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MODIFICATION OF EUCALYPTUS AND SPRUCE ORGANOSOLV LIGNINS WITH FATTY ACIDS TO USE AS FILLER IN PLA

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Abstract

Spruce (softwood) and Eucalyptus (hardwood) woods were used as raw material for lignin extraction by organosolv process. Chemical, structural and thermal characterization of the extracted lignin samples have been performed using HPLC, GPC, FT-IR, ^{31}P NMR, ^{13}C NMR, DSC and TGA. Both lignins showed high purity, being Spruce lignin (OS) which presented the highest Klason lignin content (93%) and lowest sugar (0.5%) and sulphur (0.04%) content. Extracted lignin samples were chemically modified with dodecanoyl chloride fatty acid, in order to modify its thermal properties as glass transition temperature (T_g). The noticeable increase in the molecular weight and sharp decrease of T_g can be appreciated. Esterified lignins were used as filler in poly(lactic acid) (PLA) films elaborated by solvent casting in different concentrations (1, 5, 10, 25 and 50%). Mechanical, thermal and water barrier properties of prepared films were investigated. The results showed that the addition of both modified lignins contributed to greater ductility and lower stiffness, providing plasticity to PLA.

Keywords: Organosolv lignins, fatty acids, films, poly(lactic acid), ductility

1. Introduction

Nowadays most of the plastics materials are made from petroleum. Although the development of polymeric materials has a vital importance in the society over the years and has contributed to facilitate our way of life, their use creates many potential problems due to their non-renewable nature and ultimate disposal [1]. Therefore, is necessary to develop biodegradable materials based on renewable sources with comparable properties to synthetic polymers and at equivalent cost. For this purpose, the use of lignocellulosic biomass is an attractive alternative due to their renewable origin, the biodegradability of their components and their non-human food application [2, 3].

Lignin, one of the main structural components of lignocellulosic biomass and the second most abundant macromolecule in nature, can offer a large amount of organic material that could be used in the production of biopolymers. The conversion of lignin to value-added products like biomaterials is an essential part of the integrated biorefinery concept. Although native lignin structure has been studied for years, its chemical structure has notable distinction depending on the origin, growing conditions of the plant [4, 5] and also employed isolation process. In general, lignin is a complex amorphous and heterogeneous polyphenol material with numerous functional groups such as methoxyl groups (-OCH_3), phenolic and aliphatic hydroxyl groups principally (-OH). Its abundance and biodegradability as well as the presence of appointed functional groups that could be easily modified by well-known methods, makes it a good alternative as a raw material in the polymer industry.

Several authors showed the possibility to incorporate lignin directly without any modification into other commercial synthetic [9-13] and biodegradable [14, 15] polymers to give new or improved properties to the material. However, the poor compatibility between lignin and blended polymers was often observed [16, 17], Therefore, the chemical modification can be a good alternative for the functionalization of hydroxyl groups [6]. Due to its structural features, lignin has a high potential for chemical modifications, which can lead to value-added polymeric materials with specific properties [18]. Several studies have been published about esterification of lignin in an attempt to improve the dispersion in the blends and performance in the final materials [19, 20, 21]. Hence, chemical modification of functional groups presents in lignin molecule like phenolic hydroxyl groups and aliphatic hydroxyl groups at the C-α and C-γ positions on the side chain, is a good alternative to increase its range of applications in the polymer industry area [6, 22, 23]. The esterification of lignin allows increasing the hydrophobicity of lignin and its solubility in organic solvents [24]. Moreover, lignin also possesses many disadvantages like its brittleness, poor film forming ability and difficulty of processing [25]. The natural condensed structure and strong intermolecular hydrogen bonding interactions in lignin restrict the thermal mobility and this provides high T_g value [17]. When lignin is modified by esterification, hydroxyl groups are replaced by ester substituent [26] and thus, reduce the number of hydrogen bonding and lead an increased free volume in the molecule, providing mobility of the chains [27]. In this sense, esterification is a potential route to lower the glass transition point of lignin and increase its thermoplasticity [25, 28, 29], highly desirable for current industrial polymeric processing technology.

In the present study, two types of raw materials (Spruce and Eucalyptus) were used for the lignin isolation by organosolv process. First, the determination of chemical composition, structure and thermal properties of extracted lignins were analysed. Here, the determination of functional groups of the lignins, like aliphatic and phenolic hydroxyl groups are an important factor, due to provide the total content of potential active sites in the lignin polymer structures able to be modified. The knowledge of the lignin chemical structure is very important for its chemical modification and therefore for new materials elaboration.

Moreover, esterification reaction of obtained lignins was carried out using fatty acid as reagent with a long aliphatic chain (12C). This modification is highlighted for its short period without using temperature. This strategy was developed with two different objectives. First, to analyse the changes in the thermal properties of lignins, as glass transition temperature and thermal stability. And the second one, to try to improve the low ductility of the poly(lactic acid) (PLA) using modified lignins as filler in different concentrations to overcome the major drawbacks of PLA for some applications (brittleness and stiffness). In fact, PLA is a brittle and rigid polymer, which has very low ability to plastic deformation (~3%). The brittleness is one of the important weaknesses of the PLA [30] due to it presents low deformation at break and high modulus that limits its applications in packaging industry [31]. Besides that, in this work, the effect of esterified lignin incorporation in the PLA thermal stability, mechanical properties and water barrier properties has been analysed. Although some works have been published about lignin application into some polymeric materials systems, the incorporation of esterified lignin by fatty acids as well as its application as filler into PLA for the improvement of its material properties and the elaboration of completevely renewable material result highly interesting.

2. Materials and methods

2.1. Materials

Two different raw materials were used for lignin extraction; Spruce and Eucalyptus wood, provided by KTH University in Sweden. PLA (Nature-Works® PLA Polymer 3051D) was from NatureWorks LCC (Glass Transition Temperature 55-65 ºC, Melt Temperature 150-165 ºC, Mw: 169.000 g/mol). Ethanol absolute (99.9%), N,N´-dimetilformamide (99%), pyridine (99%), dodecanoyl chloride (98%) and hydrochloric acid (37%) were used as supplied by Panreac and Sigma-Aldrich.

2.2.Lignin isolation

Both raw materials were subjected to organosolv extraction process. The extractions were carried out in a 4 L pressure (20Ba) stainless steel batch reactor with constant stirring (EL0723 Iberfluid) with electronic control unit for pressure and temperature control. Spruce was treated with a mixture of ethanol-water (50/50 w/w) for lignin extraction (OS). In this case, H_2SO_4 was used as catalyst (1.2% w/w). The treatment was carried out at 180 °C for 60 min and the solid to liquid ratio was 1:7 (w/w) [32]. Dissolved lignin was isolated by precipitation with four volumes of cold water. For Eucalyptus lignin (OE) extraction, a mixture of ethanol-water (60/40 w/w) was used. The treatment was carried out at 180 °C for 90 min. The solid to liquid ratio was 1:10 (w/w) [32]. Dissolved eucalyptus lignin was isolated by precipitation from the obtained liquor with two portions of acidified water (pH= 2) adjusted with sulphuric acid. The lignins were recovered by filtration, washed until neutral pH and then were dried at 50 °C.

2.3. Synthesis of lignin-fatty acid derivates

0.5 g of lignin was dissolved into 15 mL of DMF in a two-necked flask with a magnetic stirrer. Pyridine (2.75 mL) was used as a catalyst and dodecanoyl chloride was added (0.9 mL~~.~~). The reaction was conducted at 20 °C for 2 h. After that, the solution was poured into 650 mL of 2% ice-cold hydrochloric acid. The precipitate was filtered and washed with excess distilled water and ethanol to remove unreacted fatty acids. The samples were then dried in vacuum at 35 ºC overnight. The esterification reaction is summarized in Fig. 1.

2.4. Films elaboration

The films were elaborated by poly(lactic acid) (PLA) as matrix and different percentages of modified lignins (1, 5, 10, 25, 50%) as filler. Films have been prepared by solvent casting using chloroform (15 ml) as solvent for its ability to dissolve PLA. When PLA was totally solubilized, the requiered amount of modified lignin was added. The total amount of dry substance (PLA and modified lignin) in each film was kept constant at 0.5 g.

2.5.Characterization

Acid-insoluble lignin (i.e Klason lignin) (TAPPI T222 cm-98) and soluble lignin (with UV (band 205 nm) was determined. Carbohydrate contamination was measured by analysing the hydrolysate using High Performance Liquid Chromatography (HPLC) [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 mL). High purity standards of D-(+)-glucose, D-(-)-xylose, and D-(-)-arabinose (provided by Fluka, with 99% of purity) were used for calibration.

Elemental analysis was performed using 1-3 mg samples dried in a vacuum oven at 40 °C for 48 hours, using a Flash EA 1112, Thermo Finnigan, USA elemental analyzer (external service provided by the Elemental Analysis Unit of the Santiago de Compostela University, USC, Santiago de Compostela, Spain). The ashes were determined using thermogravimetric analyses up to 800 °C under oxygen atmosphere.

Size exclusion chromatography analysis was used to evaluate the average molecular weight (Mw) and polydispersity (Mw/Mn) 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 ºC, using a Jasco Inc. chromatograph provided with an LC-NetII/ACD interface, a column oven CO-2065Plus and a RI-2031Plus intelligent refractive index. 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 g/mol. The weight increase (WI %) after lignins modification was also measured as follows:

$$WI\ (\%) = [(m_1 - m_0)/m_0] \times 100 \qquad (1)$$

where m_0 is the initial weight of dried lignin sample (g) and m_1 is the weight of lignin after esterification reaction (g).

The FT-IR analysis of unmodified and esterified lignins was performed on a PerkinElmer UATR Two FT-IR spectrophotometer. A total of 8 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}.

For ^{13}C NMR analysis, 100 mg lignin was acetylated in 1 mL of anhydrous pyridine and 1 mL of acetic anhydride. After that, solution was poured into 20 mL of ethanol and removed the solvent under reduced pressure (3 times). The same procedure was performed with toluene and chloroform until pyridine was completely gone. For the quantitative ^{13}C NMR, the concentration of lignin was 20% in DMSO-$_{d6}$ as solvent. A 90° pulse width, 1.4 s acquisition time, and a 1.7 s relaxation delay were used. Chromium (III) acetylacetone (0.01 M) was added to the lignin solution to provide a complete relaxation of all nuclei. A total of 200.000 scans were collected. All integrations were performed assuming the integration of aromatic region (160-100 ppm) as 6 carbon atoms.

Phosphorus-31 Nuclear Magnetic Resonance (^{31}P NMR) analysis with 90-degree pulse angle, an inverse gated proton decoupling, and a delay time of 10 seconds was used for the identification and quantification of hydroxyl and carboxyl groups of lignins. Prior to analysis, a 20 mg sample of the respective lignin fraction was functionalized using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in a 1/1.6 mixture ($_V/_V$) of $CDCl_3$ and pyridine for 2 hours at room temperature [33].

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. Unmodified and esterified lignins were analysed to determinate their thermal stability. Samples about 5-10 mg were tested under nitrogen atmosphere at a heating rate of 10 ºC/min from 25 ºC to 600 ºC. PLA and elaborated films with modified lignins as filler were also analysed to determinate their thermal stability. Samples about 5-10 mg were tested under nitrogen atmosphere at a heating rate of 10 ºC/min from 25 ºC to 600 ºC.

The glass transition temperature of unmodified and modified lignins was determined by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5-10 mg were tested under nitrogen atmosphere at a heating rate of 10 ºC/min. The isolated lignins were heated from 25 ºC to 200 ºC. Each sample was first heated from 25 to 100 ºC (10 min) and cooled down to 25 ºC to eliminate any interference of water. However, chemical modified lignins were analysed from -60 ºC to 200 ºC. The results for each sample were reported as the average of the two runs.

The PLA/esterified lignin composites 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. Samples were prepared according to standard ASTM D-1708. Thicknesses of samples range between 50-90 μm. The starting distance between the clamps was 22.9 mm. Samples with 6 cm long were prepared, with a width of 4.75 mm. The values quoted are the average of eight measurements.

WVP of films was determined according to ASTM E96-00 [34]. The sample was cut into a circle of 7.40 cm diameter and the test area was 33 cm^2. The setup was subjected to a temperature and relative humidity of 38 ºC and 90 %, respectively. Water vapour permeability rate (WVTR) was calculated as follows:

$$\mathrm{WVTR} = G/(t \cdot A) \qquad (2)$$

where, G is the change in weight (g), t is time (h), and A is the test area (m^2).

WVP was calculated as:

$$\mathrm{WVP} = (\mathrm{WVTP} \cdot T)/\Delta P \qquad (3)$$

where, T is the thickness of the test specimen (mm) and ΔP is the partial pressure difference of the water vapour across the film. WVP of three specimens for each sample was calculated and reported.

3. Results and discussion

3.1. Chemical composition of isolated lignins

The chemical composition of isolated lignins was determined in terms of Klason lignin, acid soluble lignin (ASL), ashes, and sugars content. Elemental analysis was used to determine sulphur content. The impurities of lignins are usually composed by residual carbohydrates and ashes. As can be observed in Table 1, OS presented the highest lignin and less sugar content, however, the ash content is similar for both lignin samples. The high sulphur content for OS (0.20) can be due to the sulphuric used as catalyst during isolation process.

3.2. Molecular weight

Weight average (M_w), number average (M_n), polydispersity index (PDI) and weight gain (WI %) of isolated and modified lignins are reported in Table 2. Lignin structure and the weight average could be quite different depending on the feedstock and used extraction process [20, 35]. OE presented higher molecular weight and higher polydispersity index than OS, probably related to the use of H_2SO_4 as catalyst for OS isolation. Also, OE showed higher sugar content than OS, it can influence the molecular weight results. It has already been 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 by GPC [36, 37]. As expected, after esterification of lignins with dodecanoyl chloride, a significant increase in M_w was observed. This demonstrated that fatty acid has been successfully aggregate to the lignins. It is known that the 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 [38]. In the case of the weight gain values, it was recovered more than twice introduced lignin in the reaction in both cases, indicating that once again that lignin has been succesfully modified in a short period of time without temperature.

3.3. Structure analysis

The high content of aliphatic and phenolic hydroxyl groups is essential for the chemical modification of lignin. Aliphatic and total phenolic hydroxyl groups signals appear at 149-146 ppm and 144-137.5 ppm respectively. The peaks at 139.5 and 142.5 are assigned to guaiacyl and syringyl units respectively. Condensed guaiacyl OH groups can be found between 144-141 ppm and at 135 ppm signal is assigned to carboxyl groups [39, 25]. C_5 substituted condensed phenolic OH (β-5, 5-5´, 4-O-5 linkages) were integrated into the region between 144.7-142.8, 141.7-140.2 and 142.8-141.7, respectively [40]. In Eucalyptus, lignin (OE) spectra can be observed a peak at 142.5 ppm, which corresponds to syringyl units which are not visible in Spruce lignin (OS). This result agrees with those found in literature [7], and confirm that Eucalyptus hardwood lignin is composed by S-G units, while Spruce softwood lignin is basically formed by G units. Although both type of lignins presented similar hydroxyl groups content, OE had higher aliphatic OH and less phenolic OH in its structure than OS. The high content of aliphatic OH groups in OE may be due to the presence of carbohydrates. The less content of phenolic OH in Eucalyptus could be associated with the units presents in hardwoods which are preferentially linked through phenolic hydroxyls to form ether bonds like β-O-4 and 4-O-5 [8]. Regarding to condensed structures, it can be observed remarkable higher content of 5-5´ and condensed guaiacyl units in OS and 4-O-5 bonds in OE. These results can be related to the general percentages of linkages presents in both types of woods found for other authors [41]. This is usually to find in softwood lignins, higher content of β-5 and 5-5´ which contributing to degree of condensation in lignin molecule [42]. Lignins with high guaiacyl content present more condensable structure. However, for chemical modification, the lignin reactivity depends on the S/G ratio and the existence of uncondensed phenolic OH groups, among other factors [7]. The reactivity of phenolic OH groups, which are the most reactive groups in lignin molecule, can be reduced by the steric hindrance generated by the presence of syringyl units, which have the C3, and C5 substituted by methoxyl groups as well as by the presence of the condensed phenolic OH groups. In general, guaiacyl units are more reactive than syringyl units due to G units present the C5 free. However, the condensation of phenolic OH groups (typical of G units) has also a vital importance. Uncondensed OH groups have C5 position free which makes that this OH groups has less steric hindrance and could be easily modified. As found by other authors, organosolv pulping generated lignins with low amounts of carboxylic groups [43] (Table 3).

Quantitative ^{13} C NMR spectra of acetylated lignin samples were carried out in order to know the distribution of functional groups of each lignin per one C_9 unit. The signals were assigned according to the chemical shift assignment reported for other acetylated lignin samples found in literature [42, 44-47]. The obtained results are given in Table 4. The content of phenolic and aliphatic hydroxyls groups determined after acetylation lignin samples showed the same trend that calculated by ^{31}P NMR. The S/G ratio for OE was 1.5, while in Spruce lignin no syringyl units have been detected. In addition, OE showed higher content of methoxyl groups than softwood lignin due to the presence of syringyl units in its structure. Aromatic C-O content could be related with the ether bonds, so the less content of aromatic C-O in softwood lignin may be due to the less content of ether bonds in its structure. Less ether bonds content is attributed with higher phenolic OH content in OS structure. The content of aromatic C-H in lignins is widely associated to degree of condensation (DC). Moreover, depending on plant origin, softwood lignin presented higher DC than hardwood lignin due to its structural composition almost based on guaiacyl units.

The chemical modification was confirmed by FTIR and is shown in Figure 2. Both isolated lignin samples showed a wide absorption band at 3400 cm^{-1} indicated the presence of O-H stretching vibrations in aromatic and aliphatic O-H groups. Bands around 2930 and 2840 cm^{-1} can be assigned to C-H stretching in $-CH_2-$ and $-CH_3$ groups [20]. The small band al 1710 cm^{-1} showed the presence of non-conjugated carboxylic acids [26]. Signals between 1400 and 1700 cm^{-1} are attributed to the aromatic skeletal vibrations. The peaks at 1595 and 1510 cm^{-1} are due to C=C of aromatic skeletal vibrations. The bands found at 1460 and 1420 cm^{-1} are attributed to the C-H deformation in $-CH_2-$ and $-CH_3$ groups, and C-H aromatic ring vibrations, respectively. The band at 1365 cm^{-1} corresponds to aliphatic C-H stretch in $-CH_3$ groups. The band at 1325 cm^{-1} can be attributed to the presence of syringyl units (C-O stretch), only could be found in Eucalyptus lignin (OE). However, the peak at 1265 cm^{-1} assigned to guaiacyl (C-O stretch) ring breathing appears in both samples but could be observed with high intensity in Spruce lignin (OS). Some characteristic bands associated to syringyl and guaiacyl units in lignin were detected at 1220, 1110 and 1030 cm^{-1} corresponding to C-C, C-O and C=O stretch (G), aromatic C-H in plane deformation (S) and aromatic C-H in plane deformation (G > S) [48, 49, 50]. FTIR spectra of modified lignins confirmed that the estherification process was successful at studied conditions. Modified lignins showed that the signal around 3400 cm^{-1} which corresponds to O-H stretching vibrations in aromatic and aliphatic hydroxyl groups was reduced and the appearance of two new peaks at 1740 $cm^{-1}$and 1760 cm^{-1} are clearly seen. They are assigned to aliphatic and aromatic ester bonds, respectively. The intense increase of peaks at 2930 cm^{-1} and 2840 cm^{-1} are assigned to long chain alkyl groups (aliphatic carbon) which are present in fatty acid chloride. Moreover, the absence of characteristic bands of dodecanoyl chloride (1800 cm^{-1} which is related to COCl) and dodecanoyl acid at 1700 cm^{-1} (COOH), showed that the modified lignins do not contain traces of free fatty acid. Therefore, the used washing method was suitable for removing impurities from the final product.

The esterification 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=C of aromatic skeletal vibrations band at 1510 cm^{-1}, which was taken as reference (H_{ref}) [26]. The reaction conversion was calculated from the equation as follows [51]:

$$\alpha = 1 - [(H_{OH}/H_{ref})_{t=2h} / (H_{OH}/H_{ref})_{t=0}] \cdot 100 \qquad (4)$$

The esterification reaction has been very similar in both cases. The performance achieved was 80% and 82% for OS_{12C} and OE_{12C}, respectively.

3.4. Thermal analysis

The DSC curves of isolated and modified lignins are shown in Fig. 3(a,b). DSC is the most accepted method to define the glass transition temperature of lignin molucule. These thermal parameter provide important information to use lignins in polymer applications but it is often difficult to determine. This difficulty is attributed to the heterogeneity of the lignin chemistry and broad molecular weight distributions. Normally, the T_g values of various nonderivatized lignins range from 90 to 180 ºC [32, 52]. Both isolated lignin samples had a relatively high glass transition temperature (110-125 ºC) due to the condensed rigid phenolic moieties and strong intermolecular hydrogen bonding interactions which restrict the thermal mobility of lignin molecules and result in its high T_g [17]. However, modified lignins presented a great reduction of the glass transition temperature, being 15.8 ºC for OS_{12C} and 17.4 ºC for OE_{12C}. In the esterification reaction, hydroxyl groups were replaced by ester substituent. Thus, reduce the number of hydrogen bonding and lead an increase free volume in the molecule and thus the mobility of the chains [27].

The thermal degradation in polymers is also an important parameter to know during thermal processing and to establish the service life conditions [24]. The thermogravimetric (TGA) curves obtained for isolated and modified lignins under nitrogen atmosphere are presented in Fig. 4. Isolated lignins had a small weight loss (0-3%) below 100 ºC due to the gradual evaporation of moisture, however, modified lignins did not show any weight loss due to moisture confirming that the esterified lignins were more hydrophobic than originals ones. Thermal stability of the samples was assessed as the onset temperature (referred to 5% weight loss) and maximum degradation temperature together with the loss weight in this range and the obtained results are summarized in Table 5. The obtained thermograms of original and modified lignins were indicative of the alterations in chemical structure and thermal stability.

Both modified lignins presented lower initial degradation temperature ($T_{5\%}$) than original lignins. Isolated lignins only presented a single wide degradation step. This main weight loss stage occurs in the temperature range between 200-600 °C [43] and in this case are centered around 385 °C for OS and 353 ºC for OE. The main stage is associated with the fragmentation of inter-units linkage [12] like cleavage of typical ether linkages among the aromatic units. Then, cracking of aliphatic side-chains and cleavage of functional groups occurs [6, 53, 54]. However, modified lignins presented less thermal stability than originals one. They started to decompose ($T_{5\%}$) before than original lignins and showed two main degradation steps. The first one can be observed between 220-240 ºC and the second one between 370-395 ºC (Fig. 4). the first weight loss is associated with the cleavage of the C-O bond present in the ester linkage and the consequent loss of the introduced long aliphatic chain. In other studies, where other biomass components like cellulose was modified with the same reactive (dodecanoyl chloride), it was also observed two degradation steps [55, 56]. The first one could be observed at similar temperatures to this study. Modified lignins also exhibithed higher weight loss betwen 200-600 ºC than original lignins, 70-75% and 50%, respectively. This is due to the lower content of phenolic OH groups in their structure of modifies lignins. On the other hand, the amount of char residue is lower for modied lignins.

The thermal properties of elaborated films with modified lignins were also analized by TGA (Fig. 5). The initial degradation temperature ($T_{5\%}$), the maximum weight loss temperature (T_{max}) and char residue of the films are presented in Table 6. The addition of lignins decreases initial degradation temperature of PLA, when the modified lignin content increases in the PLA/modified lignin films. However, all studied composites showed higher maximum decomposition temperature than PLA and it increases at high percentages of lignin.

3.5. Mechanical properties

Tensile tests have been performed to study the effect of modified lignins on mechanical properties of PLA. The Young's modulus, elongation at break, stress at break and stress at yield of the different samples are shown in Fig. 6. The analysed mechanical properties demonstrated that neat PLA show very low elongation at break (about 3%) and high elastic modulus (E = 2 GPa), indicating a brittle behaviour. Both types of used lignins provide similar properties to the PLA. The addition of esterificated lignins (1-50%) into the PLA matrix showed a progressive reduction in the elastic modulus with increased esterified lignin content, evidencing the reduction of the rigidity of the films. On the other hand, the elongation at break of the PLA/esterified lignin films, strongly increased with the adittion of lignins up to 25%, particularly in the case of Spruce lignin (OS_{12C}), showing an important enhancement in ductility. Probably, OS_{12C} provided greater ductility or ability to deform plastically due to it had lower molecular weight than $OE_{12C.}$ Other authors have demonstrated that low molecular weight plasticizer (poly(ethylen glycol) provides greater plasticizing effect to the material [57]. However, a higher content than 25%, the material became brittle, especially in the case of OE_{12C}, probably because of a lack of cohesion between lignin and PLA [31]. On the other hand, films endured less stress at break and stress at yield than original PLA and decreased with increased lignin content. Other studies also showed that the addition of plasticizers decrease Young modulus and stress at break of final materials [31,58]. The plastificant effect of modified lignin could be attributed to esterification, as esters usually act as plasticizers [59].

3.6.Effect of modified lignin addition on WVT

PLA and films with OS_{12C} as filler were selected to analyse their water vapour permeability and the obtained results are given in Table 7. The assay was carried out at 38 ºC and 90% RH. High temperature and high humidity conditions promote the transferring of water vapor, thus leading to much higher WVT values at 38 ºC and 90% RH compared to those at less hard conditions (23 ºC and 50% RH) [60]. As can be seen, pure PLA films showed better WVP values (poner valor) than found in other studies for biobased materials [61, 62] and some convectional plastics like PET, PP, PS and LDPE. On the other hand, although examined films did not show a clear trend, is possible to observe that the water vapor permeability was not worsened with the addition of modified spruce lignin. Siparsky et al. (1997) [63] studied water transport in PLA and PLA/PEG blends. The polymer blend of PEG and PLA behaves like a hydrophilic polymer. It has a high permeability coefficient due to the presence of hydrophilic groups in the PEG component of the blend. In this case, the introduction of esterified lignin (hydrophobic component) did not contribute to the water sorption capacity of the PLA.

4. Conclusions

Chemical composition, structure and thermal properties of organosolv lignins extracted from Spruce and Eucalyptus were studied. Both lignins were esterified by fatty acid with a long chain (12C) to modify their thermal properties and to use as filler in PLA matrix to improve material properties such as the brittleness. The success of the modification reaction of lignins was confirmed by FTIR and GPC. The modification involves a significant decrease in glass transition temperature in both lignins. Although the introduction of esterified lignins into PLA decrease the initial degradation temperature of the neat PLA, the elongation at break, strongly increased when lignin is added up to 25%. The incorporation of esterified lignin into the PLA decrease considerably the rigidity, showing an important enhancement of the ductility, especially in the case of Spruce lignin (OS_{12C}). Water vapor permeability is not affected by the addition of modified Spruce lignin.

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Figures

Fig. 1. Reaction schemes for the synthesis of the esterified lignins.

Fig. 2. FTIR spectra of isolated and modified lignins (a) isolated and chemical modificated Spruce lignin and (b) isolated and chemical modificated Ecalyptus lignin.

Fig. 3. Differential scanning calorimetry (DSC) of (a) isolated and chemical modificated Spruce lignin and (b) isolated and chemical modificated Ecalyptus lignin.

Fig. 4. TGA and DTG curves of extracted and modified lignins.

Fig. 5. TGA curves of elaborated films with 1% and 25% of both modified lignins.

Fig. 6. Mechanical properties of PLA and PLA/esterificated lignin films.

Fig. 1

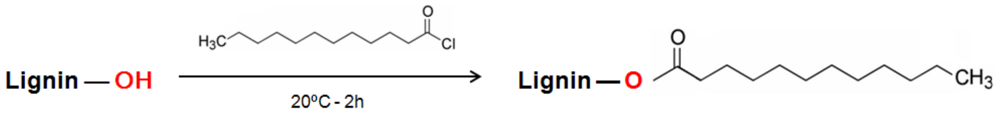


Fig. 2

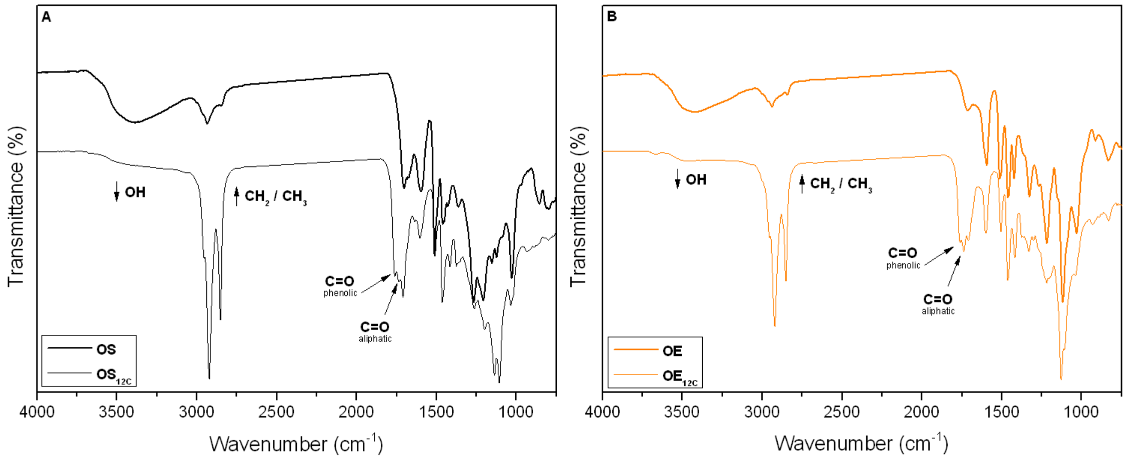

A
Transmittance (%)
OH
CH$_2$ / CH$_3$
C=O phenolic
C=O aliphatic
OS
OS$_{12C}$
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})
B
Transmittance (%)
OH
CH$_2$ / CH$_3$
C=O phenolic
C=O aliphatic
OE
OE$_{12C}$
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

Fig. 3

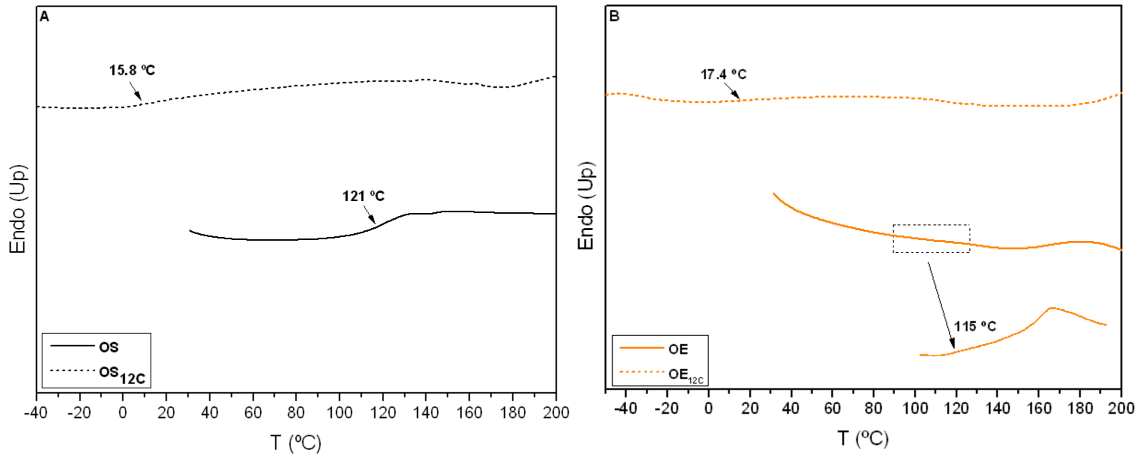
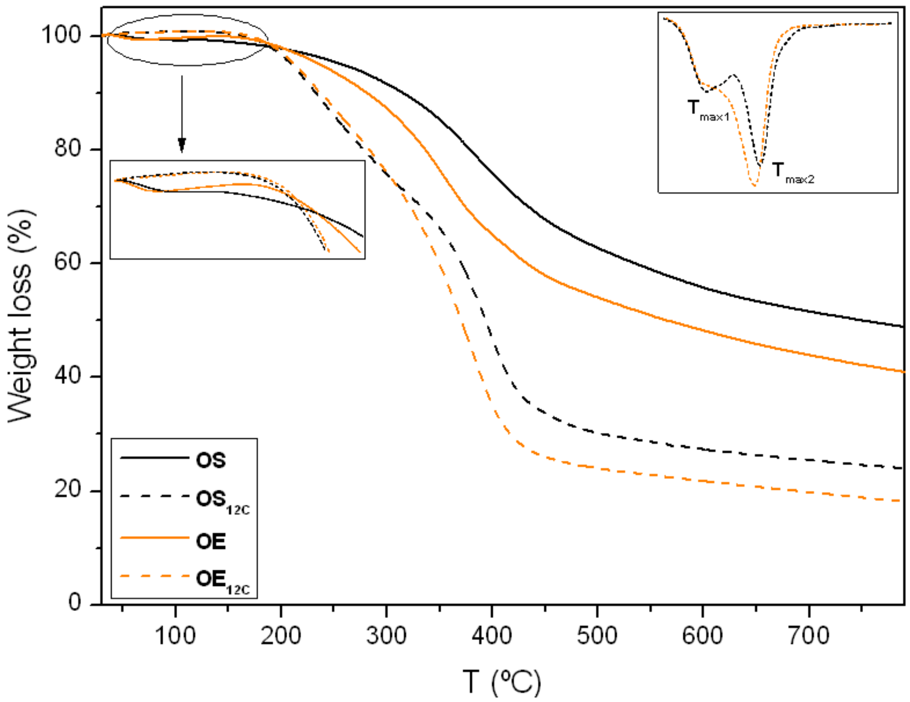

A
15.8 °C
121 °C
Endo (Up)
OS
OS12C
-40 -20 0 20 40 60 80 100 120 140 160 180 200
T (ºC)
B
17.4 °C
115 °C
Endo (Up)
OE
OE12C
-40 -20 0 20 40 60 80 100 120 140 160 180 200
T (ºC)

Fig. 4



Weight loss (%)
100
80
60
40
20
0
T (ºC)
100
200
300
400
500
600
700
T_{max1}
T_{max2}
OS
OS_{12C}
OE
OE_{12C}

Fig. 5

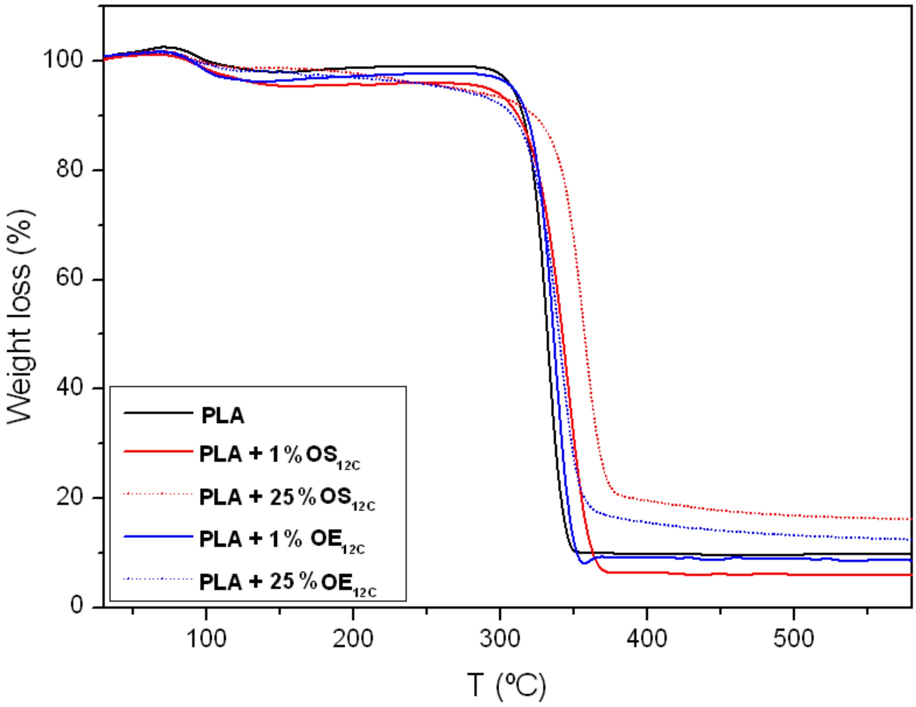
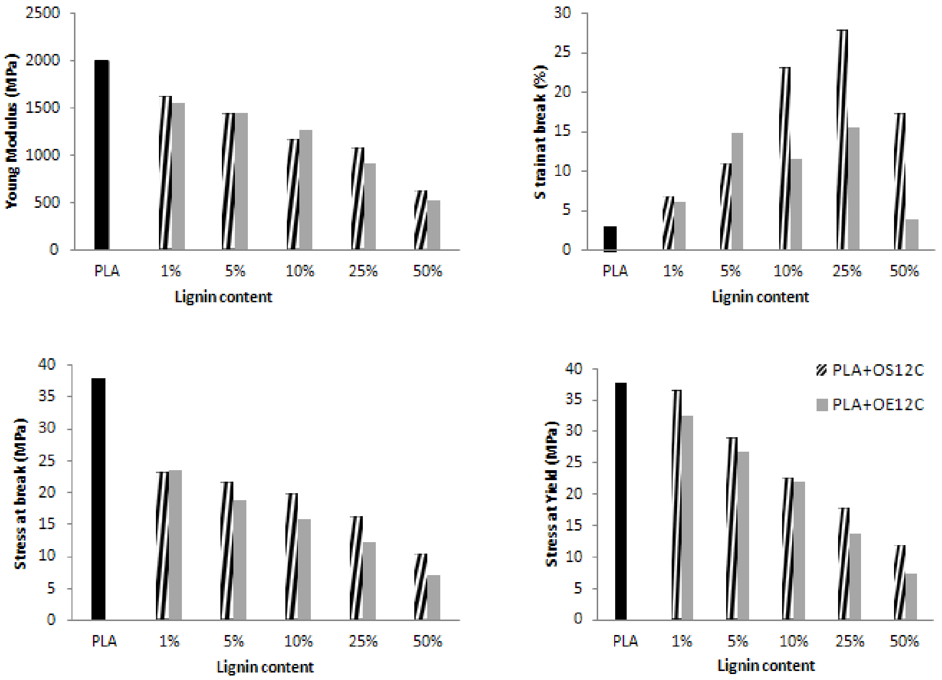

Weight loss (%)
T (ºC)
0
20
40
60
80
100
100
200
300
400
500
PLA
PLA + 1 % OS$_{12C}$
PLA + 25 % OS$_{12C}$
PLA + 1 % OE$_{12C}$
PLA + 25 % OE$_{12C}$

Fig. 6



Young Modulus (MPa)
2500
2000
1500
1000
500
0
PLA
1%
5%
10%
25%
50%
Lignin content
Strain at break (%)
30
25
20
15
10
5
0
PLA
1%
5%
10%
25%
50%
Lignin content
Stress at break (MPa)
40
35
30
25
20
15
10
5
0
PLA
1%
5%
10%
25%
50%
Lignin content
Stress at Yield (MPa)
40
35
30
25
20
15
10
5
0
PLA
1%
5%
10%
25%
50%
Lignin content
▨ PLA+OS12C
■ PLA+OE12C

Tables

Table 1. Chemical composition of isolated lignins.

Table 2. Weight average (Mw), number average (Mn) and polydispersity index (Mw/Mn) of isolated lignins and modified lignins.

Table 3. Contents of functional groups (mmol/g) determined by ^{31}P NMR.

Table 4. ^{13}C NMR of the acetylated lignin samples.

Table 5. Thermogravimetric parameters of different lignin samples.

Table 6. Temperatures and char residue characteristics of composites.

Table 7. Water vapour permeability of PLA film and PLA/OS_{12C} films.

Table 1

Sample	OE	OS
Klason Lignin %	83.7	94.3
ASL %	1.6	3.1
Ash %	3.6	3.2
Total Sugars %	2.9	0.5
C (%)	61.4	68.8
H (%)	6.0	6.3
N (%)	0.13	0.08
S (%)	0.06	0.20

Table 2

	M_n	M_w	PDI	WI%
OS	896	3124	3.5	
OS$_{12C}$	2774	10300	3.7	114.5
OE	1498	9490	6.3	
OE$_{12C}$	3192	25837	8.1	113.2

Table 3

Functional groups (mmol/g)	OE	OS
Aliphatic OH	1.58	0.75
Phenolic OH	2.12	2.99
S[a] OH	0.69	ND
G[a] OH	0.80	1.79
Condensed G[b]	0.63	1.20
β-5	0.49	0.38
5-5´	0.36	0.59
4-O-5	0.66	0.35
Total OH	3.70	3.74
COOH	0.11	0.23

[a] G: guaiacyl, S:syringyl

[b] Area between 144 and 140.5 ppm minus area of syringyl phenolic [43]

Table 4

Functional groups per C_9			
Assignment	**(ppm)**	**OE**	**OS**
Aromatic C-O	*160-140*	1.84	1.74
Aromatic C-C	*140-123*	2.16	2.41
Aromatic C-H	*123-100*	2.00	1.88
Aliphatic C-O	*90-58*	2.14	1.31
Methoxyl OCH_3	*57-54*	1.19	0.70
CH_3 acetyl	*20*	1.25	0.93
Primary OAc γ	*170*	0.33	0.15
Secondary OAc α	*169.4*	0.33	0.02
Phenolic OAc	*168.1*	0.46	0.63
S/G[a]		1.5	nd
Degree of condesation[b]	*123-100*	1.00	1.12

[a] Based on the assumption that hardwood lignin lignin is made up of only G and S units and softwood for G units.

[b] Calculated from 3.00-$I_{123-106}$ [42]

Table 5

	$T_{5\%}$	T_{max1}	$wt_1\%$	T_{max2}	$wt_2\%$	Residue at 800 ºC (%)
OS	257.8	385.8	41.8	---	---	48.7
OS_{12C}	209.8	237.6	27.8	393.4	48.5	23.7
OE	261.6	353.4	49.5	---	---	40.8
OE_{12C}	213.2	222.2	23.9	376.2	57.6	18.5

Table 6

	$T_{5\%}$	T_{max}	Residue at 600ºC
PLA	309.7	331.6	9.7
PLA + 1%OS_{12C}	292.2	346.1	5.9
PLA + 25%OS_{12C}	270.7	357.1	16.1
PLA + 1%OE_{12C}	309.8	336.3	8.4
PLA + 25%OE_{12C}	266.7	339.1	12.5

Table 7

	g/m^{2}day	WVP ·10^{13} (gcm/cm^{2}sPa)
PLA	175.3±10.3	1.89 ± 0.11
PLA + 10%OS12C	150.8 ± 3.2	1.78 ± 0.10
PLA + 25%OS12C	166.8 ± 5.0	1.85 ± 0.30