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Effects of N-octyl lactate as plasticizer on the thermal and functional properties of extruded PLA-based films

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ABSTRACT

Films of poly(L-lactide) (PLA) plasticized with varying levels of N-octyl lactate (NOL) were prepared by extrusion. The thermal and functional properties of the blends were investigated by SEM, DSC, TGA, tensile, opacity, water vapor permeability, and water contact angle tests. The compatibility of the plasticizer with PLA was confirmed by DSC and SEM analysis. A higher plasticizing effect on the thermal properties of PLA was generally observed with the increase in NOL content. Additionally, the mechanical properties were improved with the increase in NOL content. The mechanical resistance of the films could be related to their glass transition temperature. The effect of the concentration of plasticizer on the opacity of the films was negligible. The water vapor permeability of the PLA/NOL composite films increased with the increase in the concentration of NOL; however, the values observed were still lower than the water vapor permeability of commercial LDPE films. In conclusion, the extruded PLA-based films with NOL plasticizers could be used as food-packaging materials.

1. Introduction

The environmental problems caused by non-biodegradable petrochemical-based packaging materials have led to the research and development of biodegradable materials [1–3]. This trend suggests that polymers derived from renewable sources have the potential to be used as alternatives to petroleum-based polymers in the production of packaging materials on a commercial scale. Poly(L-lactide) (PLA) is a biodegradable aliphatic polyester that is produced from lactic acid, either by the direct polycondensation of lactic acid or via the ring-opening polymerization of lactide [4–6]. PLA may reasonably be substituted for some of the conventional polymers used to develop structural and food-packaging materials [7,8]. PLA is currently commercialized and used in the food packaging of fresh products as containers, drinking cups, salad cups, overwrap and lamination films, and blister packages [9]. In many food-packaging applications, polymer-film materials are prepared by extrusion methods. However, their poor mechanical properties and relatively low resistance to oxygen and water vapor permeation prevent PLA films from being applied for practical food-packaging purposes.

For many practical food-packaging applications, it is desirable that the polymer matrix be modified; indeed, many modifications for improving the performance of PLA have been studied [10]. Plasticizers play an important role in determining film properties. The addition of plasticizers is necessary to overcome the brittleness of films, improve flexibility, increase toughness, prevent the films from cracking during packing and transportation, and to improve the water vapor barrier property of biopolymer films [11]. Modifiers added to a polymer should be miscible with the polymer matrix. Thus, it is necessary to analyze the effects of plasticizers on the thermal stability of PLA composites. In structural terms, the use of plasticizers can increase the free space between polymer chains and reduce intermolecular forces throughout the polymer matrix [12,13].

The selection of a plasticizer for specified biopolymer films is normally based on the compatibility and biodegradability of the plasticizer, the amount of the plasticizer required for plasticization, and the desired functional properties of the films [8,11,14]. Therefore, new and old plasticizers should continuously be studied in the field of food-packaging materials. N-octyl lactate (NOL) is an ester that is formed from octyl alcohol and acetic acid. It is primarily found in oranges and other citrus products. NOL is a viscous liquid with a low T_g and an inability to crystallize. The melting point of NOL is approximately −38.5 °C. NOL is a non-toxic substance that is suitable for food-contact applications and can be considered a plasticizing agent for food-packaging materials [30]. NOL

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has demonstrated to be an attractive potential plasticizer for PLA. To the best of our knowledge, however, there are no reports on the use of N-octyl lactate as a plasticizer for the development of PLA-based food-packaging films.

The objective of this study was to study the thermal properties, tensile, opacity, water vapor permeability, and water contact angle of extruded PLA-based films produced at various contents of NOL.

2. Materials and methods

2.1. Materials

Poly(L-lactide) (PLA, M_w = 280 kDa, M_w/M_n = 1.98) was obtained from Natureworks LLC (Nebraska, USA). N-octyl lactate was selected for its food-contact approval and purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Sample preparation

Prior to blending, the PLA was dried in vacuum at 80 °C for 24 h to eliminate any water that may have absorbed on the surface of the polymer particles. PLA was blended with NOL by adding NOL to the PLA matrix in different amounts (0, 2.5, 5, 7.5, 10, and 12.5% (w/w)) and extruding the mixture using a torque rheometer (XXS-300, Kechuang Rubber Plastics Machinery Set, Shanghai, China) operated at 40 rpm. The die diameter was 30 mm, and its gap thickness was 100 μm. The pulling speed was 357.2 mm/min. The temperatures of the feeding zone, the intermeshing zone, and the final zone of the extruder were maintained at 150, 170, and 160 °C, respectively, and the die exit temperature was 150 °C. The films were quenched at room temperature and stored in desiccators for characterization.

2.3. Film thickness

Film thickness was measured by a digital micrometer (Mitotuyo No. 7327, Tokyo, Japan). The average thickness of the films was 0.05 ± 0.005 mm.

2.4. Scanning electron microscopy (SEM)

SEM (Quanta 200, Chicago, USA) was used to observe the cross-sectional morphology of the plasticized PLA films at an acceleration voltage of 20 kV. Before SEM examination, all of the film surfaces were coated with a thin, conductive gold layer measuring 20 nm thick.

2.5. Thermal properties

Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC-200PC (Netzsch, Germany). An empty pan was used as a reference. After being dried in a vacuum oven at 40 °C for 48 h, circular samples were cut from the plates and accurately weighed (10 mg) into aluminum pans. DSC measurements were carried out under nitrogen flow from 20 °C to 200 °C at a heating rate of 10 °C/min. The glass transition temperature (T_g), peak crystallization temperature (T_c), and melting temperatures (T_m) of the PLA composite films prepared by extrusion with different NOL contents were evaluated.

The thermal stability of the samples was evaluated using a TA Instruments DSC-200PC (Netzsch, Germany). After being dried in a vacuum oven at 40 °C for 48 h, samples weighing approximately 10 mg were sealed in an aluminum pan. Thermogravimetric analysis (TGA) was performed at 10 °C/min from 30 °C to 600 °C in a nitrogen atmosphere.

2.6. Mechanical properties

The tensile strength (TS), tensile modules (TM), and elongation to break (E) of the films were measured on a universal testing machine (WDW-10, Shanghai Jadaronson M&C System Co., Ltd., Shanghai, China) using ASTM Method D 882-88. The initial grip separation was set to 50 mm, and the cross-head speed was set to 100 mm/min [15]. The measurement was performed immediately after each sample was removed from the desiccator. TS, TM, and E measurements for each film were repeated at least eight times, and the averages were taken as the results.

2.7. Opacity

The film opacity was determined by measuring the absorbance at 600 nm using a UV–vis spectrophotometer (T90, Beijing Purkinje general instrument Co., Ltd. Beijing, China) [16]. Each sample was cut into a rectangle section (0.7 cm × 1.5 cm) and directly placed in a spectrophotometer test cell. An empty test cell was used as the reference [17]. The film opacity was calculated as follows:

$$\text{Opacity} = \frac{\text{Abs}_{600}}{d} \tag{1}$$

where Abs_{600} is the absorbance at 600 nm and d is the film thickness (mm) [18].

2.8. Water vapor permeability (WVP)

The WVP of the films was determined gravimetrically in triplicate according to the ASTM E96-95 standard method [19]. The test films were previously equilibrated at 25 °C and 50% RH for 2 h. Then, the films were sealed with paraffin and rubber on the test acrylic cups, which measured 40 mm in diameter and 25 mm in depth. The weight loss of each cup was considered to be equal to the water transferred through the film and adsorbed by the desiccant. The weight loss of each cup was recorded as a function of time for 12 h [20]. The *WVP* was calculated as follows [21]:

$$\text{WVP} = \frac{\text{WVTR} \times d}{\Delta P} \tag{2}$$

where *WVTR* is the water vapor transmission rate (g/m^2 s) through the film, d is the average film thickness (m), and ΔP is the partial water vapor pressure difference (Pa) between the two sides of the film.

2.9. Contact angle

Contact angle measurements of the extruded films were conducted on a surface tension meter (Dataphysics OCA-H200, Germany) at room temperature. The contact angle was measured by randomly placing 10 drops of distilled water (3 μl) on the surface of each film sample using a syringe needle. Five samples were tested for each specimen.

2.10. Statistical analysis

Data were analyzed as the mean and standard deviation (mean ± SD) of three test replicates for each sample. The statistical analysis was performed by analysis of variance (ANOVA) using SPSS version 13.0 at the 0.05 significance level.