

DOI: <https://doi.org/10.1016/j.indcrop.2015.01.055>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Industrial Crops and Products* 72: 46-53 (2015). To access the final edited and published work see <https://doi.org/10.1016/j.indcrop.2015.01.055>

© 2015. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <https://creativecommons.org/licenses/by-nc-nd/4.0/>

Kraft lignin as filler in PLA to improve ductility and thermal properties

Oihana Gordobil^a, Rafael Delucis^b, Itziar Egüés^a, Jalel Labidi^{a,*}

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

^b *College of Materials Engineering, Technology Development Center (CDTec), Federal University of Pelotas, 809, Félix da Cunha Street, Postal Code: 96010-000, Pelotas, Rio Grande do Sul, Brazil*

**Email: jalel.labidi@ehu.es*

Abstract

Kraft lignin (KL) and acetylated Kraft lignin (AKL) were used as filler for the elaboration of composites with poly(lactic acid) (PLA) in different concentrations (0.5, 1, 5, 10 and 20%) by extrusion method at 200 °C. Characterization of both lignins has been performed using HPLC, FT-IR, GPC, DSC and TGA. KL presented only 0.3% of ash content and molecular weight around 2000 g/mol. The esterification increased the molecular weight and decreases the polydispersity of the lignin (AKL). Also, AKL had lower T_g and higher thermal stability than unmodified Kraft lignin. Lignin content increased the thermal stability of PLA, with the addition of both types of lignins. Contact angle was measured to assess the change in the hydrophobicity of PLA with the addition of lignins. Mechanical properties of different materials were also investigated in order to know the effect of lignin addition in PLA. Maximum strength was not severely affected at low concentrations of both lignins, but it decreased dramatically especially in composites with 10 and 20% of KL. Elongation at break increased with the addition of low contents of AKL, at high content of both lignins the material becomes quite brittle.

Keywords: *Kraft lignin – Acetylation – Extrusion – Poly(lactic acid) – Hydrophobicity – Mechanical properties*

1. Introduction

Lignin is a complex amorphous polyphenol molecule whose structure and properties basically depends on the raw material, growing conditions of the plant and extraction methods used (Canetti and Bertini, 2007; Morandim-Giannetti et al., 2012; Notley and Norgren, 2010). The main precursors of lignin are three monomers phenylpropanoids, namely p-coumaryl, coniferyl and sinapyl alcohols (Mansouri and Salvadó, 2006; Silva et al., 2009). The most common linkages in the lignin molecule are the β -O-4 ether linkages, followed by other types of ether and C-C linkages such as α -O-4, β -5, 5-5, 4-O-5, β -1, and β - β (Laurichesse and Avérous, 2014). Although the lignin structure has been intensely studied for many years, the different kinds of linkages in lignin and their diversity of functional groups, like methoxyl groups, phenolic and aliphatic hydroxyl groups principally, result in a complicated macromolecule (Awal and Sain, 2013). In nature lignin is associated to carbohydrates such as cellulose and hemicelluloses, so actually there is no effective method for their isolation. Industrially, the Kraft pulping method is used for the delignification of wood fibers to produce pulp and paper, is the main process who generates as by-product large quantities of lignin annually (Sahoo et al., 2011; Song et al., 2011). Thus, the so-called technical lignins are abundant by-product of pulp and paper industry and significant increase of lignin's availability is forecasted in the future with the implementation of the second generation biofuels and chemicals from biomass. The low value and abundance of the Kraft lignin makes it an attractive feedstock for many researchers to evaluate the use of this lignin in different fields which can give greater value to this natural material (Korich et al., 2012). Therefore, several authors have studied the technical feasibility of using lignin as filler for polymers (Chauhan et al., 2014) and the efficiency of lignin as flame retardant additive (Canetti et al., 2006; Canetti and Bertini, 2007). Also, lignin is utilized as a stabilizer (antioxidant) for plastics (Kadla

and Kubo, 2004). Other authors, have proved that lignin has an important influence on the thermal and mechanical behaviour in different polymers (Bertini et al., 2012; Bhat et al., 2013; Kaewtatip and Thongmee, 2013). Furthermore, lignin has been investigated as compatibilizer between natural fibers and polymer matrix (Graupner, 2008; Morandim-Giannetti et al., 2012). The effective use of lignin in composites with various synthetic polymers such as poly(propylene) (Pouteau et al., 2003), poly(ethylene terephthalate) (Canetti and Bertini, 2007), poly(vinyl alcohol), poly(ethylene oxide) (Kadla and Kubo, 2004), poly(vinyl chloride) (Mishra et al., 2007), polystyrene (Pouteau et al., 2004), low-density polyethylene and linear low-density polyethylene (Alexy et al., 2000) has been also reported in literature. Several authors have found that lignin also has great potential to produce lignin-based PU using the lignin hydroxyl groups (Chung and Washburn, 2012). In this case, lignin works like a polyol precursor in the polymerization reaction. Sometimes, the lignin reactivity can be limited due to steric hindrance (Cateto et al., 2011; Evtugin et al., 1998), so the chemical modification like oxypropylation can improve the lignin reactivity generating more reactive aliphatic OH groups (Duval and Lawoko, 2014). So it is well known that lignin has enormous potential for use as a raw material in the polymer industry. In this area, commonly one modification of lignin through chemical treatment is required in order to increase its compatibility with the polymeric matrix modifying characteristics as: the molecular weight, the surface area of the lignin and the availability of OH groups (Pouteau et al., 2003; Sadeghifar et al., 2012; Volkova et al., 2012). Another concern of the background studies it is the ratio between lignin and polymer matrix (Alexy et al., 2000). With respect to polymeric materials used as a matrix for composites are interesting features: low cost, easy to obtain a good relationship between weight and mechanical properties, chemical resistance and weather resistance. In this sense, the PLA poly(lactic acid) has been widely studied for replacing

commodity polymers because it is a material obtained from agricultural waste and have positive features such as: good melt processability, low flammability, renewability, biodegradability and relatively low cost (Auras et al., 2004; Raquez et al., 2013). Among its weaknesses are low ductility and poor thermal stability (Jamshidian et al., 2012). Other studies have observed the ability of lignin to increase the thermal stability of the different plastics materials (Bertini et al., 2012; Kaewtatip and Thongmee, 2013; Sahoo et al., 2011), as well as its plasticizing effect provided to other materials (Baumberger et al., 1998; Wang et al., 2012). Therefore, obtaining composite materials formed from PLA matrix and lignin as filler has generated much interest due the possibility of elaboration of environmentally friendly composite with relatively low production cost. In this work, composites with different concentrations of Kraft lignin were prepared by extrusion method. Kraft lignin was also acetylated to try increase the affinity with PLA and prevent a deterioration of the mechanical properties. The main object of this study was to evaluate the effect of lignin addition in PLA thermal and mechanical properties.

2. Materials and methods

The black liquor used in this work was kindly supplied by Papelera Guipuzcoana de Zicuñaga, S.A. from Hernani (Spain). Characterization of the black liquor was carried out following procedures found in literature (TAPPI T211om-93): density: 1.054g/cm³, pH: 12.9, total dry solids %: 15.8, lignin content: 67.4g/L, content of organic material %: 5.6 and content of inorganic material %: 10.2. Dissolved lignin in black liquor was isolated by precipitation with H₂SO₄ (pH around 2). The precipitated lignin was filtered through a 0.45µm nylon filter to recover lignin. After filtration, precipitate was washed twice with acidified water (pH 2) and then was dried at 50°C. PLA (Nature-Works_ PLA Polymer 3051D) was from NatureWorks LCC (Glass Transition Temperature 55-65 °C,

Melt Temperature 150-165 °C, Mw: 169.000 g/mol). Formamide (99.5%), pyridine (99%), acetic anhydride (99%) and hydrochloric acid (37%) were supplied by Panreac.

2.1. Acetylation

Acetylation was carried out using the experimental conditions described below. Dry lignin samples (1.00 g) were dispersed in formamide (25 mL) about 3 h, until complete solubilisation. 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 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 a oven at 50 °C during 24 h.

2.2. Preparation of composites by extrusion

An extruder THERMO HAAKE Minilab Rheomix CTW5 model with double screw (109.5 mm) was used for the preparation of mixtures. Process conditions were 200 °C, at rate 75 min⁻¹ and recirculation time was 10 min, optimum conditions previously determined for successful mixing of the materials. The composites are made with PLA as matrix with different concentrations of Kraft lignin and acetylated Kraft lignin (0.5, 1, 5, 10, 20 %).

2.3.Characterization of lignin and composites

2.3.1. 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 H₂SO₄ prepared with 100% deionized and degassed water was

used as mobile phase (0.35 mL/min flow, 40 °C, and injection volume of 40 mL). High purity standards of D-(+)-glucose, D-(-)-xylose, and D-(-)-arabinose (provided by Fluka, with 99% of purity) were used for calibration.

2.3.2. Fourier transform infrared spectroscopy (FTIR)

The FT-IR analysis of Kraft lignin and acetylated Kraft lignin 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 800 cm⁻¹. FTIR spectra were also used in order to determine the degree of acetylation of lignin.

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

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 °C, using a Jasco Inc. chromatograph provided with an LC-NetII/ACD interface, a column oven CO-2065 Plus 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.

2.3.4. Differential scanning calorimetry (DSC)

The glass transition temperature of Kraft lignin and acetylated Kraft lignin was determined by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5-10mg were tested under nitrogen atmosphere at a heating rate of 20 °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 20 °C/min.

2.3.5. Thermogravimetric analyses (TGA)

Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER TOLEDO. Both lignins 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 600 °C. PLA and composites with 0.5% and 5% of KL and AKL 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.

2.3.6. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis was performed on a TRITON Tritec 2000 Dynamic Mechanical Analyser in single cantilever bending mode. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) were measured as a function of temperature at a frequency of 1 Hz, heating rate of 2°C/min and temperature range of 25-120 °C. The strain was set at 0.005%. At least two samples of each material were tested and the average value of these parameters for each material was calculated and reported.

2.3.7. Contact angle

Contact angle measurements were carried out with water using a Dataphysics Contact angle system OCA 20, in order to determine the changes in the hydrophilic character of lignin, before and after modification. Uniform pellets have been used for this purpose. Composites 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 material. Sample thicknesses oscillate between 0.76-0.43 mm. All measurements were carried out with water, and each sample was measured with a minimum of five drops.

2.3.8. Mechanical properties

The PLA/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. 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 0.76-0.43 mm, and width of 3.4-1.3 mm. The values quoted are the average of nine measurements.

3. Results and discussion

3.1. Composition of lignins

Results of acidic insoluble lignin, soluble lignin, ashes and sugars content are presented in Table 1. Precipitated Kraft lignin from Zikuñaga presented high purity compared with others Kraft lignins (Bilhalva dos Santos et al., 2014). 69.7% of Klason lignin is a high value for this type of lignin that coming from Kraft processes. Generally, these types of lignins have a great amount of salt, in this case, only 0.3% of ashes have been found. Considering that polysaccharides are the most common contamination in lignin, KL presented low quantities of sugars (3.4%) confirming the high purity of lignin. Among the sugars present in lignins, xylose was the major hemicellulosic sugar in all lignins samples.

3.2. FTIR

Fourier transform infrared spectra of precipitated Kraft lignin (KL) and Kraft lignin after acetylation treatment (AKL) are shown in Fig. 1. In the case of KL, can be observed a wide absorption band at 3300 cm^{-1} indicated the presence of O-H stretching vibrations in aromatic and aliphatic O-H groups. Bands at 2930 and 2840 cm^{-1} can be assigned to C-H stretching in $-\text{CH}_2-$ and $-\text{CH}_3$ groups (Manjarrez Nevárez et al., 2011). The band at 1710 cm^{-1} showed the presence of non-conjugated carboxylic acids (Cachet et al., 2014). 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 -CH₂- and -CH₃ groups, and C-H aromatic ring vibrations, respectively. Some characteristic bands associated to syringyl and guaiacyl units in lignin were detected at 1325, 1220, 1110 and 1025 cm^{-1} corresponding to syringyl and condensed guaiacyl absorptions, guaiacyl ring breathing, C-C, C-O and C=O stretch, aromatic C-H in plane deformation (S) and aromatic C-H in plane deformation (G > S) (Garcia et al., 2012; Sun et al., 2012). Meanwhile, the signal of aromatic C-H out-of-plane deformation in G, S and H units appears at 834 cm^{-1} . Acetylated Kraft lignin showed that the signal around 3300 cm^{-1} which corresponds to O-H stretching vibrations in aromatic and aliphatic O-H groups was reduced almost completely and the appearance of two new peaks at 1735 cm^{-1} and 1760 cm^{-1} is clearly seen. They are assigned to aliphatic and aromatic ester bonds, respectively. This indicates that the acetylation process was successful (Hult et al., 2013). The absence of the characteristic bands of acetic anhydride (\approx 1823, 1121, 995 and 896 cm^{-1}) (Cachet et al., 2014) showed that the modified lignin does not contain traces of unreacted acetic anhydride. 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 3300 cm^{-1} stretching band (H_{OH}) with the height of the C=C of aromatic skeletal vibrations at 1510 cm^{-1} , which was taken as reference (H_{ref}). This band could be used to normalize the spectra (the spectra were normalized with the intensity of the absorbance peak at 1510 cm^{-1} as it was indicated by Gilarranz et al. (2001). The reaction conversion was calculated from the equation (Saralegi et al., 2013):

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

The acetylation reaction has been very successful due to the high conversion achieved. The performance achieved approximately was 93%.

3.3. GPC

Lignin structure and the weight average could be quite different depending on the feedstock and extraction process (Ciobanu et al., 2004; Manjarrez Nevárez et al., 2011). According to literature, Kraft lignins do not have high molecular weights. This may be because they come from industrial aggressive processes (Pouteau et al., 2003). Table 2 shows the values of weight average (M_w), number average (M_n) and polydispersity index (M_w/M_n) of KL and AKL. 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 (Manjarrez Nevárez et al., 2011). In this case, it happened as expected, the molecular weight of acetylated Kraft lignin increased. Although the difference in molecular weight average is not very significant, could be observed that the Kraft lignin presented two important fractions (26% of 5700g/mol and 34% of 1000g/mol). However, acetylated Kraft lignin presented less polydisperse structure than unmodified Kraft lignin. AKL presented one major fraction of approximately 65% of 3300g/mol. It can be said that the acetylation reaction generates less polydisperse lignin.

3.4. Thermal properties

The DSC curves of KL and AKL are shown in Fig. 2. DSC is the most accepted method to define the glass transition temperature of lignin and modified lignin samples. Normally, the T_g values of various nonderivatized lignins range from 90 to 180°C (Awal and Sain, 2013). The T_g of lignin is often difficult to detect due to the complex structure of this polymer. However, it is sometimes possible to detect the range of the change in the curve (Cachet et al., 2014). All unmodified lignin has a relatively high glass transition temperature because the condensed rigid phenolic moieties and strong intermolecular hydrogen bonding interactions restrict the thermal mobility of lignin molecules and result in its high T_g (Chung et al., 2013). In this case, T_g of KL has not been clearly identified,

but is thought that ranges between 115-125 °C. This may be due to the heterogeneity of the sample. However, AKL which is more homogeneous presented an easily identified T_g approximately at 105°C. It is well known that when the lignin is modified by acetylation or other ester modification, hydroxyl groups were replaced by ester substituent (Cachet et al., 2014). Thus, reduce the number of hydrogen bonding and lead an increased free volume in the molecule and thus the mobility of the chains (Lispeguer et al., 2009). The thermogravimetric (TG) curves obtained for KL and AKL under nitrogen atmosphere are presented in Fig. 3. As it can be seen, acetylated Kraft lignin showed higher thermal stability than original Kraft lignin. Besides, Kraft lignin had a small weight loss (1-8%) below 100 °C due to gradual evaporation of moisture, however, acetylated sample did not show any weight loss due to moisture because after acetylation, lignin has become more hydrophobic. The initial degradation temperature corresponding in this case to 10% weight loss ($T_{10\%}$) of acetylated lignin (AKL) is marker higher than original Kraft lignin (KL) with values of 310 °C and 215 °C respectively. The main degradation step occurs in the temperature range between 300 and 500 °C, and it is associated with the fragmentation of inter-units linkage (Bernabe et al., 2013; Bertini et al., 2012). The maximum weight loss rate in acetylated Kraft lignin could be observed at 372 °C, while Kraft lignin showed a temperature of 369 °C. The amount of char residue at 600 °C was found to be 40.5% and 39.5% for AKL and KL respectively. On the other hand, the TGA and DTG curves, obtained under nitrogen atmosphere, of pure PLA and PLA/lignins composites are shown in Fig. 4. The initial degradation ($T_{5\%}$), the maximum weight loss temperature (T_{max}) and char residue are presented in Table 3. Addition of both type of lignins, KL and AKL, increases the thermal stability of the PLA. PLA and composites with 0.5% and 5% of KL and AKL were analyzed. All composites showed an increase in the temperature for the onset of thermal degradation of 70-80 °C. Also,

composites presented higher maximum decomposition temperature than PLA. Indeed, both types of lignins, acetylated and unmodified lignin, 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 (Morandim-Giannetti et al., 2012). Thus, composites with acetylated Kraft lignin exhibited slightly lower temperatures ($T_{5\%}$ and T_{max}) than composites with unmodified Kraft lignin. On the other hand, char residue, in general, decreased with the addition of lignin into the composites.

DMTA measurements of the pure PLA and composites with 5% of unmodified and acetylated Kraft lignin was performed to give information about the effect of lignin in dynamical mechanical properties of PLA against temperature. Fig. 5a and b shows the dynamic relative storage modulus and $\tan \delta$ as a function of temperature of composites with 5% of KL and AKL. The relative storage modulus of pure PLA remained almost constant up to the glass transition temperature. However, the storage modulus of the elaborated composites showed higher temperature dependence before glass transition temperature. The drop of storage modulus is more pronounced in the case of composites made with acetylated Kraft lignin. The addition of lignin seems to increase the ductility of PLA in both cases, especially with the addition of acetylated lignin. The reason may be that the introduction of lignin (amorphous in nature) affected the interactions among the PLA chains, generating greater free volume between them, and thus improving the movement of the chains when a load is applied.

Martini and Avérous (2001) reported that the usage of plasticizer in PLA generated a decrease of the storage modulus, obtaining a higher ductility of the material. However, Kowalczyk et al. (2011) have developed composite made of PLA and cellulose nanofibers obtaining an increase of the storage modulus, and thus, greater rigidity of PLA. However, the results obtained in this study, showed that lignin does not improve the performance of PLA for temperature above T_g . On the other hand, the rise of E' around 85 °C is due to the crystallization. Composites seem begin to crystallize around 90 °C. In a previous work, it was demonstrated that the addition of lignin can retard the crystallization of PLA (Gordobil et al, 2014). Moreover, no significant change in glass transition temperature (T_g) of the samples was found as it remained fairly constant with a very small increase in the case of composite with acetylated Kraft lignin.

3.5. Contact angle

Contact angle measurements of Kraft Lignin and acetylated Kraft lignin were performed in order to know the change in the hydrophobicity of lignin. Phenolic hydroxyls are among the main reactive groups of lignin and through acetylation, these groups are substituted with non-polar COCH_3 to improve the hydrophobic character and solubility in organic solvents of the lignin (Martinez et al., 1997). Fig. 6 shows that acetylated Kraft lignin presented higher hydrophobicity than original Kraft lignin. Moreover, it can be observed that non-modified lignin displayed a greater reduction in contact angle values through time, proving major affinity with water. Contact angle of elaborated composites at $t=0$ are reported in fig. 7. PLA showed contact angle values of $72.5 \pm 2.5^\circ$ at initial time which is consistent with those found in literature. In general, both type of composites, PLA with Kraft lignin and PLA with acetylated Kraft lignin, presented higher contact angle values, obtaining a slight improvement in hydrophobic character of PLA. Contact angle measurements demonstrate that most of the composites containing acetylated Kraft

lignin have higher contact angle than composite with unmodified Kraft lignin. It can be observed that to the 5% of both lignins the contact angle increased, especially in composites with acetylated Kraft lignin. However at more high concentrations (10-20%) begins to decrease, being in any case always more hydrophobic composite elaborated by PLA and AKL. This may be due to increased roughness of the samples.

3.6.Mechanical properties

Tensile tests have been performed to study the effect of both lignins on mechanical properties of PLA. The Young's modulus, elongation at break and tensile strength at break of the different materials are shown in fig. 8. The strength at break was not severely affected with low concentrations (0.5-5%) of both types of lignin (KL and AKL). However, at concentrations greater than 5%, the maximum strength decreased with increasing lignin content, especially in materials formed by PLA and unmodified Kraft lignin. There was a big difference between composites elaborated with PLA and KL and composites with AKL addition. Other study in which was elaborated a PLA/unmodified commercial lignin composite by similar methods were also observed a decrease in the stress at concentrations of 5% and 10% (Domenek et al., 2013). This may be the result for the best interaction between PLA and acetylated Kraft lignin than PLA with unmodified lignin. 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 (Manjarrez Nevárez et al., 2011). Moreover, it can be observed that the elongation at break remained practically constant to 5% of KL, with a very small decrease. However, the elongation at break decreased significantly upon the addition of high concentrations (10-20%) of unmodified Kraft lignin, becoming the material more brittle and difficult to handle. In the case of composites with AKL, it can be seen an improvement respect to

composites with unmodified Kraft lignin. These composites, at low concentrations presented greater ductility than neat PLA. However, at high concentrations this property also decreased, although not as much as composites with KL. The improvement in ductility on compatibilization can be attributed to esterification as esters act like internal plasticizers (Wang et al., 2012). Other author (Baumberger et al., 1998) also demonstrated a slight increase in the deformation of films formed with starch and lignin. The Young's modulus shows a slight increase in all cases especially at high contents of lignin.

4. Conclusions

In this work Kraft black liquor has been used as a resource for Kraft lignin extraction. This lignin presented a high purity with low content of ashes and sugars. Acetylation process of lignin was successful with high yield. Acetylated lignin was found to be less polydisperse and have higher molecular weight than original Kraft lignin. Also, presented high thermal stability. The addition of both lignins in PLA, increased thermal degradation temperatures ($T_{5\%}$ and T_{max}) and hydrophobicity. However, the mechanical performance of PLA against temperature could not be improved above T_g as shown by DMTA. On the other hand, maximum strength remain similar to those of pure PLA at low concentrations of both lignins, however, decreased dramatically especially in materials with 10 and 20% of KL. Elongation at break increased with the addition of low contents of AKL, at high content of both lignins the material becomes quite brittle. Thus, improvement in the compatibility between the two components is reflected in the mechanical properties.

Acknowledgements

The authors are grateful for the financial support received from the University of the Basque Country (postdoctoral fellow grant no. ESPDOC14/3 and doctoral grant of Ms. Gordobil Grant no. PIF 13/050) and from the Department of Education, Universities and Investigation of the Basque Government (IT672-13).

5. References

- Alexy, P., Kosiková, B., Podstránska, G., 2000. The effect of blending lignin with polyethylene and polypropylene on physical properties. *Polymer*. 41, 4901-4908.
- Auras, R., Harte, B., Selke, S., 2004. An Overview of Polylactides as Packaging Materials. *Macromol Bio*. 4, 835-864.
- Awal, A., Sain, M., 2013. Characterization of Soda Hardwood Lignin and the Formation of Lignin Fibers by Melt Spinning. *J. Appl Polym Sci*. 129, 2765-2772.
- Baumberger, S., Lapiere, C., Monties, B., 1998. Use of kraft lignin as filler for starch films. *Polym Degrad Stab*. 59, 273-277.
- Bhat, R., Abdullah, N., Din, R.H., Tay, G-S., 2013. Producing novel sago starch based food packaging films by incorporating lignin isolated from oil palm black liquor waste. *J. Food Eng*. 119,707-713.
- Bernabe, G., Kobelnik, M., Almeida, S., Ribeiro, C.A., Crespi, M.S., 2013. Thermal behavior of lignin and cellulose from waste composting process. *J Therm Anal Calorim*. 111, 589-595.
- Bertini, F., Canetti, M., Cacciamani, A., Elegir, G., Orlandi, M., Zoia, L., 2012. Effect of ligno-derivatives on thermal properties and degradation behaviour of poly(3-hydroxybutyrate)-based biocomposites. *Polym Degrad Stab*. 97, 1979-1987.
- Bilhalva dos Santos, P., Erdocia, X., Gatto, D.A., Labidi, J., 2014. Characterisation of Kraft lignin separated by gradient acidprecipitation. *Ind Crop Prod*. 55, 149-154.
- Cachet, N., Camy, S., Benjelloun-Mlayah, B., Condoret, J., Delmas, M., 2014. Esterification of organosolv lignin under supercritical conditions. *Ind Crop Prod*. 58, 287-297.
- Canetti, M., Bertini, F., 2007. Supermolecular structure and thermal properties of poly(ethylene terephthalate)/lignin composites. *Compos Sci Technol*. 67, 3151-3157.
- Canetti, M., Bertini, F., De Chirico, A., Audisio, G., 2006. Thermal degradation behaviour of isotactic polypropylene blended with lignin. *Polym Degrad Stab*. 91, 494-498.
- Cateto, C.A., Barreiro, M.F., Rodrigues, A.E., Belgacem, M.N., 2011. Kinetic study of the formation of lignin-based polyurethanes in bulk. *React Funct Polym*. 71, 863-869.
- Chauhan, M., Gupta, M., Singh, B., Singh, A., Gupta, V., 2014. Effect of functionalized lignin on the properties of lignin–isocyanate prepolymer blends and composites. *Euro Polym. J*. 52, 32–43.

- Chung, Y., Olsson, J.V., Li, J.R., Curtis W.F., Waymouth, R.M., Billington, S.L., Sattely, E.S., 2013. A Renewable Lignin–Lactide Copolymer and Application in Biobased Composites. *Sustainable Chem Eng.* 1, 1231-1238.
- Chung, H., Washburn, N.R., 2012. Chemistry of lignin-based Materials. *Green Mat.* 1, 137-160.
- Ciobanu, C., Ungureanu, M., Ignat, L., Ungureanu, D., Popa, V.I., 2004. Properties of lignin–polyurethane films prepared by casting method. *Ind Crop Prod.* 20, 231-241.
- Domenek, S., Louaifi, A., Guinault, A., Baumberger, S., 2013. Potential of lignins as antioxidant additive in active biodegradable packaging materials. *J. Polym Environ.* 21, 692-701.
- Duval, A., Lawoko, M., 2014. A review on lignin-based polymeric, micro- and nano-structured materials. *React Funct Polym.* 85,78-96.
- Evtuguin, D.V., Andreolety, J.P., Gandini, A., 1998. Polyurethanes based on oxygen-organosolv lignin. *Eur Polym J.* 34, 1163-1169.
- Garcia, A., Erdocia, X., Gonzalez Alriols, M., Labidi, J., 2012. Effect of ultrasound treatment on the physicochemical properties of alkaline Lignin. *Chem Eng Proces.* 62, 150-158.
- Gilarranz, M., Rodriguez, F., Oliet, M., Garcia, J., Alonso, V., 2001. Phenolic OH groupestimation by FTIR and UV spectroscopy. Application to organosolv lignins. *J.Wood Chem Technol.* 21 (4), 387-395.
- Gordobil, O., Egüés, I., Llano-Ponte, R., Labidi, J., 2014. Physicochemical properties of PLA lignin blends. *Polym Deg Stab.* 108, 330-338.
- Graupner, N., 2008. Application of lignin as natural adhesion promoter in cotton fibre-reinforced poly(lactic acid) (PLA) composites. *J. Mater Sci.* 43, 5222-5229.
- Hult, E., Ropponen, J., Poppius-Levlin, K., Ohra-Aho, T., Tamminen, T., 2013. Enhancing the barrier properties of paper board by a novel lignin coating. *Ind Crop Prod.* 50, 694-700.
- Jamshidian, M., Tehrany, E.A., Imran, M., Akhtar, M.J., Cleymand, F., Desobry, S., 2012. Structural, mechanical and barrier properties of active PLA-antioxidant films. *J Food Eng.* 110, 380-389.
- Kadla, J.F., Kubo, S., 2004. Lignin-based polymer blends: analysis of intermolecular interactions in lignin-synthetic polymer blends. *Compos PartA.* 35, 395-400.
- Kaewtatip, K., Thongmee, J., 2013. Effect of kraft lignin and esterified lignin on the properties of thermoplastic starch. *Mater Des.* 49, 701-704.

- Korich, A.L., Fleming, A.B., Walker, A.R., Wangm J., Tang, C., Iovine, P.M., 2012. Chemical modification of organosolv lignin using boronic acid-containing reagents. *Polymer*. 53, 87-93.
- Kowalczyk, M., Piorowska, E., Kulpinski, P., Pracella, M., 2011. Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers. *Compos PartA*. 42, 1509-1514.
- Laurichesse, S., Avérous, L., 2014. Chemical modification of lignins: Towards biobased polymers. *Prog Polym Sci*. 39, 1266-1290.
- Lispeguer, J., Perez, P., Urizar, S., 2009. Structure and thermal properties of lignins: characterization by infrared spectroscopy and differential scanning calorimetry. *J. Chil Chem Soc*. 54,460-463.
- Manjarrez Nevárez, L.A., Ballinas Casarrubias, L., Celzard, A., Fierro, V., Muñoz Torres, V., Camacho Davila, A., 2011. Biopolymer-based nanocomposites: effect of lignin acetylation in cellulose triacetate films. *Sci Technol Adv Mater*. doi:10.1088/1468-6996/12/4/045006
- Mansouri, N.E., Salvado, J., 2006. Structural characterization of technical lignins for the Production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Ind Crop Prod*. 24, 8-16.
- Martin, O., Avérous, L., 2001. Poly(lactic acid): plastification and properties of biodegradable multiphase systems. *Polym*. 42, 6209-6219.
- Martinez, J.M., Reguant, J., Montero, M.A., Montane, D., Salvado, J., Farriol, X., 1997. Hydrolytic pretreatment of softwood and almond shells. Degree of polymerization and enzymatic digestibility of the cellulose fraction. *Ind Eng Chem Res*. 36, 688-696.
- Mishra, S.B., Mishra, A.K., Kaushik, N.K., Khan, M.A., 2007. Study of performance properties of lignin-based polyblends with polyvinyl chloride. *J. Mater Proces Technol*. 183, 273-276.
- Morandim-Giannetti, A.A., Agnelli, J.A.M., Lancas, B.Z., Magnabosco, R., Casarin, S.A., Bettini, S.H.P., 2012. Lignin as additive in polypropylene/coir composites: Thermal, mechanical and morphological properties. *Carbohydr Polym*. 87, 2563- 2568.
- Notley, S.M., Norgren, M., 2010. Surface Energy and Wettability of Spin-Coated Thin Films of Lignin Isolated from Wood. *Langmuir*. 26 (8), 5484-5490.
- Pouteau, C., Baumberger, S., Cathala, B., Dole, P., 2004. Lignin-polymer blends: evaluation of compatibility by image analysis. *C. R. Biol*. 327, 935-943.
- Pouteau, C., Dole, P., Cathala, B., Averous, L., Boquillon, N., 2003. Antioxidant properties of lignin in polypropylene. *Polym Degrad Stab*. 81,9-18.
- Raquez, J., Habibi, Y., Murariu, M., Dubois, P., 2013. Polylactide (PLA)-based nanocomposites. *Prog Polym Sci*. 28, 1504-1542.

Sadeghifar, H., Cui, C., Argyropoulos, D.A., 2012. Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries. *Ind Eng Chem Res.* 51, 16713–16720.

Sahoo, S., Misra, M., Mohanty, A.K., 2011. Enhanced properties of lignin-based biodegradable polymer composites using injection moulding process. *Composites: Part A* 42, 1710-1718.

Saralegi, A., Rueda, L., Fernandez-d'Arlas, B., Mondragon, I., Eceiza, A., Corcuera, M^a. A., 2013. Thermoplastic polyurethanes from renewable resources: effect of soft segment chemical structure and molecular weight on morphology and final properties. *Polym Int.* 62, 106-115.

Silva, R., Haraguchi, S.H., Muniz, E.C., Rubira, A.F., 2009. Aplicações de fibras lignocelulósicas na química de polímeros e em compósitos. *Quím Nova.* 32, 661-671.

Song, P., Cao, Z., Fu, S., Fang, Z., Wu, Q., Ye, J., 2011. Thermal degradation and flame retardancy properties of ABS/lignin: Effects of lignin content and reactive compatibilization. *Thermochim Acta.* 518, 59-65.

Sun, S., Li, M., Yuan, T., Xu, F., Sun, R., 2012. Sequential extractions and structural characterization of lignin with ethanol and alkali from bamboo (*Neosinocalamus affinis*). *Ind Crop Prod.* 37, 51-60.

Volkova, N., Ibhahim, V., Hatti-Kaul, R., Wadso, L., 2012. Water sorption isotherms of Kraft lignin and its composites. *Carbohydr Polym.* 87, 1817-1821.

Wang, K., Bauer, S., Sun, R., 2012. Structural transformation of *Miscanthus- giganteus* lignin fractionated under mild formosolv, basic organosolv, and cellulolytic enzyme conditions. *J. Agric Food Chem.* 60, 144-152.

Tables captions

Table 1. Lignin purity analysis.

Table 2. Weight average (Mw), number average (Mn) and polydispersity index (Mw/Mn) of Kraft lignin (KL) and acetylated Kraft lignin (AKL).

Table 3. Temperatures and char residue characteristics of blends.

(1)

Kraft lignin	
Klason Lignin %	69.7
Soluble Lignin %	9
Ashes %	0.3
Total Sugars %	3.4
Xylose	3.1
Arabinose	ND
Glucose	0.3

(2)

	M_n	M_w	M_w/M_n
KL	579	2013	3.5
AKL	787	2276	2.9

(3)

	T_{5%}	T_{max}	Char Residue %
PLA	269	314	6.5
PLA+0.5KL	340	365	0.5
PLA+5KL	337	367	2.1
PLA+0.5AKL	328	364	0.2
PLA+5AKL	333	366	1.4

Figure captions

Fig. 1. Fourier transform infrared spectra of Kraft lignin (KL) and acetylated Kraft lignin (AKL).

Fig. 2. DSC of KL and AKL.

Fig. 3. TG curves of KL and AKL.

Fig. 4. TG and DGT curves of PLA and blends with 0.5% and 5% of KL and AKL.

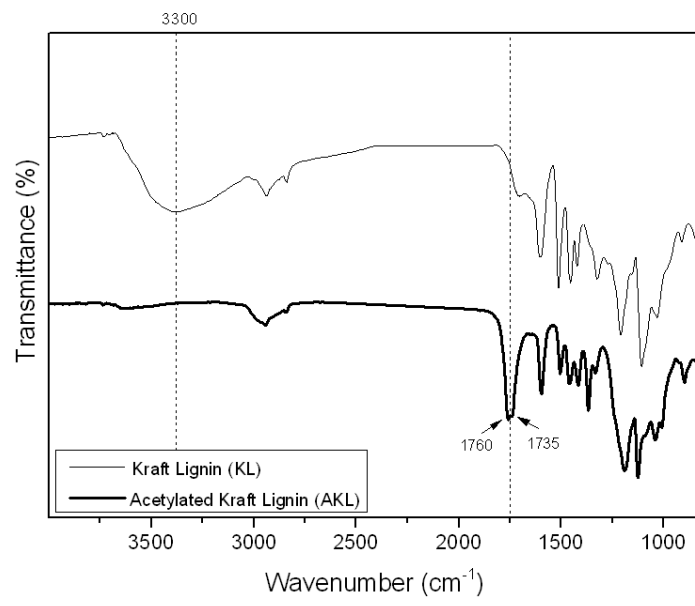
Fig. 5. Temperature dependence of (a) relative storage modulus (%) and (b) $\tan \delta$ for PLA and composites with 5% of KL and AKL.

Fig. 6. Contact angle of Kraft lignin (KL) and Acetylated Kraft lignin (AKL).

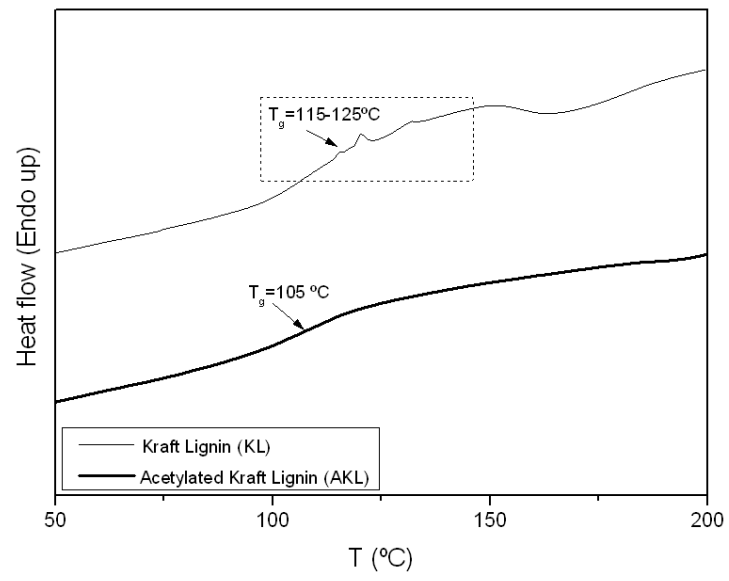
Fig. 7. Contact angle of PLA, PLA+Kraft lignin and PLA+Acetylated Kraft lignin.

Fig. 8. Mechanical properties of PLA and blends.

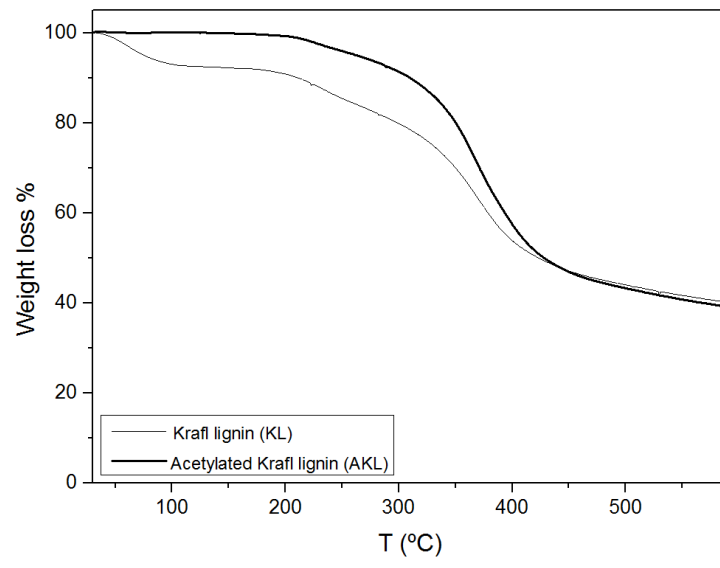
(1)



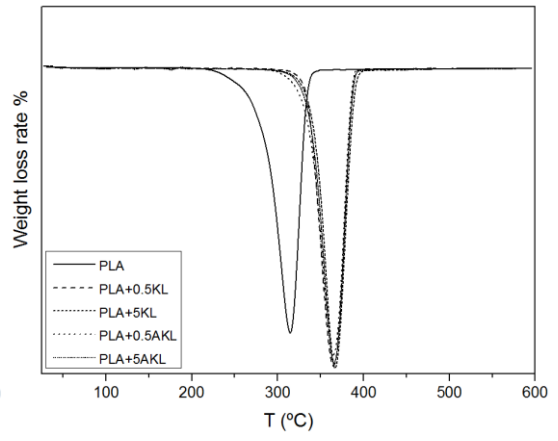
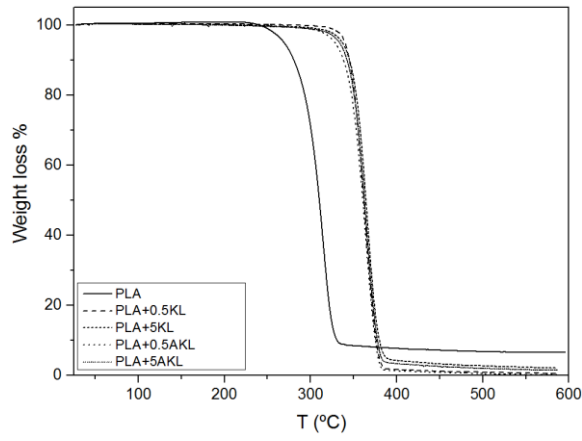
(2)



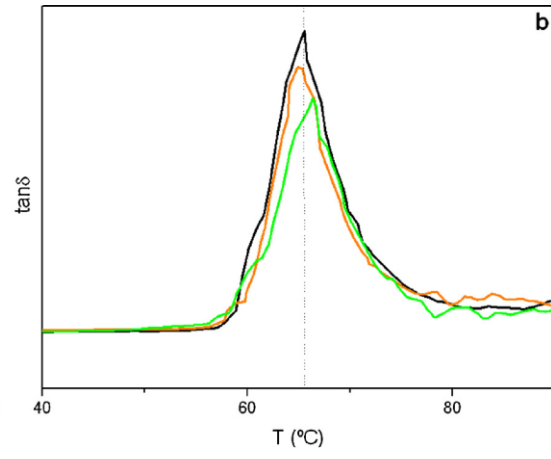
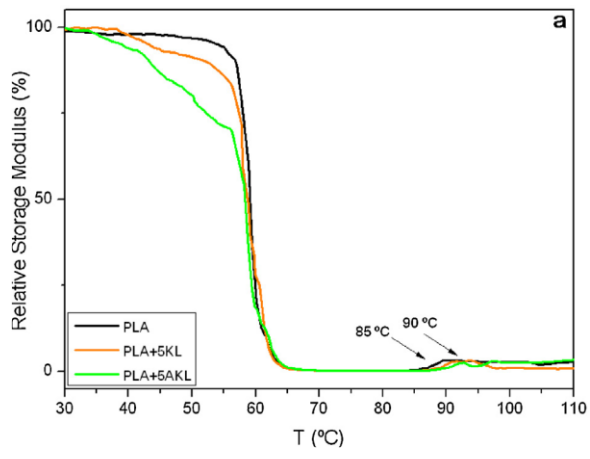
(3)



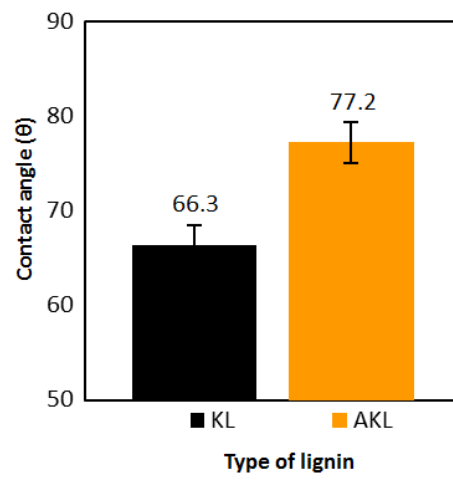
(4)



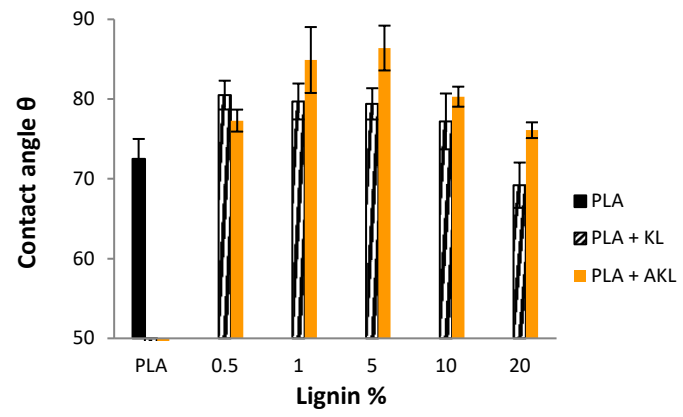
(5)



(6)



(7)



(8)

