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Whey protein layer applied on biodegradable packaging film to improve barrier properties while maintaining biodegradability

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A B S T R A C T

The aim of the present study was to verify that a whey protein-based layer can improve oxygen barrier properties of commercial compostable plastic film, while not hindering the biodegradability of the compostable film as well as not affecting the quality of the compost. The whey protein-based coating was applied on a biodegradable commercial film certified to meet the requirements of EN13432. Oxygen barrier properties were significantly improved by the presence of the whey protein layer. This result is particularly important since biodegradable packaging generally lack in maintaining barrier properties and the use of not degradable materials to improve barrier to gas and water vapour compromises the composting of the final packaging. In addition to that, it was important to assess the biodegradability of the whey protein layer itself since natural polymers may became not degradable if cross-linked or blended with not degradable additives. The material based on denatured whey protein and plasticizer presented fast biodegradability even after application on the commercial film. These positive results have potential to be used in new cost effective and ecological food packaging designs.

1. Introduction

In packaging protection and safety of the product are very important since the packed food product binds significantly more resources than its packaging and insufficient protection of the product leads to the spoilage of food which causes much higher CO_2 emissions than the reduction of packaging material could save [1]. For several sensitive food packaging applications, a high gas and water vapour barrier are the prerequisite conditions for preserving the quality of the products throughout their lifecycle, from manufacturing to consumption. These performances are commonly achieved by the utilization of multilayers films.

Nevertheless combination of different polymers in various layers hampers recyclability as mono-materials of high purity are needed for reprocessing. In addition to that, these polymers are neither renewable nor biodegradable [2,3]. For example a commonly used barrier polymer is ethylene vinyl alcohol (EVOH) which provides high oxygen barrier properties when incorporated in multilayer structures for food packaging applications in order to protect oxygen sensitive food products. In order to replace non renewable materials with low carbon footprint materials, current research actions are focused on the development of systems based on natural polymers such as proteins, both from animal [4–6] and vegetal sources [7–9].

Proteins have been evaluated for applications in the field of packaging, since they can be converted using versatile process options, and additives [4,10], and present appropriate barrier properties to water and gas permeation. Several studies have been published on the use of whey protein for application in packaging

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and it resulted very promising as barrier to moisture and oxygen [11–20], in particular after a denaturation process [21] or in blends with other polymers [22]. Whey is a by-product 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. Worldwide about 180 to 190 $\times$ 10^6 tons of whey are produced every year but only 50% is further processed [23].

Whey protein-based coating combines high barrier properties and good processing when blended with appropriate plasticizers such as polyols [24,25], and thus is suitable to act as part of new eco-efficient food packaging concepts.

The time when whey was considered as only a waste product is long gone. But only 50% of the accruing cheese-whey is treated and transformed into different food and feed products whereby about half of this amount is utilized in liquid form, 30% as powdered cheese-whey, 15% as lactose and its by-products and the remaining as whey protein concentrates or isolates [26,27].

Whey protein can be separated and purified from the liquid whey in an efficient membrane filtration process followed by spray drying to obtain either Whey Protein Concentrate (WPC, protein concentration 65–80% in dry matter), or Whey Protein Isolate (WPI, protein concentrations over 90% in dry matter).

A number of authors have also reported the good barrier properties of whey proteins based coating on paper and on plastic substrates [28–30]. Previous studies of application of whey based layer in multi layers films based on polyethylene terephtalate and polyethylene, have outlined that the whey layer is able to achieve superior barrier properties compared to other bioplastics and approached those of synthetic barrier layers, such as ethylene vinyl alcohol (EVOH) [31].

The present research addresses a preliminary development and assessment of a completely biodegradable packaging solution combining whey proteins based coatings with commercial biodegradable films based on blends of co-polyester and poly lactic acid (PLA). Indeed while PLA blends allows the formation of biodegradable films and foils, its potential to substitute, for example polyolefin films, could be increased using whey based formulations to improve PLA's resistance to gas permeation which, among PLA functionalities, is often the limiting factor for packaging applications. The combination of a carrier film such as PLA with a whey protein-based coating as coated film is promising and relevant for the compatibility studied here. Such bi-layers could be further laminated in order to create final laminates for real industrial applications.

Furthermore, it is well known that protein layers cannot be used in packaging applications as standalone films due to their brittleness, which can be tackled by the use of plasticizers or blends with other polymers and their water sensitivity, which can be addressed by crosslinking or using them in a sandwich configuration [32–39]. Modification of natural materials such as denaturation, blending with additives, crosslinking etc can affect the final biodegradability of the resulting protein-based material. It was thus important to assess that the layer of whey protein was not affecting the compostability of the final material.

2. Experimental

2.1. Materials and preparation

Multi layer films were produced using as substrate a commercial film under the trade name Bio-FlexR F 2110 (prev. Bio-FlexR 467F) provided by FKuR Kunststoff GmbH, Willich, Germany, of thickness 58 μm. The BIO-FLEX® trade name indicates blends of co-polyester and PLA CAS 9051–89–2, this film is hereafter referred to as PLA.

The aqueous coating solution used for testing, and hereafter referred to as Whey, mainly comprises whey protein isolate (WPI) BiPro (10 wt% in aqueous solution) of Davisco Foods International (Le Sueur, MN, USA) (dry protein pureness 97.4%; N $\times$6.38). Sorbitol, supplied by Merck KG (Darmstadt, Germany), was used as plasticizer at 100 wt% based on protein content in the aqueous solution and mixed with the denatured whey protein solution as reported elsewhere [13,40,41].

The layer of whey protein was coated onto the substrate film using an A4-A3 sample size control coater of Erichson GmbH & Co. KG, Hemer, Germany. The Whey dry coating thickness was 10 μm leading to a total laminate structure (PLA/Whey) thickness of 68 μm.

The films were dried at 23 °C and 50% RH until the samples reached the equilibrium moisture content at the given temperature and humidity but at least for one week. These samples were used for measurements of permeability, mechanical properties and degradation.

2.2. Methods

Oxygen permeability of the substrate and the coated PLA/Whey films were measured according to DIN 53380-3 (DIN, 1998) at 23 °C and 50% RH using an Ox-Tran 2/20 (Mocon Inc., Minneapolis, MN, USA). 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 $cm^3 (STP)\cdot m^{-2}\ d^{-1}\ bar^{-1}$ and used for further calculations regarding permeability of the single whey protein layer. A Whey-coated polymer film can be considered as a 2-layer-structure, comparable to a laminated material [14,26]. The following equations (1) and (2) can be used:

$$\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \quad (1)$$

$$\frac{1}{Q_{tot}} = \sum \frac{d_i}{P_i} = \frac{1}{Q_1} + \frac{1}{Q_2} + \frac{1}{Q_3} + \ldots \quad (2)$$

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 Whey layer 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 according to the following equation (3).

$$Q_{100} = Q * (d/100) \quad (3)$$

Film thicknesses were measured with the instrument Mahr Millimar C1216 of Mahr GmbH (Göttingen, Germany) after oxygen transmission tests. The thickness of the whey layer coating was calculated by subtracting the base for PLA film. Five random positions on the film were measured and averaged.

Samples of PLA films and PLA/Whey films were stamp cut in dog bone shaped specimen: 11.5 cm length, 2.5 cm wide; 4.0 cm neck length, 0.6 cm neck wide and used for tensile tests with an Instron 4302 tensile machine (Instron, Norwood, MA, USA), 1 kN cell Load, running at 10 mm/min.

Scanning electron microscopy (SEM) was a JEOL JSM-5600LV (Tokyo, Japan), samples were gold sputtered before the analysis with an Edwards Sputter Coater (Edwards Ltd., Crawley, England).

Film samples with PLA and Whey were analysed for total organic carbon (TOC) content by a modified method of EN13137 (coulometric). The carbon dioxide released by the combustion in