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Material properties

Effect of cooling and coating on thermoplastic starch/poly(lactic acid) blend sheets

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ABSTRACT

The influence of the processing conditions (cooling rate) and coating on the physicochemical properties of thermoplastic starch/poly(lactic acid) blend sheets was studied. Two cooling rates were used: fast and slow, and in the latter case the sheets were both non-coated and coated with cross-linked chitosan. The physicochemical properties investigated were crystallinity, morphology, water affinity (moisture sorption isotherm, water vapor permeability, water solubility and contact angle) and mechanical properties. In general, the sheets cooled at the slow rate were more crystalline, less permeable and less soluble in water than those cooled at the fast rate. They also produced a more homogeneous morphology. The coated sheets were less soluble in water and mechanically stronger than uncoated sheets cooled at the slow rate. The concentration of plasticizer in the TPS affected only the sorption isotherm and contact angle since a higher plasticizer content caused a greater affinity for water.

1. Introduction

Research has been focused on biodegradable and natural polymers in order to replace synthetic polymeric materials. Thermoplastic starch (TPS) is a low cost material of high availability, which can be processed using equipment for conventional plastics. However, its mechanical properties are dependent on the relative humidity, limiting its application as food packaging.

To decrease the affinity between TPS and water, starch modification and the formation of composites and blends have been studied. Several blends of TPS/biodegradable polymers, such as polycaprolactone [1], polyhydroxybutyrate [2], poly(butylene adipate-co-terephthalate) [3] and poly(-lactic acid) [4], are notable for their ability to maintain the biodegradability of the final product.

Poly(lactic acid) (PLA) is a commercial polymer with biodegradable and hydrophobic characteristics, and it presents equivalent properties as those of conventional materials. However, its application is limited by its high cost. In this regard, the use of TPS/PLA blends is one option to improve the cost-benefit and obtain a material with better performance.

Besides the raw materials used to obtain the blends, the processing parameters can influence the final properties of the material obtained [5]. For example, the cooling rate during the specimen molding can alter the degree of crystallinity, which in turn can affect the physical, mechanical and barrier properties [6]. Sarasua et al. [7] studied sheets of PLLA/PDLA blends with different component compositions and varied the cooling rates in order to evaluate the relationship between the crystallinity and the mechanical properties. They found that the crystallinity ranged from 7 to 50%, according to the composition. The sheets that were cooled at lower rates achieved higher crystallinity values (40–50%). On the other hand, the sheets cooled in water, had

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7% crystallinity. In general, with a higher degree of crystallinity there was an increase in the Young's modulus and a decrease in the elongation-at-break.

Another way to control the blend properties is by applying a coating of another biodegradable polymer on the sheet surface. Hoagland and Parris [8] produced chitosan laminates coated with pectin, which had higher storage and loss moduli than uncoated laminates. Bangyekan, Aht-Ong and Srikulkit [9] coated starch films with chitosan. The mechanical properties of the films were modified on increasing the chitosan concentration of the coating, and the water uptake decreased due to the hydrophobic characteristic of the chitosan.

In this study, different approaches to improving the properties of TPS/PLA blend sheets were evaluated. The molded sheets were cooled from 150 °C at room temperature applying slow and fast cooling rates and then coated with a biodegradable cross-linked polymer prior to evaluating the physicochemical properties.

2. Materials and methods

2.1. Materials

Native cassava starch (amylose 20.8 ± 0.6 wt%) was supplied by Indemil (Brazil), poly(lactic acid) by Cargill (Natureworks LLC, USA) and chitosan (medium molecular weight, 75–85% deacetylated) by Sigma–Aldrich (USA). Glycerol and glutaraldehyde were supplied by Dinâmica (Brazil) and Nuclear (Brazil), respectively. All chemicals were used without further purification.

2.2. PLA/TPS blends

Previously prepared thermoplastic starch pellets with 0.25 g or 0.30 g of glycerol per gram of starch were extruded with PLA at a constant TPS/PLA ratio of 70/30 (w/w), denoted by B25 and B30 (the numbers 25 and 30 relating to the glycerol content of the thermoplastic starch).

The blends were extruded in a single-screw extruder (BGM, model EL-25, Brazil) with a screw diameter of 25 mm and L/D of 30, at 150 °C (in all three zones) and a screw speed of 35 rpm. These extrusion parameters were the same as those applied in a previous study by Soares et al. [10].

2.3. Sheet molding

The blend pellets were thermopressed in a hydraulic press (Schulz, model PHS, Brazil) at 150 °C and 2.6 MPa, and the specimens were cooled at room temperature applying two procedures: the molded sheet was (i) kept in and (ii) removed from the heating system. The cooling procedure (i) took 3 h and procedure (ii) took only 20 min, and these are referred to herein as slow and fast cooling, respectively.

The temperature decrease as a function of time for each cooling procedure is illustrated in Fig. 1. In order to represent the sheet cooling process, the temperature was adimensionalized and the experimental data were fitted according to Equation 1.

$$\frac{T_{(t)} - T_\infty}{T_0 - T_\infty} = Je^{-kt} \quad (1)$$

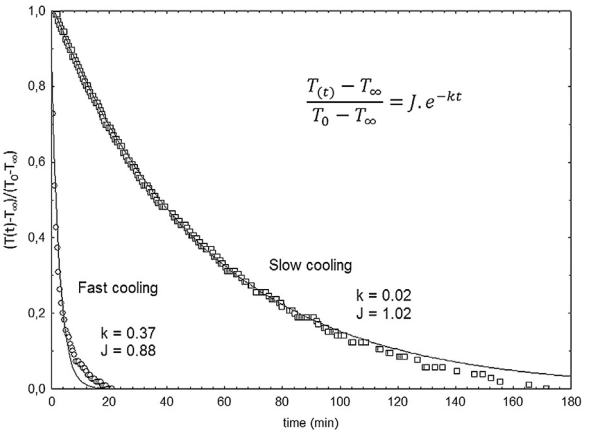

Fig. 1. Temperature decrease as a function of time for fast and slow cooling process.

where $T_{(t)}$ is the center temperature of the sheet at time t; T_∞ is the final temperature; T_0 is the initial center temperature of the sheet, t is time and J and k are model parameters.

The fitting of the model to the experimental data was carried out using non-linear regression and Statistica 8.0 software (Statsoft, USA).

2.4. Coating

The procedure to coat the sheets involved a spray method, as described in a previous report by Soares et al. [10]. The two sides of the TPS/PLA sheets were coated with chitosan solution (0.1% of chitosan dissolved in aqueous acetic acid solution of 0.1% v/v) and subsequently with an aqueous glutaraldehyde solution of 0.5% v/v, in order to cross-link the chitosan.

2.5. Characterization of the sheets

2.5.1. X-ray diffraction

X-ray patterns of the specimens were obtained on a Philips X'Pert diffractometer (Netherlands), with Cu (Kα) radiation (λ = 1.5418 Å), operating at room temperature, 30 mA and 40 kV. The scanned region ranged from 2θ = 2–60°, and the pitch was 0.05° s^{-1}. The relative crystallinity index was evaluated from the relative areas of the crystalline and amorphous regions.

2.5.2. Morphological analysis

The specimens were fractured under liquid nitrogen. The fractured samples were subjected to different treatments: one part was placed in a desiccator while another part was placed in a test tube and sufficient chloroform was added to cover the specimen which was then left to stand for 24 h. The specimens were coated with gold and analyzed using a scanning electron microscope (Philips XL-30).

2.5.3. Moisture sorption isotherms

The moisture sorption isotherms were determined through the static method, using saturated saline solutions