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Biodegradable multilayer barrier films based on alginate/polyethyleneimine and biaxially oriented poly(lactic acid)

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ABSTRACT

A layer-by-layer (LBL) approach was used to assemble alternating layers of sodium alginate (ALG)/polyethyleneimine (PEI) on biaxially oriented poly(lactic acid) (BOPLA) films in order to produce bio-based all-polymer thin films with low gas permeability. Increasing the depositing of ALG and PEI from 0 to 30 layers results in large thickness variations (from 0 to 3.92 μm). After 30 ALG/PEI layers are deposited, the resulting assembly has an OTR of 1.22 $cm^3/(m^2$ day atm). When multiplied by thickness, the resulting oxygen permeability (OP) is found to be less than 3.8×10^{-17} cm^3 cm/cm^2 s Pa, which is almost 3 orders of magnitude lower than that of uncoated BOPLA film (1.8×10^{-14} cm^3 cm/cm^2 s Pa). At the same time, the resulting multilayer-coated BOPLA films maintain high optical clarity and tensile properties. This unique barrier thin film has become a promising alternative to non-biodegradable synthetic food packaging materials.

1. Introduction

The growth of environmental problems and exhausting natural resources caused by non-biodegradable petrochemical-based packaging materials has raised a renewed interest in developing biodegradable materials (Liu & Berglund, 2012). The results suggest that polymers derived from renewable sources have the potential to be used as alternatives to petroleum based polymers in packaging applications (Picard, Espuche, & Fulchiron, 2011; Vartiainen, Tammelin, Pere, Tapper, & Harlin, 2010). Among the renewable source-based biodegradable plastics, poly(lactic acid) (PLA) film is one of the most promising materials since it can achieve excellent mechanical properties, biodegradability and biocompatibility (Fortunati et al., 2012; Rhim, Hong, & Ha, 2009; Yu et al., 2012). However, compared with the conventional non-biodegradable polymer resins, PLA exhibits low resistance to oxygen and water vapor permeation (Delpouve, Stoclet, Saiter, Dargent, & Marais, 2012; Jamshidian et al., 2012; Marais, Kochumalayil, Nilsson, Fogelstrom, & Gamstedt, 2012). Therefore, many studies have focused on improving the gas barrier properties of PLA by different modified methods, such as the incorporation of other nano-scale materials (Rhim et al., 2009; Sanchez-Garcia & Lagaron, 2010), organic–inorganic hybrid coatings (Bang & Kim, 2012; Iotti, Fabbri, Messori, Pilati, & Fava, 2009; Park et al., 2012) and the lamination of other polymers (Cho, Gallstedt, & Hedenqvist, 2010).

Recently, a developed alternative strategy using a bottom-up layer-by-layer (LBL) process has been employed as a powerful way to assemble gas barrier multilayer thin films by sequential adsorption of oppositely charged polyelectrolytes or particles (Koch, Akhave & Bharadwaj, 2003), as shown in Fig. 1. The LBL technique presents a great advantage over many other coating techniques in that the coatings of nanometer-thickness can be tailorable simply by adjusting some factors such as the deposition pH and the number of dipping cycles (Guzman et al., 2011; Priolo, Gamboa, & Grunlan, 2010). From the perspective of packaging applications, LBL assembly films can be made to exhibit flame retardant behavior (Li et al., 2010), super mechanical properties (Podsiadlo, Tang, Shim, & Kotov, 2007; Sui, Huang, Podsiadlo, Kotov, & Kieffer, 2010), antimicrobial behavior (Dvoracek, Sukhonosova, Benedik, & Grunlan, 2009) and gas barrier properties (Jang, Rawson, & Grunlan, 2008). LBL technique has been used to create multilayer coatings consisting of negatively charged clay and cationic polymer on a poly(ethylene terephthalate) (PET) substrate resulting oxygen barrier dramatically increased (Priolo, Gamboa, Holder, & Grunlan, 2010). More recently, this concept has been applied to clay–biopolymer assemblies on biodegradable PLA films that exhibits high oxygen barrier (Laufer, Kirkland, Cain, & Grunlan, 2012; Svagan et al., 2012). These environmental benign nanocoated PLA films can be developed as an ideal candidate for food packaging to be competitive with the synthetic plastics (e.g., PET).

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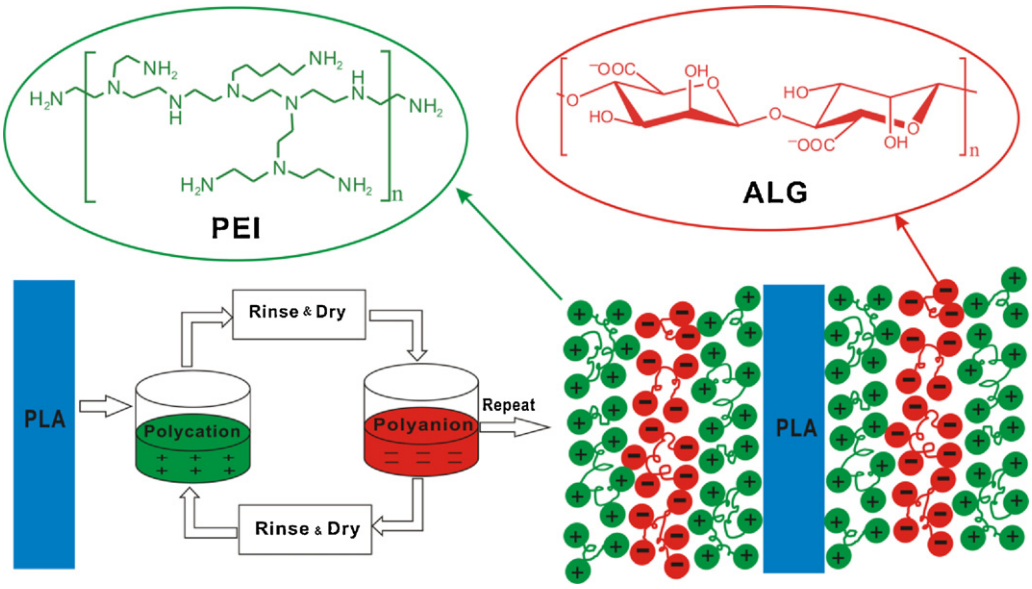

Fig. 1. Schematic of the LBL deposition process and a simplified image of the resulting multilayer ALG/PEI structure deposited on the BOPLA films.

New biodegradable all-polymer multilayer coatings have been deposited via LBL technique to impart mechanical properties (De Mesquita, Donnici, & Pereira, 2010; Rossier-Miranda, Schroen, & Boom, 2010), biocompatibility (Xie, Wang, & Yao, 2009), antifog properties (Nuraje, Asmatulu, Cohen, & Rubner, 2011). To our knowledge, there are only a few publications on the gas barrier properties of all-polymer multilayer films on PET (Carneiro-Da-Cunha et al., 2010; Yang, Haile, Park, Malek, & Grunlan, 2011). These coated PET films may, however, not be ideal for biodegradable food packaging applications because they are either nonbiodegradable or possessing relatively low barrier properties. Earlier investigations have indicated that it is possible to assemble cationic polyelectrolytes and natural polysaccharides to form multilayers on the biodegradable substrate (e.g., PLA) in biomedical engineering (Zhu, Gao, He, Liu, & Shen, 2003; Zhu, Ji, Tan, Barbosa, & Shen, 2003). The build-up of multilayers using all-polymer biodegradable polymers may also be applied to food packaging field, and to the best of our knowledge, multilayer build-up of both oxygen and water vapor barrier films using biomaterials on biodegradable BOPLA has not previously been reported.

In our work, novel biodegradable all-polymer multilayer-coated BOPLA films are constructed through LBL technique to improve the oxygen barrier of the BOPLA film significantly. Water vapor barrier properties, mechanical properties and transparency are also researched, which will assist in competing with non-biodegradable plastic (e.g., PE, PET) in food packaging application.

2. Experimental

2.1. Materials

Sodium alginate (ALG, at 0.2 wt%, pH = 7) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Chitosan (CS) with a degree of deacetylation of 90% (viscosity = 152 mPa s at 0.2 wt%, w/w, in 3%, v/v, acetic acid solution with a pH of 3) was supplied by Golden-Shell Biochemical Co., Ltd. (China). Branched polyethylenimine (PEI) (Mw = 10,000 g/mol) was purchased from Aladdin chemistry Co., Ltd., China and dissolved into distilled water to create a 0.1 wt% solution (pH = 9.5). The pH was adjusted using 1 mol/L sodium hydroxide or 1 mol/L hydrochloric acid solution, respectively. The BOPLA films were provided by Shenzhen Esun Industrial Co., Ltd., China. The films had a thickness of 27 μm, a typical film thickness used in the production of packaging bag for food packaging.

2.2. Preparation of multilayers on BOPLA

The overall multilayer assembly process is shown in Fig. 1. Prior to LBL assembly, each BOPLA film of 10 cm × 10 cm piece, rinsed with ethanol/water (1:1, v/v) solution for 2 h, followed by a thorough rinsing with distilled water (pH = 7), was immersed in PEI solution for 3 h at room temperature, and then washed with a large amount of distilled water. The aminolyzed BOPLA films were treated with HCl (pH = 4) solution for 3 min at room temperature and then washed with a large amount of distilled water, and dried to constant weight. The modified BOPLA substrate was initially dipped into the polyanion (ALG) solution for 5 min. Then the substrate was rinsed with distilled water for 3 min and dried with blowing air. After the first layer of negatively charged polymer was adsorbed, the substrate was dipped into the polycation (PEI or CS) solution for another 5 min followed by another rinsing and drying cycle. The above procedure was repeated for subsequent layers using 5 min dip times until the desired number of layers was achieved. All coated films were dried at 30 °C under reduced pressure prior to characterization.

2.3. Film growth

Contact angles of the nanocoated film surface were measured by a video contact angle meter (OCA-20, Kruss, Germany) using the sessile drop method. A 3 μL droplet of MilliQ water was placed on the horizontal surface with a 50 μL glass syringe. Measurements were made at equilibrium after drop deposition and duplicate measurements were performed on three different areas of each sample at room temperature (25 °C). The UV–vis analyses were performed using a UV-vis spectrophotometer (Jasco 560, Germany) and were used to follow the multilayer films construction. The absorbance was measured at 260 nm on dried films.

2.4. Film properties

The oxygen transmission rate (OTR, $cm^3/(m^2\ day\ atm)$) values were performed with a VAC-V_1 gas permeability tester (Labthink Instruments Co., Ltd., China). The tests were carried out at 23 °C, and