



Influence of colloidal silica nanoparticles on pullulan-coated BOPP film



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ABSTRACT

The influence of two different types of colloidal silica (CS) nanoparticles in a main pullulan coating on bi-oriented polypropylene (BOPP) was evaluated in this work with the goal of exploring new and more advantageous applications in the food packaging sector. It was observed that the addition of the nanoparticles did not affect the friction properties of the pristine pullulan coating, with the static and kinetic coefficient mean values being 0.35 and 0.22, respectively. An improvement in the barrier properties against O₂ and CO₂ was observed for all the tested nanocomposite coatings. The best performance was provided by the particles with the highest surface area (750 m² g⁻¹) (O₂TR ~30 mL m⁻² 24 h⁻¹ and CO₂TR ~80 mL m⁻² 24 h⁻¹ at 23 °C under dry conditions) compared to the pristine pullulan-coated BOPP (O₂TR ~480 mL m⁻² 24 h⁻¹ and CO₂TR ~1245 mL m⁻² 24 h⁻¹). Noteworthy, the change in the permeability properties ultimately yielded a decrease of the CO₂/O₂ selectivity towards 1. The addition of CS nanoparticles did not modify the optical attributes of the pullulan coating, with the final haze values being approximately 1.5% for all nanocomposite layers. The wettability of the final coatings was influenced by the addition of the CS nanoparticles, with a remarkable decrease of the water contact angle to ~19° for the formulation loaded with the lowest concentration of silica nanoparticles that have the smallest size and the highest surface area. The potential application of the pullulan-CS coatings for MAP-packaged fruit and vegetables is suggested.

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1. Introduction

Pullulan is one of the biopolymers that has attracted much attention in recent years as potential food packaging material due to its unique characteristics. This non-ionic exopolysaccharide is obtained from the fermentation medium of black yeast like *Aureobasidium pullulans* under limiting conditions (e.g., nitrogen). Dry pullulan is white, nontoxic, tasteless, odorless, and biodegradable, with high film-forming abilities (Trovatti et al., 2012). The α-(1 → 6) linkage between maltotriose residues contributes to the structural flexibility and high solubility of pullulan, whereas the presence of hydroxyl groups on the molecular skeleton is responsible for the extensive inter-molecular hydrogen bonding and the marked hydrophilicity (Leathers, 2003). Another important feature of pullulan is its high transparency in the form of a thin layer, which is a sought-after property to allow consumers to see through the packaging.

As with most biopolymers directly extracted from biomasses (e.g., pectins, gelatin, chitosan, etc.) and that are inherently polar in nature, pullulan suffers sensitivity to external moisture that dramatically affects its performance. In addition, high production cost is one of the main factors hindering its application in the food packaging sector (Farris et al., 2012). Blending pullulan with other (bio)polymers has been shown to be a valid approach to address these issues (Xiao, Lim, & Tong, 2012; Wu, Zhong, Li, Shoemaker, & Xia, 2013). Another strategy for improving the final packaging performance without significantly impacting its final cost is the development of pullulan coatings (Farris, Uysal Unalan, Introzzi, Fuentes-Alventosa, & Cozzolino, 2014). Pullulan nanocomposite coatings were successfully produced using natural montmorillonite (Na⁺-MMT) (Introzzi et al., 2012b) and graphene (Uysal Unalan et al., 2015) to improve the oxygen barrier properties even at high relative humidity values, or in combination with microfibrillated cellulose (MFC) (Cozzolino, Cerri, Brundu, & Farris, 2014) and borax (Cozzolino, Campanella, Türe, Olsson, & Farris, 2016) to produce biocoatings with enhanced mechanical and permeability properties. Sophisticated pullulan-based coatings were also obtained from an integrated 'sol-gel/intercalation' approach (Fuentes-Alventosa et al., 2013). Pullulan was also proposed as an anti-

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fog coating on the internal side of plastic materials used for freshly-cut and ready-to-eat fruits and vegetables (Introzzi et al., 2012a). More recently, hybrid coatings based on pullulan have also been developed to improve the oxygen barrier properties of coffee capsules made of polypropylene (Cozzolino, Pozzoli, La Vecchia, Piergiovanni, & Farris, 2015).

Colloidal silica is a dispersion of nanosized particles of amorphous silica, where SiO_2 is the discontinuous phase in a continuous dispersion medium, such as water (Dos Anjos, Ismael, de Oliveira, & Pandolfelli, 2008). Colloidal silica particles are typically spherical in shape and have sizes in the nanometer range, generally between 1 nm and 100 nm in diameter, which prevents the final suspension from being affected by gravitational forces (Kroschwitz, 2004). The typical surface area of colloidal silica particles ranges between $900 \text{ m}^2 \text{ g}^{-1}$ and $30 \text{ m}^2 \text{ g}^{-1}$. Standard colloidal silica dispersions are stable against gelling and settle within the pH range of 8–10.5. Stability is achieved by dispersing the particles in alkali medium (e.g., sodium hydroxide and ammonium hydroxide) to achieve a final pH of 9–11 (Bergna & Roberts, 2005). Under these conditions, negative charges on the surface of the colloidal silica particles dominate, which provide the necessary electrostatic repulsion for long-term stability (Björkengen, Nordstierna, Törnrona, Persson, & Palmqvist, 2015). Partial substitution of silicic acid ($\text{Si}(\text{OH})_4$) on the silica surface with the hydrated aluminum anion ($\text{Al}(\text{OH})_4^-$) brings an extra negative charge because of the lower valence of the aluminum. This negative charge, which is independent of pH, allows the sol to remain stable even in acidic conditions (Blute, Pugh, van de Pas, & Callaghan, 2007). Although forming a stable sol, colloidal silica particles tend to grow spontaneously by the Ostwald ripening process, which will decrease the surface area of the colloid (Iler, 1979). In addition, pH variations below 7 as well as the presence of cationic species (e.g., ions and polyelectrolytes such as cationic starch) lead to the fast precipitation of silica particles (Lidén, Karlsson, & Tokarz, 2001). The different methods of production that are now available can lead to sols with distinct solids concentration, particle size and shape, and pH, thus fulfilling the industrial need for characteristics specifically tailored for particular applications (Singh et al., 2014).

Colloidal silica has applications in different fields, such as papermaking, construction, electronics, photography, metal casting, and the production of paints, beverages and polishes (Ullmann & Bohnet, 2009; Blute, Pugh, van de Pas, & Callaghan, 2007). With regard to the food packaging sector, colloidal silica is suggested in water-based coating formulations to enhance some specific functions of plastic films. Coatings containing colloidal silica are claimed to allow the plastic web easily to run on hot surfaces (e.g., those found in filling machines) without sticking due to both an increased coefficient of friction and a high anti-blocking property (AkzoNobel, 2016). Moreover, colloidal silica enhances the plastic's wettability and the ink adhesion of water-based inks due to an increased surface hydrophilicity. Finally, the presence of silica particles makes coatings harder, more durable, and more scratch-resistant, which are sought-after properties, especially for the protection of printings and for special decorative operations (e.g., embossing) (AkzoNobel, 2016). Very recently, the potential migration of colloidal silica nanoparticles from food packaging materials has been assessed (Bott, Störmer, & Franz, 2015). According to the worst-case scenario set up by the authors, it was concluded that the migration of silica particles with 20 nm in diameter from low-density polyethylene (LDPE) into food would not occur.

Surprisingly we have not found research literature on composite coatings including silica nanoparticles for potential food packaging applications. The aim of this work was to evaluate the changes induced by the addition of colloidal silica in pullulan

coatings laid on a polypropylene film, a plastic that is commonly used for food packaging applications. In particular, the addition of the nano-filler was evaluated in terms of its oxygen and carbon dioxide barrier properties as well as its frictional, optical, and wettability properties.

2. Materials and methods

2.1. Materials

Biaxially oriented coextruded polypropylene (BOPP) plastic film ($20.0 \pm 0.5 \mu\text{m}$ thickness, one flame-treated side) was provided by Metalvuoto Spa, Italy. Pullulan powder (PF-20 grade, Mn ~ 200 kDa) was purchased from Hayashibara Biochemical Laboratories Inc. (Okayama, Japan).

Two aqueous dispersions of colloidal silica (Bindzil[®], AkzoNobel, Netherlands) were used and coded as: 1) CS_{15/500} (particle size: 5 nm; dry matter: 15 wt%; specific surface area: $500 \text{ m}^2 \text{ g}^{-1}$ at pH = 10.0); 2) and CS_{15/750} (particle size: 4 nm; dry matter: 15 wt%; specific surface area: $750 \text{ m}^2 \text{ g}^{-1}$ at pH = 10.5).

2.2. Nanocomposites coatings preparation

A fixed amount of pullulan (5 wt%) was dissolved in distilled water at 25 °C for 1 h under gentle stirring (500 rpm) using a digital ceramic plate stirrer (mod. AREC, Velp, Italy). Two different amounts of colloidal silica were added to the pullulan solution (600 rpm \times 3 h) eventually to obtain pullulan: colloidal silica ratios of 1:0.15 and 1:0.45. The final four formulations were coded as P/CS_{15/500}(1:0.15), P/CS_{15/500}(1:0.45), P/CS_{15/750}(1:0.15), and P/CS_{15/750}(1:0.45). The pullulan–colloidal silica solutions were poured on the flame-treated side of BOPP with an automatic applicator (Mod. 1137, Sheen Instruments, Kingston, UK) equipped with a steel, horizontal, wire-wound rod enabling the deposition of a layer having a nominal thickness of 24 μm . Coating deposition was performed according to ASTM D823-07-Practice C, at a constant speed of 150 mm min^{-1} . Evaporation of the solvent was achieved by a constant and perpendicular flux of mild air (25.0 ± 0.3 °C for 2 min) at a distance of 40 cm from the applicator, after which dry coatings of nominal thickness of $\sim 1.5 \mu\text{m}$ were obtained. All films were stored in a vacuum chamber containing calcium chloride at 23 ± 0.5 °C for an additional two weeks before analysis.

2.3. Friction properties

The static (μ_s) and kinetic (μ_k) coefficients of friction (COF) of bare BOPP and the coated films were determined according to the typical 'coating vs. coating' and 'coating vs. metal' configuration, with the goal of simulating the friction between the plastic web against itself and the metallic parts of the equipment used during the manufacturing process, respectively. Tests were carried out according to the ASTM D882-02 at 23 ± 0.5 °C and $50 \pm 2.0\%$ relative humidity (RH), by means of a dynamometer (mod. Z005, Zwick Roell, Ulm, Germany) fitted with a 100 N load cell. For each parameter, the final results are the mean of three replicates.

2.4. Atomic force microscopy (AFM)

The surface morphology of pristine pullulan coatings and pullulan–CS nanocomposite coatings was analyzed using an atomic force microscope (Nanoscope V MultiMode, Bruker) in tapping mode. Measurements were carried out in the air using a silicon tip (resonance frequency ≈ 300 kHz, spring constant 40 N/m). The images were recorded with a resolution of 512×512 pixels. The root mean square roughness S was also evaluated for each sample

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