the multilayer packaging incorporating a whey-based barrier layer can be composted when using biodegradable polymeric substrates. Overall, use of whey-based layers could reduce CO2 emissions and consumption of resources in packaging production [28].

2. Materials and Methods

2.1. Materials. Whey protein isolate (WPI), BiPro of Davisco Foods International (Le Sueur) (dry protein pureness 97.4%; N × 6.38), was used for formulating the whey-based coatings in the present study. Glycerol and sorbitol used as plasticizer were supplied by Merck Schuchardt OHG (Hohenbrunn) and Merck KGaA (Darmstadt), respectively. Polyethylene terephthalate (PET) films of 50 μm and 12 μm thickness (Melinex of DuPont Teijin Films, SA) were used as substrate for whey protein coating application. Resulting coated films were laminated with polyethylene (PE) film of 20 μm thickness as a sealing layer, with Liofol UK 3640/UK 6800 by Henkel KGaA (Düsseldorf) used as an adhesive.

2.2. Formulation Preparation. Besides using BiPro, different types of whey proteins were isolated by membrane filtration in order to obtain pure whey protein with suitable film-forming properties. Various modification techniques, like chemical modification, enzymatic hydrolysis, and high-pressure treatment were evaluated to improve film-forming behaviour [13].

As shown in the literature [9, 13, 20, 22, 25, 29, 30], the denaturation of the proteins is essential to achieving the necessary barrier properties. Denaturation leads to a protein network via disulphide bonds, hydrogen bonds, and hydrophobic and electrostatic interactions, which furthermore allows the formation of proper whey protein films [15, 31].

Thus, standard denatured protein formulations were prepared by heating aqueous WPI solutions (10% w/v) to 90°C for 30 min (above their denaturation temperature of around 58–60°C as measured by DSC) using an electronic stirrer with heating, Thermomix 31-1, from Vorwerk Elektrowerk GmbH & CoKG (Wuppertal). After cooling the solutions to room temperature in a water bath, glycerol (66.7% on dry matter, dm) or sorbitol (100% on dm) was added and stirred for another 30 min (at 200 rpm). Degassing was performed via ultrasonication in each stage.

2.3. Coating and Curing. The WPI coating formulations were applied on corona pretreated PET films (thickness 12 μm; surface energy > 40 mN/m). At lab scale, a control coater, Erichson GmbH & CoKG (Hemer), was used to apply the solution evenly at a speed of 4 m/min. Depending on the kind of grooved rod used, film wet coating thicknesses varying between 10 and 30 μm were achieved. Coated polymer films were dried in an oven, Kelvitrone T 6120 from Heraeus Thermo Electron Corporation (Langenselbold), at 105°C for 10 min.

Pilot plant trials were performed on a lacquering and laminating plant. Corona-discharge-treated PET films (12 μm) were coated with whey protein solution by use of a comma bar roller coaster system and laminated with PE (20 μm). Whey protein layers of up to 10 μm could be achieved.

2.4. Fast Screening of Formulations Based on Mechanical and Optical Properties. The properties of coated films were characterized using a light microscope, Diplan of Leitz (Incident light; 200-fold zoom-in), in terms of aspect (transparency), brittleness, scratch resistance, and surface finish after mechanical stress. Therefore, a method according to a rating scale was implemented. The 4 criteria were rated according to 5 levels (5 = best result). For each formulation investigated for performance, films of 40 × 15 mm were prepared. In order to analyze resistance of the coating against mechanical stress, one piece of each film was twisted about-face (180°) four times. For analysis of scratch resistance, films were scratched 7 times using a standardized brush (angle approximately 40°). Samples were then analyzed regarding scratches or damage and classified according to the aforementioned rating scale.

2.5. Thermomechanical Properties. For the Dynamic Mechanical Thermal Analysis (DMTA), the samples coated and uncoated (coating removed by biodegradation) were used to evaluate the elastic modulus of the total structure and of the substrate.

The width of the sample was 10 mm and the thickness varied for each sample. The load cell used was 100 N and a pretension was applied. The temperature scans were carried out from 0 to 250°C with a heating rate of 5°C/min and a frequency of 1 Hz.

2.6. Adhesion. The bond strength measurement method measures the interlaminar strength that keeps together two different surfaces and was applied to the laminate samples (PET/WHEY_LAYER/Adhesive/PE). The equipment is composed by the same machine and the same clamps used as those for the common tensile and tear test (sample holder according to EN ISO 4624 and EN ISO 527-1). For each test, two samples with dimensions of 100 mm per 15 mm were prepared and cut according to either the machine or the transverse direction. The two surfaces were then supposed to split up for a length of 40 mm and be kept in constant conditions of 23°C and 50% relative humidity. The ends of the samples were positioned into the clamps of the tensile machine and the bond strength was measured. The number of the sample for each trial was more than 10 to ensure statistically reliable results.

In addition to that, the adhesion between the whey layer and the substrate was measured according to the International Standard EN ISO 4624:2002, paints, varnishes and plastics (pull-off test). This standard evaluates the adhesion/cohesion of a single or a multilayer coating system
2.7. Optical Properties. Film transparency is known to be an important feature for the packaging industry. First, qualitative evaluation was done visually using human cognition; this was then complemented by the quantitative measurement of light transmittance of the films using the spectral photometer PMQ 3 Carl Zeiss (Grosskuchen) with a wavelength of 600 nm (to correlate with the visible eye perception).

2.8. Barrier Properties. Oxygen permeability of PET films coated with the previously described whey-based formulations was measured according to DIN 53380-3 (DIN, 1998) at 23°C and 50% RH using an Ox-Tran 2/20. The coated side of the films was exposed to flowing oxygen gas and the other side to flowing nitrogen gas. Resulting oxygen permeability of multilayer films was deduced in terms of cm³/m²·d·bar and used for further calculations regarding permeability of the single whey protein layer. A WPI-coated polymer film can be considered as a 2-layer-structure, comparable to a laminated material [9, 17]. The following equations can be used:

\[
\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2},
\]

\[
\frac{1}{Q_{tot}} = \sum \frac{d_i}{P_i} = \frac{1}{Q_1} + \frac{1}{Q_2} + \frac{1}{Q_3} + \ldots,
\]

where \(d\) represents the thickness of each layer, \(i\) \((d = \Sigma d_i)\) and \(P\) is the oxygen permeability of each layer. Subscript 1 stands for the polymer film and subscript 2 for the WPI coating on the surface.

Oxygen permeability values of whey-based coatings are converted to a thickness of 100 μm \((Q_{100})\) in order to allow direct comparison of different materials independently of the coating thickness. Film thicknesses were measured with the instrument Mahr Millimar C1216 of Mahr GmbH (Göttingen) after oxygen transmission tests. WPI coating thickness was calculated by subtracting the base for PET film. Five random positions on the film were measured and averaged.

3. Results and Discussion

3.1. Fast Screening of Formulations. In light of the prior art previously reported, the whey-based layer formulations were developed in order to reach the best compromise between barrier properties and flexibility [9–11, 17, 21, 31–33]. As mentioned in Section 2, different types of whey protein were used and formulated with variable amounts of different additives (marked w1–w12 in Table 1 and Figure 2).

The nature and amount of plasticizer were varied in order to obtain films with good integrity and flexibility while containing as little plasticizer as possible so as not to jeopardize barrier performance. The film properties, as assessed through the previously explained rating scale in terms of the 4 criteria of interest, are reported in Figure 2. Aside from w6 and w12, the scratch resistance of the formulations tested is rather low, but such a coating may still be suitable as an intermediary layer in a multilayer configuration. This analysis resulted in the determination of the most suitable formulations for the target and for further testing.

3.2. Optical Properties. The transparency of the films was measured by light transmittance using the spectral photometer PMQ 3 Carl Zeiss (Grosskuchen). The transmittance spectrum was recorded over the whole wavelength range \((250–1000\ \text{nm})\). As shown in Figure 3, no difference in light transmittance was observed between pure PET and coated PET (over the whole spectrum and especially at 600 nm). All the samples reached a transmittance over 90% and appeared transparent, even though a slight haze could be recognized by the eye.

3.3. Thermo-Mechanical Properties. Isolating the value of the elastic modulus of PET and considering its contribution in the modulus of the total structure made it possible to calculate the Young’s Modulus of the coating. The Young’s Modulus, \(E\), of the whey-based layer was determined applying the theory of composite materials in “isodeformation conditions” [34]; the load applied during the DMTA analysis on the coated sheet leads to a uniform deformation on the different layers of the material and the interface between the two different layers remains unchanged. Using the “rule of the mixtures of binary composites,” it is possible to calculate...
the elastic modulus of a composite material when the elastic modulus of the matrix and the fibres and their volume fractions are known.

Thus, the DMTA tests allowed the modulus of the whey-based layer to be calculated. The tests showed that the layer is much stiffer than the substrate used and it is possible to observe that it contributes to increasing the rigidity of the coated film (Figure 4). The high stiffness of the whey-based layer could be related to the high cross-linking density of the structure formed by the proteins.

3.4. Adhesion. Using the laminate bond strength method, it was not possible to separate the layers since the substrate (PET) broke at 5.5–6 N/15 mm earlier. Therefore the adhesion measurement method according to the International Standard EN ISO 4624:2002 (pull-off test) was performed.

Results of the pull-off test showed that whey-based coating displays excellent adhesion to the corona pretreated substrates on which it was applied. Resulting peeling forces were over the standard and only cohesive failures in the substrates were observed, as opposed to adhesive fractures at the whey-based layer/substrate interface. The two surfaces separated at the level of coextruded PET and thus appeared clear and shiny. The average value of strength $\sigma$ was 15 N/mm².

3.5. Barrier Properties. As expected, it was shown that formulations with higher plasticizer content had lower barrier properties.

Indeed, due to the increase of the mobility of the polymer chains between cross-links, diffusion coefficient $D$ and solubility coefficient $S$ increase. Consequently, the permeation coefficient, as defined in (2) below, also increases:

$$P = D \cdot S. \tag{2}$$

This directly influences the permeability of the polymer, which is directly proportional to the diffusion coefficient, as described by

$$Q = \frac{P}{d}. \tag{3}$$

Nevertheless, with the optimum plasticizer content and for the formulation selected according to the previously
4. Conclusion

For the optimized whey-based formulations developed in the present study, their high transparency without surface defect, temperature stability, mechanical performance, and flexibility, along with their adhesion on the substrates, made them suitable for packaging applications. A whey protein layer is able to serve as a good oxygen barrier and can either be used as an upper layer or as a sandwich layer in a composite, as the lamination tests showed it is possible to obtain proper composites with whey-protein-coated polymer films. Depending on its position in the multilayer, the whey-based layer (seal or interim layer) has to meet different demands. Therefore a suitable formulation can be chosen according to factors such as the packed good, product shelf life, or consumer demands. Whey proteins are thus a promising resource for the packaging industry in that they provide a sustainable, recyclable packaging material that meets all the performance requirements of packaging materials.

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