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PHYSICOCHEMICAL PROPERTIES OF PLA LIGNIN BLENDS

Oihana Gordobil, Itziar Egués, Rodrigo Llano-Ponte, Jalel Labidi

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

*E-mail: jalel.labidi@ehu.es, tel.:+34-943017178; fax: +34-943017140

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 favour the crystallization of PLA. Maximum strength decreased with high percentages of original lignins. However, PLA/acetylated lignin blends remains fairly constant, even at high percentages. In all cases, the elongation at break was increased.

Keywords: Lignin • Acetylation • Poly(lactic acid) • Extrusion • Mechanical properties

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 behaviour 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 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 lignins 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 because is thought to be one of the most promising environmentally 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 engaged 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, Mw: 169.000).

2.1. Characterization of raw material

The almond shells used for lignin extraction were milled to obtain particles between 0.25-0.40 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 (70wt%) 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 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 (109.5mm) 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 mix 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)]; 0.005M H₂SO₄ prepared with 100% deionized and degassed water was used as mobile phase (0.35 mL/min flow, 40°C, and injection volume 40 μ L). 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 spectras 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 determined by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5-10mg 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.

The effect of different lignins on the crystallization behaviour of PLA was also studied using differential scanning calorimetry (DSC). In the DSC study, 5–10mg of the samples were heated at 5°C/min from ambient temperature to 200°C during 3 min, then temperature was decreased to ambient and reheated to 200°C. The absolute degree of crystallinity (X_c) of the PLA and composites was calculated by:

$$X_c = (\Delta H_m / \Delta H_m^\circ) \cdot (100/w) \quad (1)$$

where ΔH_m is the enthalpy of the sample, ΔH_m° is the enthalpy of fusion for 100% crystalline PLA (93 J/g), w is the weight fraction of PLA in the blend [22, 23].

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. Unmodified (CL and OL) and acetylated lignin (ACL and AOL) were analyzed to determine their thermal stability. Samples about 5-10mg were tested under nitrogen atmosphere at a heating rate of 10°C/min from 25°C to 400°C. PLA and blends with 5% lignins were also analyzed to determine their thermal stability. Samples about 5-10mg were tested under nitrogen atmosphere at a heating rate of 10°C/min from 25°C to 600°C.

2.5.5. Mechanical properties

The PLA/lignin blends were mechanically tested by MTS Insight 10 equipment provided with pneumatic clamps (Advantage Pneumatic Grips) and with a loading cell

of 250 N with a speed of 5 mm/min. The stress/strain measurements were performed using a video extensometer with digital video camera attached to a PC. The starting distance between the clamps was 25 mm. Samples with 6 cm long were prepared, with thicknesses between 0.25-0.8mm, and width of 2.5-5 mm. The values quoted are the average of eight measurements.

2.5.6. Hydrolytic degradation

The pure PLA and blends with 5% of non acetylated and acetylated lignin were analyzed. Hydrolytic degradation of the samples (100mg of dry weight) were carried out at 58 °C in a 25ml phosphate-buffered solution (pH=7.1). Hydrolytic degradations of the products were determined gravimetrically and visually [24, 25]. The weight of the sample was carefully measured before the measurement. After being placed into the solution, the samples were periodically removed, washed with fresh water and dried in an oven for 6 h, and then the samples were carefully weighed to evaluate the degree of hydrolytic degradation. The results are given as weight loss%.

2.5.7. Contact angle

Contact angle measurements were also carried out with water using a Dataphysics Contact angle system OCA 20, in order to determine changes in the hydrophilic character of each lignin, before and after modification. All lignins were tested at different times (0, 15, 30, 45 and 60s). Uniform pellets have been used for this propose. Blends were also analyzed in order to determine changes in the hydrophilic character of each sample, before and after hydrolytic degradation. The contact angle was read immediately in order to determine the hygroscopicity of each blend. Sample thicknesses oscillate between 0.25-0.8mm. All measurements were carried out with water, and each sample was measured with a minimum of five drops.

2.5.8. Blend morphology

Blends containing 5% lignin both unmodified and acetylated were analyzed by means of optical microscope (OM) Nikon Eclipse E600 working with the incidence of light in reflection, in order to know their morphology and analyze compatibility between PLA matrix and both types of lignins (unmodified and acetylated). Atomic force microscopy (AFM) Nanoscope IIIa scanning probe microscope from Digital Instruments was also employed to determine only the morphology of composites containing acetylated lignin systems which were studied working in tapping mode at room temperature. For this purpose, both samples were dissolved in chloroform and it was prepared by spin-coating (Spincoater P6700) at 2000 rpm for 120 s.

3. Results and discussion

3.1. Characterization of raw material

The chemical composition of almond shells was determined, and it was obtained following values: moisture content 10.8 ± 0.1 , ashes 0.9 ± 0 , extractives 0.07 ± 0 , Klason lignin 52.6 ± 3.7 , Celluloses 41.3 ± 2.2 and hemicelluloses 8.6 ± 0.8 .

3.2. Composition of Lignins

Results of acids insoluble lignin and sugars content are presented in Table 1. All the used lignins for blends elaboration, both modified and non-acetylated, showed high purity ($>80\%$). Also, considering that polysaccharides are the most common contamination in lignin, all lignins presented low quantities of sugars (0.3-3.8%) confirming the high purity of lignins. Commercial lignin (CL) indicated a lower sugar content (1.2%) than lignin extracted from almond shells (OL) (3.8%). Among the sugars present in lignins, xylose was the major hemicellulosic sugar in all lignins samples.

In both cases, acetylated lignins reflected increased purity and a reduction of sugar content. This may be due to degradation of sugars in the acetylation process.

Table 1. Lignin purity analysis.

	CL	ACL	OL	AOL
Klason Lignin %	82.6	88	81.4	90.2
Total Sugars %	1.2	0.3	3.8	0.7
Xylose	1	0.3	3.6	0.7
Arabinose	0.2	-	-	-
Glucose	-	-	0.1	-
Acetic acid %	0.4	7.5	0.9	7.8

3.3. FTIR

The wavenumbers and important bands identifications of unmodified and acetylated commercial and organosolv lignins are shown in Table 2 [26, 27]

Table 2. Bands assignments of the unmodified and acetylated lignins.

Assignment	Peak Wavenumber (cm⁻¹)			
	CL	ACL	OL	AOL
O-H stretching	3300	---	3300	---
C-H stretch in -CH ₃ and -CH ₂ -	2930, 2836	2940,2835	2941, 2836	2935,2834
C O stretching (acetylation)	---	1735	---	1740
C=C of aromatic skeleta vibrations (S>G)	1595	1595	1595	1595
C=C of aromatic skeleta vibrations (G>S)	1510	1510	1504	1504
C-H deformation in -CH ₃ and -CH ₂ -	1450	1450	1454	1459
C-H aromatic ring vibrations	1424	1415	1420	1419
Aliphatic C-H stretch in CH ₃	1364	1364	1374	1364
S ring (or G ring condensed) breathing	---	---	1330	1330
G ring breathing	1260	---	1270	---
C-C, C-O, and C=O stretch	1210	1214	1220	1219
Aromatic C-H in plane deformation (S)	1128	1119	1119	1124
Aromatic C H in plane deformation (G >S)	1024	1029	1024	1033
Aromatic C H out-of-plane deformation in C, S and H units	859	853	828	828

Although both unmodified lignins present similar spectra, only organosolv lignin showed a small peak at 1330 cm⁻¹ that indicates the presence of syringyl units. Also, it can be seen that the peak at 1260-1270 cm⁻¹ which appears in both spectra (OL and CL) is greater in commercial lignin spectra. This indicates that in the organosolv lignin

structure predominate syringyl units (S) and commercial lignin present predominance of guaiacyl units (G). Acetylated samples (ACL, AOL) showed that the signal around 3400 cm^{-1} was reduced completely and around 1735 cm^{-1} appeared an intense peak due to stretching of carbonyl groups generated after acetylation indicating that the acetylation process was successful. The spectra of acetylated lignins showed the disappearance of the peak at 1260 cm^{-1} indicating G ring breathing loss. The acetylation reaction yield was calculated using a FTIR spectroscopy. Absorbance changes were related to conversion, by measuring the height of the hydroxyl group at 3400 cm^{-1} stretching band (H_{OH}) with the height of the C-H symmetric stretching band at 2836 cm^{-1} , which was taken as reference (H_{ref}). The reaction conversion was calculated from the equation [28]

$$\alpha = 1 - [(H_{OH}/H_{ref})_{t=30} / (H_{OH}/H_{ref})_{t=0}] \cdot 100 \quad (2)$$

The acetylation reaction has been very successful in both cases due to the high conversion achieved. The performance achieved was 96% and 98% for ACL and AOL, respectively.

3.4.GPC

Lignin structure and the weight average mainly depend on the feedstock and extraction process [29]. According to the literature, organosolv process allowed to obtain lignins with higher molecular weight as compared to those extracted with alkaline solutions [30]. It has been also reported that the carbohydrates chains linked to lignin can increase the hydrodynamic volume of lignin and therefore increase the apparent molecular weight of the lignin when it was measured using GPC [1, 30]. Table 3 shows the values of weight average (Mw), number average (Mn) and polydispersity index (Mw/Mn) of unmodified and acetylated lignins. Unmodified lignins presented a little more high weight average than acetylated lignins. Among two unmodified lignins, OL showed the

higher Mw with 16167g/mol while weight average of CL was 10324g/mol. Acetylated commercial lignin and acetylated organosolv lignin had Mw 9295g/mol and 14974g/mol respectively. According to the literature, weight average should increase when lignin is modified with ester groups; also the molecular weights increase with the increase in the length of the ester substituent. In this case, the weight average decreased may be affected by the loss of hemicellulose sugars in the acetylation process.

Table 3. Weight average (Mw), number average (Mn) and polydispersity index (Mw/Mn) of different lignins.

	Mn	Mw	Mw/Mn
CL	1129	10324	9.14
ACL	1598	9295	5.81
OL	1953	16167	8.28
AOL	2409	14974	6.22

On the other hand, unmodified lignins showed greater heterogeneity than acetylated samples with Mw/Mn between 8 and 10 while acetylated lignins had values between 5 and 7. It was observed the elimination of small fractions during acetylation process so obtaining more homogeneous lignins.

3.5. Thermal properties

The DSC curves of all lignins are reported in fig. 1. In both cases, a decrease in the glass transition temperature of the acetylated lignins with respect to the unmodified lignins can be appreciated. After acetylation process, hydroxyl groups were replaced by ester substituent. Thus, reduce the number of hydrogen bonding and lead an increased free volume in the molecule and thus the mobility of the chains [31]. Commercial lignin and organosolv lignin shows a Tg value around 158 °C and 144 °C respectively. However, acetylated commercial and organosolv lignins o showed lower glass transition temperatures, 127 °C and 132 °C, respectively.

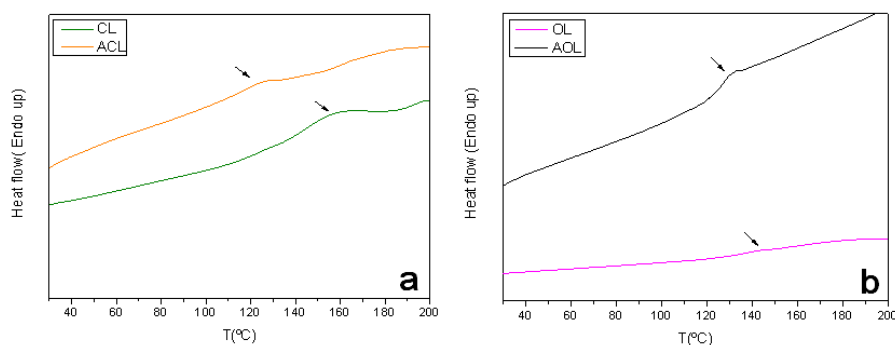


Fig. 1. DSC of (a) CL and ACL and (b) OL and AOL.

The thermogravimetric (TG) and 1st derivative thermogravimetric (DTG) curves obtained for unmodified and acetylated lignins under nitrogen atmosphere are presented in Fig 2. The initial degradation temperature, the maximum weight loss temperature and char residue are reported in Table 4. Both unmodified lignins had a small weight loss (1-4 %) below 100 °C due to gradual evaporation of moisture, however, acetylated samples didnot show any weight loss due to moisture. As it can be seen in Table 5, the initial degradation temperature corresponding to 5% weight loss ($T_{5\%}$) of both acetylated lignins is marked higher than unmodified lignins with values of 259 °C and 182 °C for CL and OL respectively. Acetylated lignins presents values 266 °C for ACL and 297 °C for AOL. The main degradation step occurs in the temperature range between 300-500°C, and it is associated with the fragmentation of inter-units linkage [8]. Also, it can be observed an improvement in the thermal stability of acetylated lignins with respect unmodified lignins, appreciating further improvement in the case of acetylated organosolv lignin. The amounts of char residue at 800 °C were found to be 52, 44, 36 and 42% for CL, ACL, OL and AOL respectively. According to the DTG curves, the decomposition of all lignins can be divided into various stages due to different molecular weight fractions present in lignins.

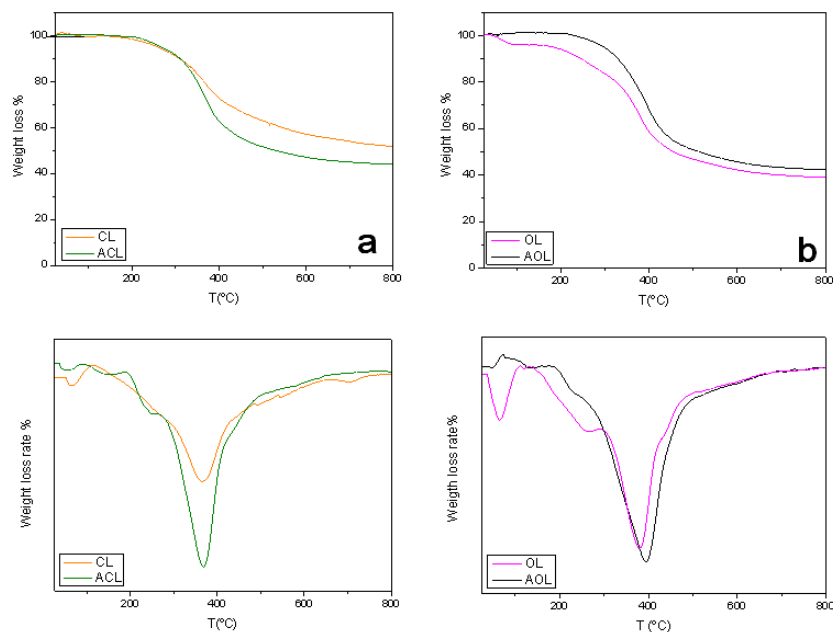


Fig. 2. TG and DGT curves of (a) OL and AOL and (b) CL and ACL.

Table 4. Temperatures and char residue characteristics of TG.

	$T_{5\%}$	T_{max}	Char residue %
CL	259	365	52
ACL	266	367	44
OL	182	380	36
AOL	297	395	42

On the other hand, the TGA and DTG curves, obtained under nitrogen atmosphere, of pure PLA and PLA/lignins blends are shown in fig. 3. The initial degradation ($T_{5\%}$), the maximum weight loss temperature (T_{max}) and char residue are presented in Table 5. Addition of different lignins increases the thermal stability of the PLA, all the blends, showed higher degradation onset and maximum decomposition temperature than PLA. Indeed, both types of lignins, acetylated and unmodified lignins, presented high thermal stability than PLA. The high thermal stability of lignin is due to the presence of complex phenylpropanoid units, which consist of aromatic phenyl groups. These aromatic structures are very stable mainly due to the overlapping of p-orbitals which

allows complete delocalization of the π electrons. Moreover, the presence of several hydroxyl groups also contributes to stability since the unpaired electrons also come into resonance, increasing the stability of the aromatic structure and impeding its break, which occurs only at high temperatures [10]. Thus, blends with acetylated lignins exhibited lower temperatures ($T_{5\%}$ and T_{\max}) than composites with unmodified lignins. On the other hand, char residue, in general, increased with the addition of lignin into the composites as reported in other studies [4].

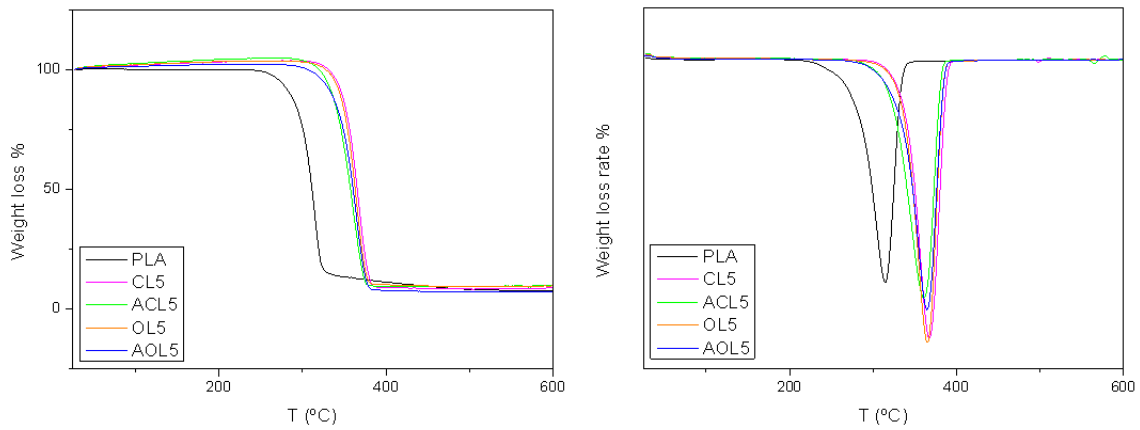


Fig. 3. TG and DGT curves of PLA and composites 5%.

Table 5. Temperatures and char residue characteristics of composites

	$T_{5\%}$	T_{\max}	Char Residue %
PLA	264	314	7.5
CL5	337	367	8.6
ACL5	325	360	9.5
OL5	335	365	9.7
AOL5	318	365	7.3

The effect of lignin on the crystallization and melting behaviour of blends was studied in non-isothermal DSC experiments. With the aim to cancel previous thermal history, the melting was carried out at 200 °C for 3 min. The DSC of PLA and blends containing 5 % lignin are depicted in fig. 4. Glass transition temperature (T_g), melt temperature

(T_m), crystallization temperature (T_c), endothermic enthalpy of melting (H_m), and exothermic enthalpy of crystallization (H_c) of the samples were displayed in Table 6. The pure PLA exhibited a T_g at 59.2 °C and a melting temperature (T_m) around 146 °C. Calculated PLA crystallinity according to Equation (1) was 35.9%, and crystallization temperature (T_c) was around 106 °C. Similar results were obtained by other authors [32]. No significant change in glass transition temperature (T_g) of the samples was found as it remained fairly constant with a very small increase. Two melting peaks can be observed in the thermogram; when two or more melting peaks were observed in a DSC thermogram, we assumed that the lowest melting peak was a real melting peak, while the other peaks were ascribed to the melting of the crystallites formed or thickened during DSC scanning. As it can be observed, PLA/lignin blends presented an increase in cold crystallization temperatures between 14 to 17 °C and in melting temperature between 3 to 4 °C. The normalized heat of fusion decreases with lignin addition in the blends. This behaviour may point to a lower nucleation density, then to the formation of poorer and fewer crystals. The introduction of lignin (amorphous in nature) affected the interactions among the PLA chains. This change affects greatly the crystallization behaviour causing that the PLA chains have a lower mobility and crystallize with greater difficulty and higher temperatures. The crystallinity degree decreases for all blends except CL5 which remains fairly similar.

Table 6. Thermal properties of blends containing 5% of unmodified and acetylated lignins.

	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c
PLA	59.2	106.4	146.5	33.4	32.0	35.9
CL5	59.3	120.2	149.5	31.4	30.5	35.6
ACL5	59.8	124.5	150.5	25.3	24.0	28.7
OL5	59.8	123.2	150.5	26.4	26.5	29.9
AOL5	59.5	123.0	150.1	27.0	26.8	30.6

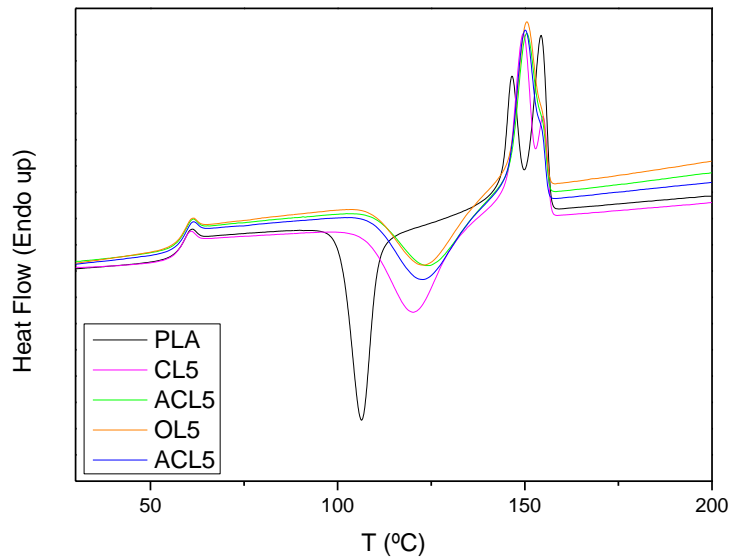


Fig. 4. DSC thermogram of PLA, composites with unmodified lignins and acetylated lignins (*2^o heating*)

3.6. Hydrolytic degradation

3.6.1. Weight loss and composites appearance

Fig. 5 exhibits the optical images of different samples after being hydrolyzed in four weeks. Changes in the appearance of the specimens are remarkable; a significant change in the samples opacity could be noticed, already after one week of immersion in buffered solution. Besides the loss of transparency of the PLA and loss of gloss of other blends, was also observed in the first week that composites became extremely brittle. All samples have been broken before the assay end. This prevented carrying out the mechanical tests of samples after hydrolytic degradation and getting an exact of mass losses of blends formed with commercial lignin (unmodified and acetylated). The modification of the opacity of samples, which is a consequence of degradation, can be explained by various phenomena occurring all along the degradation. Indeed, the changes in appearance are directly related to the light diffusion through the material due to the presence of water and/or to the degradation products formed during the hydrolytic

process. Such diffusion can be altered either by the formation of holes in the bulk of the specimen during the degradation or by evolution in crystallinity of the polymer [33-35]. So, the hydrolytic degradation of the polyester chains is known to take place at a higher rate in the amorphous zones of the matrix, this phenomenon is expected to increase the relative crystallinity of the sample, which may result in increased opacity of the material. During the first two weeks of testing, the samples showed a small weight gain due to moisture absorbed during the process. Normally, the diffusion of water into the products was higher during the first period assay [36]. The third and fourth week began to be small weight loss in the composites. This may be due to the large thickness of the samples. Hydrolytic degradation test was performed with samples obtained directly from the extrusion process with thicknesses varying from 0.25-0.8mm. Therefore, it was more difficult to start hydrolytic degradation because the thickness of the sample in this test is a critical factor. After four weeks of test, the PLA lost $4\pm 0.2\%$ of mass, composites with 5% lignin obtained from almond shells by $3.8\pm 0.1\%$ and 5% composites with acetylated organosolv lignin $2.5\pm 0.2\%$. It seems that the addition of lignin can retard hydrolytic degradation of the PLA. Other authors have proven that blends of poly (hydroxybutyrate) (PHB) and lignin obtained by extrusion and buried in garden soil during 12 months showed that PHB films lost 45 wt% of mass in 12 months, while with the blend containing 10 wt% lignin, only 12 wt% of mass was lost during the same period [37]. In other study, lignin was used as filler in low-density polyethylene and polypropylene up to 30 wt% in order to know the influence of lignin in UV light degradation. The degradation process starts earlier for the pure polymer than for polymers with low concentrations of lignin blends [13].

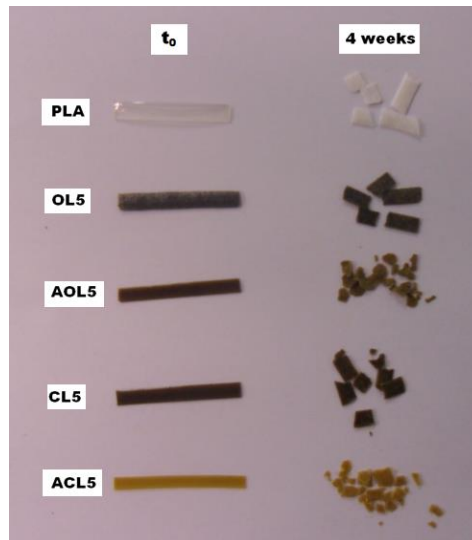


Fig. 5. Changes in sample visual aspect upon four weeks of hydrolysis for the PLA matrix and composites with 5% of lignins (acetylated and non-modified).

3.6.2. Contact angle

The blends were tested at different times (0, 2 and 5 min) before hydrolytic degradation. PLA showed contact angle values of $72.5 \pm 2.5^\circ$ at the initial time which is consistent with those found in literature. Blends formed by unmodified and modified lignins showed high contact angle values, obtaining an improvement in hydrophobic character of PLA. On the other hand, all blends showed the same trend over time, decreased around 10° the contact angle values. After degradation process during 4 weeks have only been analyzed samples of PLA and blends with unmodified lignins (CL5 and OL5). Fig. 6 shows the contact angles of the PLA and blends with unmodified lignins before and after 4 weeks of degradation. As it can be seen the contact angle decreased a lot in all cases. Besides, it was not possible to analyze the contact angle at different times due to the rapid absorption of the drop.

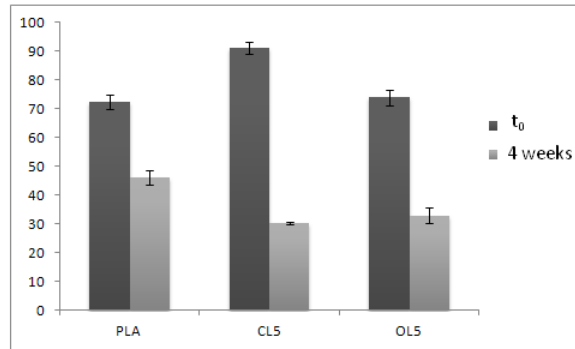


Fig. 6. Contact angle of composites before and after 4 weeks of hydrolytic degradation.

3.6.3. Morphology

Fig. 7 shows micrographs of blends with 5% lignin. It can be observed that both blends with unmodified lignin (a and c) presented aggregates due to incompatibility between PLA and lignin. After acetylation process, blends seem homogeneous at a macroscopic scale. Other author [38] obtained better compatibility between the kraft esterified lignin and wheat gluten and a less rough surface than films with wheat gluten and unesterified lignin. However, microscopic scale reveals the existence of small lignin particles (b and d). In this case, the particles were smaller than composites with unmodified lignins, so it was demonstrated that after acetylation of lignins a mixture with greater compatibility between matrix and filler and higher dispersion of lignin particles was obtained. On the other hand, AFM images (fig. 8) showed the existence of lignin nanoparticles homogeneously distributed in the PLA matrix. Particles with sizes around 100nm have found.

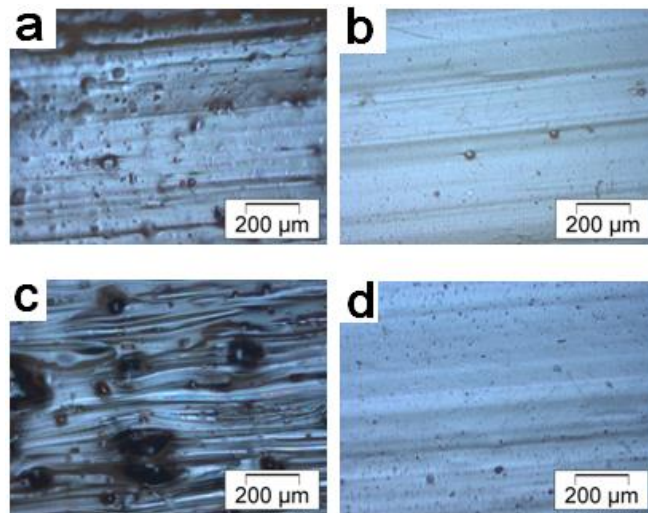


Fig. 7. Micrographs of composites (a) CL5, (b) ACL5 (c) OL5 and (d) AOL5.

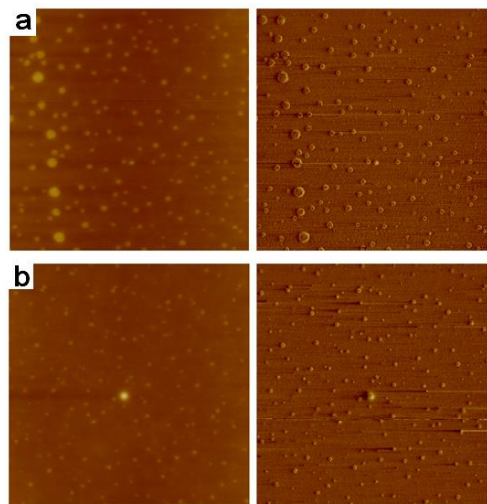


Fig. 8. AFM noncontact mode phase and height images of composites with both acetylated lignins thin films prepared by spin-coating (a) ACL5 and (b) AOL5. The data scale is 5 μm x 5 μm.

3.7. Mechanical properties

Tensile tests have been performed to study the different lignins effect on mechanical properties of PLA. Mechanical properties of blends with different percentages are showed in Fig. 9. The maximum strain was not severely affected by the low percentages (0.5-1%) of unmodified lignin, mainly in the case of organosolv lignin. However, at percentages greater than 5%, the maximum strain decreased with increasing lignin content, especially in blends formed by PLA and commercial lignin. Other study in which was elaborated a blend of PLA / unmodified commercial lignin by similar methods were also observed a decrease in the stress at percentages of 5% and 10% [16]. In the case of blends with acetylated lignin, both showed an improvement respect to composites with unmodified lignin, particularly, at high percentages. This blend with acetylated lignin presented a less rough surface without the presence of agglomerations than blends with unmodified lignin. This may be the result for the best interaction between PLA and acetylated lignins than PLA with unmodified lignins. Similar results were found with other composite formed by cellulose triacetate as polymer matrix and unmodified and acetylated lignin as filler; in this case acetylated lignin also provided an improvement over the lignin without acetylated [29]. Moreover, the elongation at break decreased upon the addition of high percentages of unmodified lignin, but blends with low content of unmodified lignin presented an improvement compared to PLA. Furthermore, have seen an increase in the deformation in all blends blended with acetylated lignin. The improvement in ductility on compatibilization can be attributed to both esterification as esters act like internal plasticizers [27]. Other author [32] also demonstrated a slight increase in the deformation of films formed with starch and lignin. The Young's modulus shows a slight decrease in all cases although the addition of acetylated lignin at high percentages (20%) enhanced these properties.

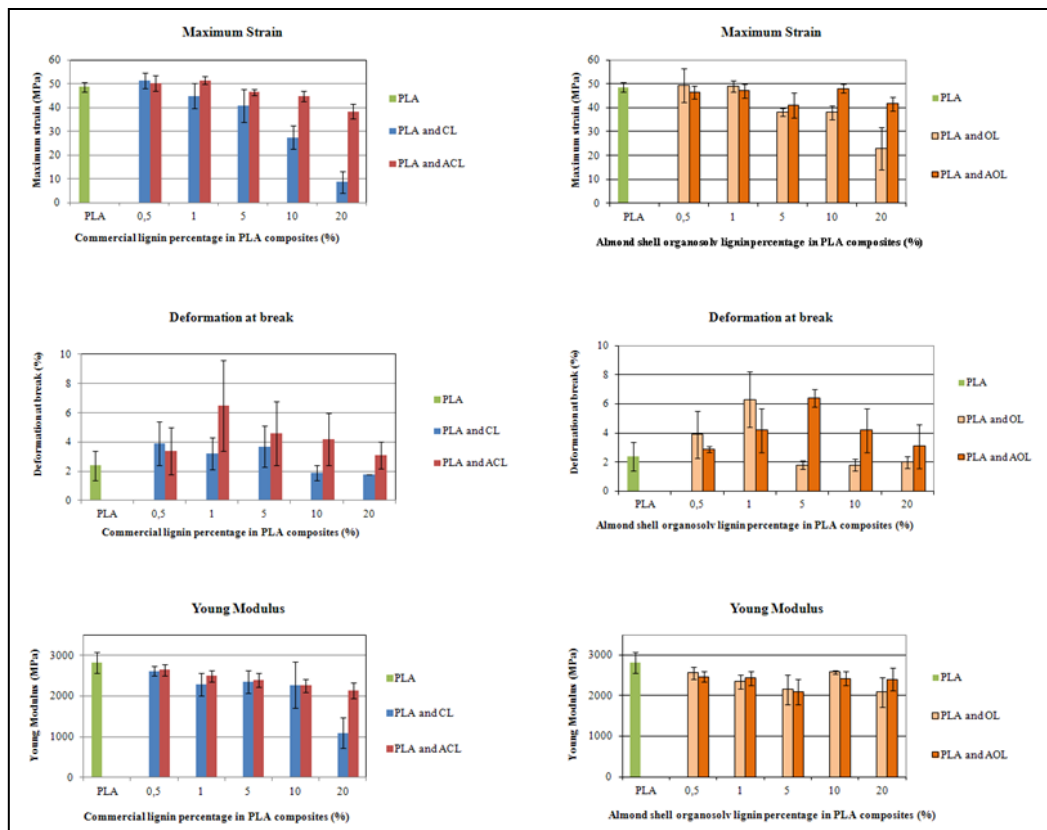


Fig. 9. Mechanical properties of PLA and blends.

4. Conclusions

In this work two different lignins were used, commercial alkaline lignin and lignin extracted from almond shells. Original and acetylated lignins were used as PLA filler. Acetylation process of lignins resulted successful with high yield and besides improvement in the compatibility between the two components of the mixture was achieved. All lignins presented high purity with very low content of polysaccharides. Acetylated lignins have lower T_g and higher thermal stability than original lignins. The addition of lignin greatly improved the thermal stability of PLA but PLA crystallization behaviour is not favoured. Although it would require a more exhaustive test, the addition of acetylated lignins appears to prevent hydrolytic degradation of PLA. Mechanical properties of PLA worsen with the addition of high percentages of lignin; however, PLA/acetylated lignin blends properties remain similar to those of pure PLA. In all cases, the elongation at break was increased.

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