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Physicochemical properties of PLA lignin blends

Oihana Gordobil, Itziar Egüés, Rodrigo Llano-Ponte, Jalel Labidi*

Chemical and Environmental Engineering Department, University of the Basque Country, Plaza Europa, 1, 20018 Donostia-San Sebastián, Spain

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ABSTRACT

Commercial alkali lignin (CL) and lignin extracted from almond shells by organosolv process (OL) were used for the preparation of blends with poly(lactic acid) (PLA) with different percentages (0.5, 1, 5, 10 and 20%) by extrusion method. Both lignins were acetylated to improve their compatibility with PLA. PLA/acetylated lignin blends exhibited greater compatibility than non-acetylated PLA/lignin. Characterization of lignins has been performed using HPLC, FT-IR, GPC, DSC and TGA. All lignins showed high purity. Acetylated lignins had lower T_g and higher thermal stability than original lignins. Thermal and mechanical properties of different blends were investigated. Morphology before and after hydrolytic degradations of blends with 5% of different lignins were also investigated. The addition of acetylated lignin appears to prevent hydrolytic degradation of PLA. Lignin content increased the thermal stability of PLA but does not favor the crystallization of PLA. Maximum strength decreased with high percentages of originals lignins. However, PLA/acetylated lignin blends remains fairly constant, even at high percentages. In all cases, the elongation at break was increased.

1. Introduction

Lignin is the second most abundant biopolymer on earth. It confers mechanical support of the plant and also provides rigidity, internal transport of water, nutrients and protection against attack by microorganisms [1–3]. The chemical structure of lignin is difficult to define because its structure and properties are largely related to isolation process and the types of sources used for its extraction. Generally, is an amorphous polyphenolic macromolecule which is composed of a large number of polar functional groups [4]. Commercially, lignin is a by-product mainly obtained from the pulp and paper industry. Most of the raw material is burnt as an energy source, although it can offer many other added value uses. This important component of biomass is less studied due to its structural complexity, however, that structure which provides multiple functionalities. Some papers described the efficiency of lignin as flame retardant additive since it is able to give a large amount of char when it is heated at high temperature in an inert atmosphere. This char reduces the combustion rate of polymeric materials [5,6]. Also, lignin is utilized as a stabilizer (antioxidant) for plastics [7]. Other authors have found that lignin has an important influence on the thermal behaviorbehavior in different composites. Lignin can also behave as a nucleating agent during the crystallization of different thermoplastic polymers and interfere on their supermolecular structure [8]. Furthermore, lignin has been investigated as compatibilizer between natural fibers and polymer matrix [9,10]. The effective use of lignin in blends with various synthetic polymers such as poly(propylene) [11], poly(ethylene terephthalate) [5], poly(vinyl alcohol), poly(ethylene oxide) [7], poly(vinyl chloride) [3], polystyrene [12], low-density polyethylene and linear low-density polyethylene [13] has been also reported in literature. However, the environmental concerns and a shortage of petroleum resources have driven efforts on the preparation of bioplastics made from renewable materials. Several works have been reported about biopolymer/lignin blends. Some authors showed that the addition of lignin into thermoplastic starch matrix (TPS), improved mechanical properties, increasing the tensile strength. Thermal stability also increased and a reduction of moisture absorption was achieved [14]. Other study, also confirmed that the use of lignin as a filler in TPS improved the mechanical and thermal properties; however a decrease in a water vapor permeability was observed [15]. Biocomposites of (3-hydroxybutyrate) (PHB) and acetylated lignin were prepared by other authors, in this case the decrease of PHB crystallization rate and the increase of thermal stability were observed [8]. Also, the potential of lignin as a natural antioxidant additive in food packaging was demonstrated [16]. This study was focused on the obtaining of composites formed by PLA and lignin as filler. Poly(lactic acid) (PLA) is a biodegradable and aliphatic polyester obtained from agricultural plants such as corn, sugar beets, wheat… among others. It is being extensively studied for the purpose of replacing commodity polymers because is thought to be one of the most promising environmentally

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* Corresponding author. Tel.: +34 943017178; fax: +34 943017140.
E-mail address: jalel.labidi@ehu.es (J. Labidi).

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friendly polymer materials in sustainable development [17–19]. Although PLA possesses good melt processability, its weaknesses include poor gas-barrier properties, low toughness and ductility, poor thermal stability and high cost so that many research studies have focused on overcoming these limitations, to increase its potential in the fabrication of attractive materials for wide industrial applications [20]. In this research, blends with different percentages of lignin were prepared by extrusion method. Two kinds of lignin were used, commercial alkaline lignin and the lignin extracted from natural resources such as almond shells. Both lignins were acetylated to increase lignin affinity with PLA because properties of blends are governed directly by the components in the blends and the interfacial interactions between them. The object of this study was to evaluate the effect of lignin addition in PLA thermal and mechanical properties.

2. Materials and methods

Almond shells are not exploited industrially. They are harder and more rigid than wood and also denser and less porous [21]. Almond shells used in this study for lignin extraction by organosolv process were provided by "Eloy Castillo Fernandez" company which is involved in the production of almond in Arnedo (La Rioja). This company uses two varieties of almond called Largueta and Marcona produced by almond-tree *Prunus amygdalus*. Commercial alkaline lignin was supplied by Sigma ALDRICH®. PLA (NatureWorks® PLA Polymer 3051D) was from NatureWorks LCC (Glass Transition Temperature 55–65 °C, Melt Temperature 150–165 °C, M_w: 169.000).

2.1. Characterization of raw material

The almond shells used for lignin extraction were milled to obtain particles between 0.25 and 0.40 mm. Chemical composition was determined following procedures found in literature: ash (TAPPI T211 cm-93), ethanol–toluene extractives (TAPPI T204 cm-97), lignin (TAPPI T222 cm-98), holocellulose (Method Wise et al.), cellulose (Method Rowell) and hemicelluloses content.

2.2. Lignin isolation

Almond shells were treated with a mixture of ethanol–water (70 wt%) for lignin extraction. The treatment was carried out at 180 °C for 90 min in a 4 L pressure stainless steel batch reactor with constant stirring (EL0723 Iberfluid) with electronic control unit for pressure and temperature control. The solid to liquid ratio was 1:6 (w/w). The liquid fraction (where lignin was dissolved) was separated from the solid fraction by filtration. Dissolved lignin was isolated by precipitation with two acidified portions of an aqueous solution (pH around 2). The suspension was centrifuged at 4000 rpm for 20 min to recover lignin which was then dried at 50 °C.

2.3. Lignin acetylation

Each lignin was chemically modified by the esterification of its hydroxyl groups in order to enhance the interaction with PLA in the composite. Commercial lignin and obtained almond shell lignin were acetylated. Acetylation of different lignins was carried out using experimental conditions described below. Dry lignin samples (1.00 g) were dispersed in formamide (25 mL) about 3 h, until complete solubilization. Pyridine (40 mL) was added, followed by acetic acid anhydride (6.6 mL). After stirring at room temperature for 3 h, another portion of acetic anhydride (6.6 mL) was added, followed by the same amount after another 3 h. After 30 h, the viscous dark solution was poured (under vigorous stirring) into 1.3 L of 2% ice-cold hydrochloric acid. The white fluffy precipitate was filtered on a buchner funnel with filter paper and washed with excess (0.5 L) deionized water and then with 0.5 L diethyl-ether. The samples were then dried in vacuum at 40 °C overnight.

2.4. Preparation of blends by extrusion

An extruder THERMO HAAKE Minilab Rheomex CTW5 model with double screw (109.5 mm) was used for the preparation of mixtures. Process conditions were the same for all blends, 165 °C, at rate 25 min^{-1} and recirculation time was 30 min, optimum conditions previously determined for successful mixing of the materials. The blends are made by PLA as matrix with different percentages of nonacetylated and acetylated lignin (0.5, 1, 5, 10, 20%). Two types of blends were prepared, in both cases, PLA was used as a matrix and was mixed with unmodified lignins (commercial and organosolv) and were also made with acetylated lignins.

2.5. Characterization of lignins and blends

2.5.1. Composition of lignins

Acid-insoluble lignin (Klason lignin) was determined. Carbohydrate contamination was measured by analyzing the hydrolyzate using High Performance Liquid Chromatography [Jasco LC Net II/ADC with a ROA Organic Acid (00H-0138-K0) column (Phenomenex) equipped with a refractive index detector (RI-2031Plus) and a photodiode array detector (MD-2018Plus)]; 0.005 M H_2SO_4 prepared with 100% deionized and degassed water was used as mobile phase (0.35 mL/min flow, 40 °C, and injection volume 40 μL). High purity standards of D-(+)-glucose, D-(+)-xylose, and D-(−)-arabinose (provided by Fluka, with 99% of purity) were used for calibration.

2.5.2. Fourier transform infrared spectroscopy (FTIR)

The FT-IR analysis of unmodified and acetylated lignins was performed on a NICOLET MODEL NEXUS 670 FT-IR spectrophotometer. A total of 20 scans were accumulated in transmission mode with a resolution of 4 cm^{-1}. The spectrum was obtained from a range of 4000 to 650 cm^{-1}. FTIR spectra were also used in order to determine the degree of acetylation of lignins.

2.5.3. Gel permeation-high performance liquid chromatography (GPC)

Size exclusion chromatography analysis was used to evaluate the average molecular weight (M_w) and polydispersity (M_w/M_n) of the obtained lignin samples. N,N Dimethylformamide (DMF) eluent was used as GPC mobile phase, at a flow rate of 0.7 mL/min and 35 °C, using a Jasco Inc. chromatograph provided with an LC-NetII/ACD interface, a column oven CO-2065Plus and a RI-2031Plus Intelligent Refractive Index Detector. A guard column and two columns PolarGel-M (Varian Inc.) were employed. Calibration was made using polystyrene standards provided by Fluka, ranging from 250 to 70,000.

2.5.4. Thermal properties

The glass transition temperature of unmodified and acetylated lignins was determinated by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5–10 mg were tested under nitrogen atmosphere at a heating rate of 10 °C/min. The samples were first heated to 110 °C to eliminate interferences due to moisture. Then, the samples were cooled to 25 °C and reheated to 200 °C at 10 °C/min.