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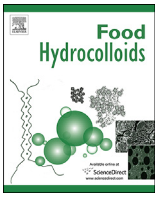

Whey protein-coated high oxygen barrier multilayer films using surface pretreated PET substrate

Eunmi Joo [a, 1], Yoonjee Chang [b, 1], Inyoung Choi [a], Seul Bi Lee [c], Dong Hoo Kim [d], Young Ju Choi [c], Chan Suk Yoon [d], Jaejoon Han [a, b, *]

[a] *Department of Biotechnology, College of Life Sciences and Biotechnology, Korea University, Seoul, 02841, Republic of Korea*
[b] *Department of Food Bioscience and Technology, College of Life Sciences and Biotechnology, Korea University, Seoul, 02841, Republic of Korea*
[c] *EverChemTech Co., Ltd., #313, 314, Human Sky Valley, 959, Gosaek-dong, Gwonseon-gu, Suwon-si, Gyeonggi-do, Republic of Korea*
[d] *Agency for Korea National Food Cluster (AnFC), Iksan, 570-749, Republic of Korea*

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ABSTRACT

Whey protein isolate (WPI)-coated multilayer films were developed using polyethylene terephthalate (PET) film as a substrate. To improve the interfacial compatibility between PET film and water-based WPI coating solution, various surface pretreatments (corona discharge, plasma, and primer coating) were applied to PET. Water contact angles of the plasma-treated PET were significantly decreased by 12.8% related to the untreated PET, suggesting an increment of hydrophilic functional groups. Oxygen transmission rates of surface-pretreated multilayer films with WPI coating layer [PET/WPI/nylon/linear low-density polyethylene (LLDPE)] were significantly lower, about 43–234 times, than the multilayer films without WPI film layer. In addition, tensile strength of the plasma-pretreated PET/WPI/nylon/LLDPE films was 13.4 and 21.8% higher, elongation at break was 29.7 and 2.6% higher than the corona discharge- and primer-pretreated films, respectively. Taken together, WPI films are promising candidates for replacing synthetic oxygen-barrier materials. Specifically, plasma-pretreated PET/WPI/nylon/LLDPE films have a high potential as high oxygen-barrier packaging materials.

1. Introduction

In recent years, oxygen-barrier films have become increasingly important in the food packaging industry. They are used to extend the shelf life of foods and to prevent food deterioration owing to problems such as lipid rancidity, microorganism growth, enzymatic browning reaction, and vitamin reduction (Bonilla, Atares, Vargas, & Chiralt, 2012; Yang & Paulson, 2000). To prevent food quality degradation due to the oxygen inflow, multilayer films composed of various polymers have been developed (Kurek et al., 2012). In food packaging materials, typical oxygen-barrier films made of synthetic polymers such as ethylene vinyl alcohol and polyvinylidene chloride are known to create excellent barriers. However, these synthetic barrier materials are relatively expensive and difficult to separate for recycling (Hong & Krochta, 2004; Scherzer, 1997; Tihminlioglu, Atik, & Ozen, 2010). Moreover, synthetic polymers release large amounts of carbon dioxide (CO_2) during incineration, whereas biopolymers produce lower amounts of CO_2 and are capable of rapid degradation (Mulhaupt, 2013). For these reasons, sustainable and alternative natural packaging materials are needed to be developed. Therefore, biological macromolecules such as carbohydrates, proteins, and lipid-based materials have been considered in the packaging and bioplastic industry.

Whey protein, a by-product of cheese production, has a high potential as a film-forming agent. Whey is a complex mixture of globular protein molecules comprising β-lactoglobulin (~50 wt %), α-lactalbumin (~20 wt %), immunoglobulins (~10 wt %), and bovine serum albumin (~6 wt %) and other minor protein or peptide components including lactoferrin, lactoperoxidase, lysozyme, and growth factors (Anandharamakrishnan, Rielly, & Stapley, 2008). WPI, one of the most important whey protein products, is a commercial powder with a high protein content (>90 wt %) normally

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Abbreviations: WPI, whey protein isolate; PET, polyethylene terephthalate; LLDPE, linear low-density polyethylene; EAA, ethylene-acrylic acid; LDPE, low density polyethylene; WCA, water contact angle; FTIR-ATR, Fourier-transform infrared with attenuated total reflection; OTR, oxygen transmission rate.

[*] Corresponding author. Department of Food Bioscience and Technology, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea.

E-mail address: jjhan@korea.ac.kr (J. Han).

[1] E.J. and Y.C contributed equally to this work.

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manufactured by ion exchange chromatography or microfiltration, followed by spray drying (Foegeding, Davis, Doucet, & McGuffey, 2002). Whey protein-based films have received increasing attention as they can be importantly used in the food packaging industry. Whey protein-based films have not only functional benefits of transparency, flexibility, lack of color, and lack of odor but also outstanding oxygen and aroma-barrier properties (Galietta, Di Gioia, Guilbert, & Cuq, 1998; Peelman et al., 2013).

Most industrial synthetic polymers are low-surface-energy (low wettability) materials and have hydrophobic surfaces. Therefore, it is very difficult to apply water-based coatings directly on such synthetic polymers. Modification of polymer surfaces for coating application by increasing their surface energy is important (Awaja, Gilbert, Kelly, Fox, & Pigram, 2009; Kostov et al., 2010). Many attempts have been made to modify polymer surfaces by using methods such as corona discharge, flame, plasma, and chemical treatments (Hong & Krochta, 2004). Plasma treatment has been widely used to synthetic polymers for improving their compatibility with surface coating materials. Through the interaction between surface and active species (excited atoms, electrons, photons, and free radicals) generated by discharges at plasma treatment, the chemical and physical modifications of polymeric plastic surfaces are performed and the modified surfaces become more reactive without losing any of their inherent characteristics. Plasma active species are combined with oxygen in air, and oxygen-containing functional groups formed on the polymeric surface lead to increase surface energy (De Geyter et al., 2008; Kostov et al., 2010; Wei, 2004). Corona discharge treatment is a surface modification technique used to treat polymeric plastic surfaces to improve their adhesive bonding, ink printability, lamination to other polymers, and wettability from the viewpoint of coating application. Surface energy, which is generated by surface oxidation and introduction of polar functional groups (phenolic hydroxyl, carbonyl, and carboxyl functionalities), was increased through corona discharge treatment (O'Hare et al., 2002). To form new functional groups on polymeric plastic surfaces, corona discharge treatment has been used conventionally. As the surface polarity increases, intermolecular forces and adhesion strength between layers' increase (Awaja et al., 2009).

Pretreatment of polymeric plastic surfaces with solvent-based primers has been attempted to improve their adhesion property. The ethylene-acrylic acid (EAA) primer solution is useful and commercially available with various acrylic acid contents, and can be used in various industrial fields. A copolymer of ethylene and acrylic acid represents combined characteristics from both of polyethylene and acrylic acid. Moreover, it is chemically resistant to organic solvents by polyethylene and widely used for preparing plastic films and for coating applications. Because it is substantially soluble in the polyethylene phase, this copolymer solution acts as an adhesion promoter. The carboxylic acid groups (–COOH) of acrylic acid act as reaction sites (Scaffaro, La Mantia, & Castronovo, 2004; Walters & Hirt, 2006).

Generally, multilayer films are used as food packaging materials rather than single films. Also, the structure of the polyethylene terephthalate (PET)/WPI/nylon/linear low-density polyethylene (LLDPE) multilayer film was designed to be similar to one of the packaging multilayer films commonly used in the food industry (PET/nylon/LLDPE). Based on the PET/nylon/LLDPE packaging system, WPI layer was added because of its high oxygen-barrier properties. Studies on the manufacture of multilayer films by applying protein-based coatings as oxygen-barrier materials have been reported. Bae et al. studied the potential of PET/fish gelatin-nanoclay composite/low density polyethylene (LDPE) laminate films (Bae, Park, Darby, Kimmel, & Whiteside, 2009). Schmid et al. (2012) reported the excellent barrier properties of whey protein-coated laminated films manufactured at a semi-industrial scale. Moreover, Shin et al. (2002) reported the fabrication of LLDPE/corn zein/ethylene vinyl acetate and LLDPE/chitosan/ethylene vinyl acetate films through plasma source ion implantation. However, multilayer plastic films manufactured by using various surface treatment methods and their comparative studies have not yet been investigated.

This study aims to develop the high oxygen-barrier multilayer films with WPI coating layer (PET/WPI/nylon/LLDPE) using PET film as a substrate and to improve compatibility of the developed films with water-based coating of WPI by applying three types of surface treatments (corona discharge, plasma, and primer coating) to hydrophobic PET film. The resulting films were investigated in terms of (1) change in wettability of PET films, (2) surface structure of the surface-pretreated PET films with WPI coating layer (PET/WPI), and (3) oxygen transmission rate (OTR), surface morphology, and mechanical properties of PET/WPI/nylon/LLDPE films.

2. Materials and methods

2.1. Materials

Commercial WPI with protein content of >90% (Hilmar 9410, Hilmar Ingredients, Hilmar, CA, USA) was used as the film-forming matrix. Sorbitol obtained from Sigma-Aldrich (St. Louis, MO, USA) was used as a plasticizer to overcome WPI film brittleness. A commercial PET film (thickness = 12 μm; Hyosung Inc., Seoul, Korea), nylon film (thickness = 15 μm; Hyosung Inc., Seoul, Korea), and LLDPE film (thickness = 70 μm; Dae Ryung Precision Packaging Industry Co., Ltd., Gwangju, Korea) were used to manufacture the proposed multilayer film with WPI coating layer.

2.2. Preparation of WPI coating solution

Dispersion stability of the WPI coating solution was adjusted by pH alteration and thermal cross-linking. These adjustments affect the final structure and function of WPI films. The WPI coating solutions were prepared by dissolving 40 g of WPI powder in 450 ml of distilled water. Finally, 40 g of sorbitol were added to this mixture as a plasticizer. To achieve complete aqueous dispersion of WPI, 10 ml of 1 N sodium hydroxide (NaOH) was added to the mixture to increase its pH from 7 to 9. The WPI coating solution was stirred at a constant speed of 300 rpm by using a mechanical stirrer, and simultaneously heated from room temperature to 90 °C by using a heating mantle. After heating for 30 min at 90 °C, the WPI coating solution was cooled to room temperature and filtered using a sieve with mesh sizes of 125 μm to remove impurities.

2.3. Surface treatments

2.3.1. Corona discharge treatment

Commercial corona discharge-treated PET films measuring 12 μm in thickness were obtained from Hyosung Inc. (Seoul, Korea). Corona discharge treatment has been widely applied to various synthetic polymers and plastic films for the purpose of their good adhesion property as to modify surface by electrical discharge. PET films were subjected to corona discharge using a Bare Roll Corona treater device (Enercon Industries Co., Menomonee Falls, WI, USA). The device generator was equipped with the Insulated gate bipolar transistor (IGBT) output amplifier and an automatic control of the frequency in 20 kHz. The gas flow rate was 20 ml/min.

2.3.2. Plasma treatment

PET films (non-corona discharge-treated, 12 μm thickness; Hyosung Inc.) were prepared for plasma treatment which was