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Effect of poly(lactic acid) coating on mechanical and physical properties of thermoplastic starch foams from potato starch

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ABSTRACT

Single-use packaging is widely used in the food industry, and is mainly made of expanded polystyrene (EPS). These packages are discarded immediately after use and generate large amounts of waste. Thermoplastic starch (TPS) foams can be used in these situations due to the fact that starch is from renewable sources and biodegradable. Despite of these advantages, TPS has great affinity with water, which makes difficult its application as packaging. Such problem can be solved by coating the TPS foam with a hydrophobic material which prevents contact of water with the starch. In this work, poly(lactic acid) (PLA) was used as a coating due to its hydrophobicity and also for being a biodegradable material. Three coating concentrations were evaluated: 2%, 4% and 6% w/v PLA. The foams were made from potato starch, water and glycerol (62/5/33% m/m). PLA coatings increased the density, tensile strength and impact strength of the foams. TPS foams with 6% w/v PLA coating exhibited an excellent reduction of 225% in water absorption when compared to TPS foam.

1. Introduction

The problems with solid waste associated with expanded polystyrene (EPS) have been motivating the study and production of new environmental friendly materials coming from renewable sources that can replace EPS. Starch-based products have attracted great interest, because starch is abundant, cheap and biodegradable. Foams made with thermoplastic starch (TPS) may replace the EPS, especially in single use food packages [1,2]. The thermoplastic starch foam can be easily made through a baking process, which involves placing a specific amount of starch, water and plasticizer into a preheated mold. Inside the mold, starch gelatinizes and the water evaporates quickly, creating a foam structure. The properties of the obtained foams will depends on the components concentrations, type of starch and the type of plasticizer used [3,4]. Previous research has shown that foams made from potato and cassava starch have lower densities and more interesting mechanical properties compared to foams made from corn starch [5].

Although it is easy and inexpensive to produce TPS foams, the moisture content and fast water absorption make a major problem for this material due to the hydrophilic character of starch. In contact with water, the TPS foam loses its physical and mechanical properties, because the moisture incoming softens the cell structure, weakening it. Also, the cell walls are destroyed and the material becomes a mass doughy. These factors limit the use of this material.

Many polymers have been used as coating or blends to reduce this problem and also to improve other properties of TPS. Biodegradable polymers more hydrophobic than starch have been mostly studied for this use due to the fact that these maintain the biodegradability of the foam and also hinder the contact of water with the starch of TPS foams and thus keeping for more time the physical and mechanical properties of these foams. [3,6–9]. One of the most interesting coatings is the poly lactic acid (PLA), since it is less hydrophilic than starch and is also biodegradable.

PLA is an aliphatic polyester derived from renewable sources, such as starch and sugarcane, and has been considered as a solution to the reduction of solid waste [10]. It is a material that has attracted great interest in the technological industry because it has good mechanical properties, is non-toxic and biocompatible with living tissue. PLA can be used in implants, sutures and drug encapsulation, since the products of its degradation are neither toxic nor carcinogenic to the human body [11–13]. It can form films, has great resistance to water contact and is a safe material to be used in packaging [14]. Preechawong et al. [15] showed that the addition of PLA decreased moisture absorption and increased mechanical strength of TPS hybrid foams. Rhim, Lee, and Ng. [16] studied PLA coating soy protein-based films and found out that the water absorption decreased with the increase in PLA concentration in the coating solution.

This study aims to evaluate the influence of the PLA incorporation

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as a coating in TPS foams based on potato starch as a barrier, and evaluate its influence on properties such as moisture absorption and water absorption. It was also evaluated the effect of the concentration of the coatings (2%, 4% and 6% w/v) on the TPS foams. Cellular structure, mechanical properties and water absorption were analyzed and correlated with the presence of PLA on the foams surface.

2. Materials and preparation

2.1. Materials

Potato starch (Giro Verde®) was purchased in a local market in Porto Alegre, Brazil. The plasticizer glycerol was provided by Dinamica Ltda. The PLA was purchased from Politech® and chloroform used in the PLA solution was provided by Synth®. The Sulfuric acid used in the of moisture determination content was provided by Química Moderna®.

2.2. TPS foam preparation

Starch, glycerol and water were mixed with a weight ratio of 62/5/33. The resulting starch paste was mixed at 70 °C until the starch mixture gelatinization and homogenization. The obtained paste was placed in a preheated mold at 180 °C and then compressed in a 2,5 tons hydraulic press for 240 s. The resulting foams were kept at room temperature in a desiccator before being coated with PLA and analyzed.

2.3. Coating

The coating solution was prepared by dissolving 2%, 4% and 6% (w/v) of PLA in 50 mL chloroform using magnetic stirring at room temperature for 2 h. The coating was done by immersing the foams in the PLA solution, and then placed to dry in a desiccator.

2.4. Foams characterization

2.4.1. Scanning electron microscopy (SEM)

Images of samples fracture surfaces were studied using a JEOL JSM 6060 Scanning Electron Microscope (SEM) operating at a voltage acceleration of 2 kV. The samples were gold metalized.

2.4.2. Infrared spectroscopy

To evaluate the chemical structure of the surface of the TPS foams with and without coating, infrared spectroscopy with Fourier transform (Perkin-Elmer frontier equipment) using the ATR accessory (FTIR-ATR). For the analysis, small pieces of the TPS foams were cut. The analyses were done by transmittance in the range of 4000–650 cm^{-1}, 30 scans, at room temperature, according to ASTM E 1252.

2.4.3. Water absorption

Samples measuring 4 cm × 2 cm were weighed and placed in distilled water for 5, 10, 20 and 40 min. Then samples were weighed again after removing the water excess by using a tissue paper. The amount of absorbed water was calculated gravimetrically, and the analysis was performed in triplicate for each formulation. [17]

2.4.4. Moisture content

Pre-dried samples measuring 4 cm × 3 cm were weighed and placed in sealed recipients with 57% and 90% relative humidity (RH) and then were placed in an oven at 25 °C. The moisture was provided by sulfuric acid solutions with a concentration of 40% w/w and 20% w/w, respectively. The absorbed moisture was calculated by the samples weight difference before and after being exposed to moisture at 24, 48, 72, 96 and 120 h [2,7]. The obtained data were adjusted according to the mathematical model suggested by Peleg [18–20], presented in Eq. (1):

$$M_{(t)} = M_0 + \left(\frac{t}{(K_1 + K_2 t)}\right) \quad (1)$$

Where $M_{(t)}$ is the moisture in time, M_0 is the initial moisture, t is the time, K_1 is the Peleg flux constant (h/(w water/w solids)), while K_2 is Peleg capacity constant (w solids/w water). The statistical program used was Statistic Statsoft for Windows 10 software. The assay was done in triplicate for each sample.

2.4.5. Density and mechanical test

The foams density were calculated by foam weight/foam volume in triplicate, following methodology from Shogren et al. [21]. The measurements of length, width and thickness of specimen test of TPS foam were made in triplicate for each sample.

The properties related to foams tensile strength were analyzed according to ASTM D638 with crosshead speed of 3 mm/min in an universal testing machine (INSTRON, model 3382). The specimen dimensions were 100 mm × 25 mm × 3 mm. Impact IZOD strength test was carried out with ASTM D256 on IMPACTOR II, using a 0,5J hammer. The samples dimensions were 60 mm × 12 mm × 3 mm. The results of both tests were obtained by averaging the measurements of nine independent samples. The experiments were performed at room temperature (25 °C) and at 40–60% relative humidity.

3. Results and discussion

3.1. Influence of PLA coating on TPS foams morphology

Selected scanning electron micrographs of TPS foams with and without PLA coating are shown in Fig. 1. The micrograph of uncoated foam (Fig. 1a) show that these have a dense outer skin with some small cells near the surface. The interior of the foam have larger cell groups with more void spaces. The cells are formed by water vapor which expands the material, and tend to be larger in the center of the foam. Researches of Cinelli et al. [1]; Willett and Shogren [3]; Glenn, Orts, and Nobes [7]; Vercelheze et al. [17] and Matsuda et al. [22] founded similar results.

Micrographs of TPS foams with PLA coating (Fig. 1b–d) show that this coating modified the structure of the foams, especially close to surface. It is noted that the coating made with the 2% w/v PLA solution (Fig. 1b) did not completely cover the material, while the coatings made with 4% and 6% w/v visibly filled the foam. With the coating, the outer layer of the foams became thicker and the empty spaces in the interior were filled with PLA, disrupting the cells and apparently making the foams more dense. Preechawong et al. [15], in the study on hybrid TPS/PLA foams, reported that TPS foams with PLA have a similar structure compared to pure TPS foams, but have smaller cells and empty spaces. In the study by Zhang et al. [31], the PLA used to cover paper containing organic nanoparticles reduced the surface porosity of the material.

The PLA coating did not show complete compatibility with the TPS foam, and in some parts the PLA was not fully trapped on the foam surface, as seen in the TPS foam with 4% w/v PLA (Fig. 1c). This possibly occurs because the starch is highly hydrophilic and the PLA is hydrophobic, which hinders compatibility. Some studies have exposed the same problems and suggested some solutions such as modifying the starch structure through butyl etherification to increase compatibility with PLA [23], or through the use of a new modified malic anhydride based compatibilizer [10,24].

3.2. Chemical composition of TPS foams surface

Fig. 2 shows the absorption spectra in the infrared region of the TPS foams with and without PLA coating. The bands found in the spectra of the foams with 2%, 4% and 6% w/v of PLA were practically identical and therefore only the spectrum with 6% w/v PLA is represented.