Biorefinery of Paulownia by autohydrolysis and soda-anthraquinone delignification process. Characterization and application of lignin

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Biorefinery of paulownia by autohydrolysis and soda-anthraquinone delignification process. Characterization and application of lignin

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Abstract

BACKGROUND:

Lignin is one of the most abundant polymers in nature. Its physical and chemical properties confer it a high potential for various uses including the production of thermoplastic matrices. In this work, characterized various types of lignin obtained by alkaline delignification of Paulownia with soda–anthraquinone in the presence and absence of autohydrolysis. The products obtained after evaporation or acidification were used to produce polylactic acid–lignin composites.

RESULTS:

Subjecting the raw material to autohydrolysis prior to alkaline delignification provided a spent liquor (black liquor) containing an increased amount of extracted lignin (11.9% more than without autohydrolysis) and possessing a higher calorific value (14 822 kJ /kg) than in the absence of a autohydrolysis stage. Thermogravimetric analysis revealed a strong impact of the autohydrolysis process, which provided residual delignification fractions containing abundant lignin and no degradation products of polysaccharides or other constituents of the raw material. Mechanical dynamics analysis of composites with lignin contents from 12.5 to 30% revealed an increased elastic (storage) modulus (E') and also that the thermal stability of the material was equivalent to the mechanical strength of polylactic acid plastic containing 30 wt% lignin in its formulation.

CONCLUSIONS:

Soda lignin has appropriate interaction with the polylactic acid, which allows it to be used for obtaining a composite with adequate physical strength characteristics.

Keywords: Lignin, composites, polilactic acid, autohydrolysis, biomass

INTRODUCTION

A biorefinery is an integral, diversified processing plant using lignocellulosic biomass as raw material to obtain and wide variety of chemicals by efficiently exploiting available resources and reducing pollution similarly to a conventional refinery.[1,2] The integral process provides carbohydrates and lignin for use as fuels, chemicals with a high added value and various other materials, thereby fulfilling the essential objective of producing virtually no waste.

Many biorefining schemes focus on a specific product (e.g. ethanol, cellulose pulp) and disregard the potential valorization of other, minor streams such as those of polysaccharides (hemicellulose) and polyphenols (lignin). However, sustainability and economic viability in these industries relies on efficient exploitation of all by-products to obtain bioproducts with a high added value.[3]

Lignin is an amorphous natural polymer highly abundant in nature that is part of the cell wall of plants.[4] Its branched polyphenol network, together with its physical and chemical properties, make it a material with a high technological potential.[5] In fact, lignin can replace petroleum chemicals in formulations of polymers, adhesives, dispersants, emulsifiers and sorbents (activated carbon).[6-9] Also, the rheological properties of lignosulfates have recently been exploited in lubricant grease thickeners[10] and the surface-active properties of lignins have enabled their use as surfactants. The organic nature of lignin additionally allows its use in thermochemical processes such as pyrolysis or gasification to obtain hydrogen-rich pyrolytic oils and synthetic gases for energy production purposes.[11] In addition, the antioxidant properties of lignin have promoted its use to obtain bioactive products for pharmaceutical or veterinarian purposes.[12]

One other way of valorizing lignin is by producing new materials such as carbon fibres [13] or using it as a polymer reinforcing agent or filler to obtain products performing as well as or even better than the original polymer.

Mixing polymers is an economical manner of obtaining materials with specific properties. To this end, lignins have been mixed with various types of natural and synthetic materials.[14] The former include soya proteins[15], starch[16] and a wide variety of synthetic polyesters together with polyhydroxyalkanes (PHA) and polylactic–polyglycolic acid polymers including polyethyleneterephthalate (PET)[17], polybutylene terephthalate (PBT)[18], polyhydroxybutyrate (PHB)[19], and poly-□-caprolactone (PLC)[20]. Lignin is expected to play a very prominent role in the replacement of petrochemical plastics with biodegradable polymers.

In developing new uses for lignin, one should bear in mind that the properties of the starting material will differ with its source and the methods used to extract it.[21] The main industrial source of lignin is black liquor from kraft and sulphite pulping processes. This lignin has the disadvantage that it contains sulphur, which restricts its use for some purposes such as the production of composites or pyrolytic processes, where thermal stability is an important requirement and sulphur emissions are undesirable.[21,22] However, sulphur-free lignin can be obtained by using organic solvents or delignification with NaOH. Both have enabled the industrial production of biomaterials from wood and non-wood raw materials.[23] The industrial value of organosolv and soda lignin can easily exceed that of kraft lignin by a factor of 5. The main advantages of organosolv of lignin over kraft lignin and lignosulfates is that they contain less ash and no sulphur and can be more readily derivatized; also, they are purer —by virtue of their decreased contents in carbohydrates—, lighter and more hydrophobic.[21]

Soda lignin has a high content in carboxylic acids, which makes it an effective dispersant of the polycarboxylate type. Also, it contains no sulphur and very little hemicellulose derivatives or degradation products, which makes it potentially useful for obtaining products with a high added value.[14,24]

Optimizing its exploitation requires using as pure and uniform lignin as possible.[8] This requires avoiding one of the constraints of lignin from cellulose pulping, namely: its containing variably degraded polysaccharides which lead to its use for energy production. Biorefining schemes overcome this shortcoming by obtaining purer fractionation streams with additional, new potential uses. This requires accurately establishing the fractionation sequence and product purification or separation processes for optimal results. In fact, the processes to be applied should be as little "stringent" as possible in order to maximize the integrity of the compounds to be valorized while ensuring an acceptable extraction yield.[25] This can be accomplished by fractionating in two steps, and extracting and valorizing as selectively as possible the more labile fraction (hemicellulose) in the first. This first, hydrolysis step should be performed under relatively mild conditions to avoid excessive degradation of cellulose fibres and be followed by delignification of the ensuing solid residue. Autohydrolysis is also possibly the most suitable choice for the integral fractionation of lignocellulosic biomass,[26-28] as it provides dissolved hemicelluloses of potential use as food additives or in the production of furfural and polymers.[29]

Autohydrolysis has been shown to accelerate delignification in subsequent alkaline steps,[30] albeit only over specific ranges of the operating conditions. In fact, severe autohydrolysis reduces the subsequent solubility of lignin, probably through repolymerization and bond-formation reactions. Soda lignin from an acid hydrolysis or autohydrolysis process can be used as a raw material for obtaining phenol, benzene, toluene, xylene and other aromatic hydrocarbons by hydrocracking or related reactions.[31]

In this work, we characterized various types of lignin obtained by alkaline delignification of the *Paulownia fortunei* x *tomentosa* x *elongata trihybrid* clone with or without prior autohydrolysis. The black liquor from the delignification process was recovered by evaporation or acidification and assessed for the production of composites with polylactic acid.

MATERIALS AND METHODS

Obtention of lignin

The raw material used was *Paulownia fortunei x tomentosa x elongata trihybrid* clone (Sun Tzu 104®) from a 3-year-old plantation in Extremadura (SW Spain) and supplied by the firm Vicedex Europa S.L. The wood was splintered and chips at least 5 mm thick were chosen in order to avoid the diffusional restrictions observed in preliminary tests. The samples were air-dried, homogenized in a single batch and stored in a dry place. The Klason lignin contents of the raw material and soluble lignin in it and in the cellulose pulp obtained by delignification were determined in accordance to Tappi 222 om-06 and Tappi 250 wd-96, respectively.

The autohydrolysis process, which involved cooking the raw material in water prior to delignification, was performed in a 2 L high-pressure Parr reactor operating at a constant temperature of 198 ºC for 15 min. The digester was equipped with external heating and internal temperature control via a coil and cooling water on–off electrovalves.

Delignification was done by using an NaOH/anthraquinone mixture under the following conditions: 20% NaOH on a dry matter basis; a reaction temperature and time of 171 ºC and 120 min, respectively; a solid/liquid ratio of 1/12 and an anthraquinone concentration of 0.1%. The process was performed in a 10 L MK-SYSTEMS reactor. The reactor included a black liquor recycling circuit equipped with external cooling and an electric heating mantle. Following cooking, the liquor, rich in lignin, was separated by filtration.

Lignin in the black liquor was separated in two different ways, namely:

(1) By adding 0.5% sulphuric acid to pH 6 in order to obtain a lignin precipitate that was subsequently dried in a stove at 60 ºC.

(2) By directly drying the liquor in a stove at 40 ºC. The resulting lignin was contaminated with polysaccharide derivatives but the process required using no sulphuric acid.

Characterization of lignin

The calorific values of the lignin and the other materials studied were determined in accordance with the CEN/TS 14918:2005 standard for solid biofuels on a Parr 6300 isoperibolic calorimeter.

Thermogravimetric analyses were conducted on a Q50 analyser from TA Instruments. Samples were heated from 50 to 600 ºC at a rate of 10 ºC/min under a nitrogen stream of 100 mL/min.

Infrared spectra were recorded on a Perkin Elmer Spectrum One Fourier Transform IR spectrophotometer, using KBr pellets containing 2 mg of sample and the wavenumber range from 4000 a 600 cm^{-1}.

Soluble lignin was determined by UV spectrophotometry on a UV/1800 spectrophotometer from Analytic Instruments Corp. To this end, a sample of black liquor obtained after filtering insoluble lignin was diluted 10 times with 4% H_2SO_4 and homogenized by stirring. Measurements were made at 205 nm against a 4% H_2SO_4 solution as blank.

Scanning electron micrographs were obtained with a Fei-QUANTA 200 microscope.

Obtention and characterization of composites polilactic acid-lignin

Composites containing polylactic acid as the matrix and lignin as reinforcing agent were prepared by using dichloromethane as diluent. To this end, an amount of 3.5 g of polylactic acid in 40 mL of dichloromethane was heated at 40 ºC and, after complete dissolution of the acid, supplied with 0.5, 1.0 or 1.5 g of Klason lignin. The mixture was thoroughly homogenized, transferred to a Petri dish and allowed to cool and solidify at room temperature. The resulting solid was used to obtain specimens containing 12.5, 22.2 and 30.0% lignin.

The specimens were subjected to mechanical dynamics analysis on a TA Instruments 2980 analyser using a film-tension clamp. Measurements were made at a frequency of 1 Hz and a heating rate of 5 ºC/min over the temperature range 25–150 ºC.

RESULTS AND DISCUSSION

Comparison of soda lignin after alkaline delignification with and without previous autohydrolysis

As can be seen from Table 1, including or excluding an autohydrolysis reaction resulted in substantial quantitative differences in lignin contents in the liquid phase (black liquor). Thus, the alkaline delignification process including prior autohydrolysis (A+D) reduced the Klason lignin content of the pulp by 69.7% vs 61.4% without autohydrolysis (D). Therefore, the Klason lignin content of the spent liquor from the A+D process was 21.5% higher than that in the liquor from D. The soluble lignin content was greater with D than with A+D, but both fractions were of little industrial value. The increased delignification obtained with the A+D process is one immediate advantage over the conventional process (D) as it provides lignin of a greater uniformity and containing less polysaccharide residues.

The increased constant-volume calorific value on a dry matter basis in soda lignin was substantially lower than that of the raw material (20 335 kJ/kg). The value for the lignin obtained with the A+D process and dried at pH 10 at 40 ºC was 14 822 kJ/kg, whereas that for D lignin dried at the same pH and temperature was 13 273 kJ/kg. Although the increased calorific value of the raw material indicates that the polysaccharide fraction contained more energy than the polyphenol fraction, the results for soda lignin remaining after alkaline delignification with or without autohydrolysis suggest that the lignin possessed a higher heat value than the hemicellulose fraction extracted from the liquid phase after autohydrolysis and also that cellulose derivatives present in the delignification liquid phase were degradation products losing most of the energy contained in the original cellulose polymer. All this confers a second advantage or added value to the lignin fraction from the A+D process in relation to D, namely: an increased energy content for conventional burning purposes. These calorific values are lower than those for solid biofuels from hardwood and softwood (approximately 18 200–20 500 kJ/kg),[32,33] but similar to those for some residual materials such as barley straw (15 700 kJ/kg)[34] or even higher than those for fruit tree residues (12 884 kJ/kg), gardening residues (13 724 kJ/kg), fruit (13 421 kJ/kg), agricultural residues (13 421 kJ/kg) or urban wastewater sludge (11 790 kJ/kg).[35]

Thermogravimetric analysis allowed thermal degradation in lignin to be assessed by measuring weight losses as the temperature was raised (see Figure 1, which shows the results for A+D and D lignin as extracted under different pH conditions). An additional process for D lignin extracted at pH 6 was conducted by extracting volatile substances prior to the thermogravimetric analysis. Since neither the A+D lignin fraction nor the D fraction was pure, the results must be interpreted with provision for the presence of additional compounds such as hemicellulose derivatives, resins, waxes, fats, chlorophyll, oils and gums.

As can be seen, there was a well-defined region from 50 to 100 ºC reflecting in a positive slope in the derivative graph (Figure 3) where the material lost 3–5% by weight as moisture. The region from 100 to 200 ºC exhibited tall peaks for A+D lignin and the D lignin obtained by evaporation at pH 10 at 40 ºC. The difference between these two curves and those for A+D and D lignin obtained at pH 6 indicates the presence of substantial amounts of impurities or non-polyphenolic compounds. Therefore, acidification at pH 6 afforded efficient separation and purification of the lignin fraction provided by both processes. Also, the substantial differences between peaks for the two types of lignin obtained by drying at 40 ºC and at pH 10 are suggestive of a strong influence on the purity of A+D lignin relative to D lignin. The increased peak area can be ascribed to compounds present in the raw material that were more thermally unstable and removed to a marked extent in the autohydrolysis step.

A third region from about 200 to 350 ºC discriminated between A+D and D lignin much more clearly than did the lignin separation method or whether it included acidification. The greater stability of the derivative weight loss curves for the A+D process further confirms an increased purity of the soda lignin fraction obtained with it. Lignin decomposed in the region from 350 to 600 ºC, with similar weight losses for both alkaline delignification and separation of the lignin but marked differences in the residual mass as the temperature was raised. Thus, the lowest contents in residual compounds measured at 500 ºC were those for D lignin separated at pH 10 at 40 ºC or pH 6 (viz. 58 and 65% , respectively, of the material as compared to 66 and 68% in A+D lignin). As confirmed by the results for D lignin separated at pH 6 after extraction of volatiles, which contained 73% residues at 500 ºC, these differences can be ascribed to the presence of other compounds in addition to lignin.

A comparison of the TGA results with those for other materials such as kraft lignin revealed that thermal decomposition started in the same temperature range: 195–200 ºC. The reaction rate (i.e. the weight derivative) increased gradually with increasing temperature to a peak between 300 and 380 ºC.[36] Other authors located the maximum at

350–450 ºC[8]; ours occurred at 250–350 ºC. This temperature region is where bonds between units are broken to form aromatic hydrocarbons, phenolic compounds, hydroxyphenols and guaiacyl–syringyl compounds. Most of the products contained phenolic hydroxyls[36]. Temperatures above 500 ºC usually cause decomposition of some aromatic rings[8,37] —those in our materials were broken at 450 ºC. The contents in residual compounds of our lignin fractions were slightly higher than those for kraft lignin and amounted to 40–50% at 600 ºC.[8] The high residual contents obtained were a result of the formation of highly condensed polymers by effect of the high thermal stability of the materials. In fact, lignin usually exhibits a high thermal stability and is difficult to decompose. Also its thermal decomposition is more markedly influenced by temperature than by the particular type of material.[38]

The different types of lignin were characterized in structural terms from the IR spectra for Klason lignin from soda-delignified pulp obtained with prior autohydrolysis and lignin in the black liquor extracted at pH 6 (Figure 3). We chose to examine the lignin obtained with prior autohydrolysis because, based on the results, it was purer than that obtained in the absence of autohydrolysis. For the same reason, we chose to use the lignin extracted at pH 6 rather than at pH 10.

The typical functional groups and IR signals for lignin from various materials have been reported by several authors.[37,39-41] The band at 3200–3600 cm^{-1} in the spectra of Figure 3 corresponded to hydroxyl groups. Although both spectra contained very similar bands, the vibrations of hydroxyl groups in Klason lignin extracted at pH 6 (Figure 3B) appeared in the region 3200–3650 cm^{-1}, whereas those in soda lignin (Figure 3A) were observed at a specific frequency: 3600 cm^{-1}. Differences in this spectral region were due to the greater severity of the extraction method used with the soda lignin; thus, the method involved quantitative acid hydrolysis in two steps and was thus bound to cause repolymerization to insoluble condensed products and elimination of methoxyl groups to produce catechols.[42]

Other signals worth noting were those for CH_2 groups in guaiacyl–syringyl units —typical of lignin— in the 2800–2650 cm^{-1} region, and methylene groups and aromatic rings in such units at 2300–2650 cm^{-1} and 1500 cm^{-1}, respectively.

As can be seen from the spectrum for soluble lignin (Figure 4), the band for hydroxyl groups at 3300–3600 cm^{-1} was broader by effect of the groups being completely free rather than reticulated to other groups. Also, the bands for hydroxyl and carboxyl groups in soluble lignin were stronger and weaker, respectively, than those in Klason lignin.

The spectrum for soluble lignin was very similar to that reported by Yang et al. ,[41] where the 1830–730 cm^{-1} region was specially prominent; thus, this region contained a group of complex IR absorbance bands for lignin suggesting that it might be rich in methoxyl-O-CH_3, C–O–C stretching and C=C stretching vibrations (aromatic rings).

Scanning electron microscopy exposed the effect of the autohydrolysis treatment and the different lignin extraction techniques used on the morphological features of the lignin. Thus, autohydrolysis increased surface uniformity and reduced surface fragmentation (see Figure 5.1). This confirms that the autohydrolysis treatment provides purer lignin. Also, our lignins have a more uniform surface than kraft lignin, which is more strongly altered by the pulping process and exhibits particle agglomeration on its surface.

Figure 6 shows the micrographs for lignin samples obtained with autohydrolysis but extracted at a different pH. As can be seen, extraction was more aggressive at pH 6 than at pH 10. The lignin extracted at the higher pH (Figure 6.1) had slightly rounder edges and less sharp surfaces. Figure 7 is a magnified view of a fragment of the lignin extracted at pH 6.

Valorization of composites of polylactic acid with lignin obtained by autohydrolysis and alkaline delignification

Based on the above-described results, we used variable amounts of A+D and D lignin extracted by evaporation at pH 10 at 40 ºC to reinforce a polylactic acid polymer. In this way, we obtained composites containing 12.5, 22.2 and 30% lignin. Their mechanical dynamics analysis revealed that the material exhibited a viscoelastic behaviour under loading (i.e. it resisted deformation by an externally applied force). Figure 8 shows the elastic (storage) modulus E', which is a measure of the ability of a material to store mechanical energy, for the pure polymer and its composites with lignin. As can be seen, using lignin in a 12.5% proportion to strengthen the polymer caused a slight decrease in E' with respect to the pure polymer. At a reference temperature of 50 ºC, increasing the amount of lignin added increased the elastic modulus from 280 MPa for polylactic acid to 170, 488 and 545 MPa for the composites containing 12.5, 22.2 and 30% lignin, respectively.

The delta tangent plot of Figure 9 illustrates the viscoelastic behaviour of the composites. The increased elastic module of the composites reflected a decreased elastic response relative to the pure polylactic acid polymer. Also, there were several peaks at the glassy transitions for the materials. The peak for polylactic acid, which typically appears at 68 º C, was shifted to 58 and 65 ºC in the composites containing 22.2 and 30% lignin, respectively, which reflects interactions between lignin and the polymer. The additional peaks observed for the composite containing 12.5% lignin indicate a reduced thermal stability by effect of the material not retaining is thermal properties. On the other hand, the composites containing 22.2 or 30% lignin were more thermally stable than the pure polymer.

As can be seen from the IR spectra for the polymer–lignin composites (Figure 10), virtually all hydroxyl groups initially present in the structure of chemically pure polylactic acid (CPPLA), which exhibit a signal at 3200–3650 cm^{-1}, disappeared. These results are suggestive of a chemical interaction between lignin and the acid.

CONCLUSIONS

Subjecting a *Paulownia fortunei x tormentosa x elongata trihybrid* clone to autohydrolysis prior to alkaline delignification provided a spent liquor containing 11.9% more lignin and having a greater calorific value (14 822 kJ/kg) than without autohydrolysis. The results of the thermogravimetric analysis revealed that the autohydrolysis step provides residual delignification fractions containing increased amounts of lignin but no degradation products of polysaccharides or other components of the raw material. This advantage reflected in scanning electron micrographs, where lignin obtained with autohydrolysis exhibited a more uniform surface and less surface fragmentation. Mechanical dynamics analysis of the composites containing 12.5–30% lignin revealed and increased elastic (storage) module (E’) and thermal stability, which were similar to those for the pure polymer in the composite containing 30% lignin. A comparison of the IR spectrum for a polymer–lignin composite with that for lignin revealed that virtually all hydroxyl groups, which typically absorb at 3200–3650 cm^{-1}, were removed. This suggests a chemical interaction between the two components that facilitates formation of the polymer.

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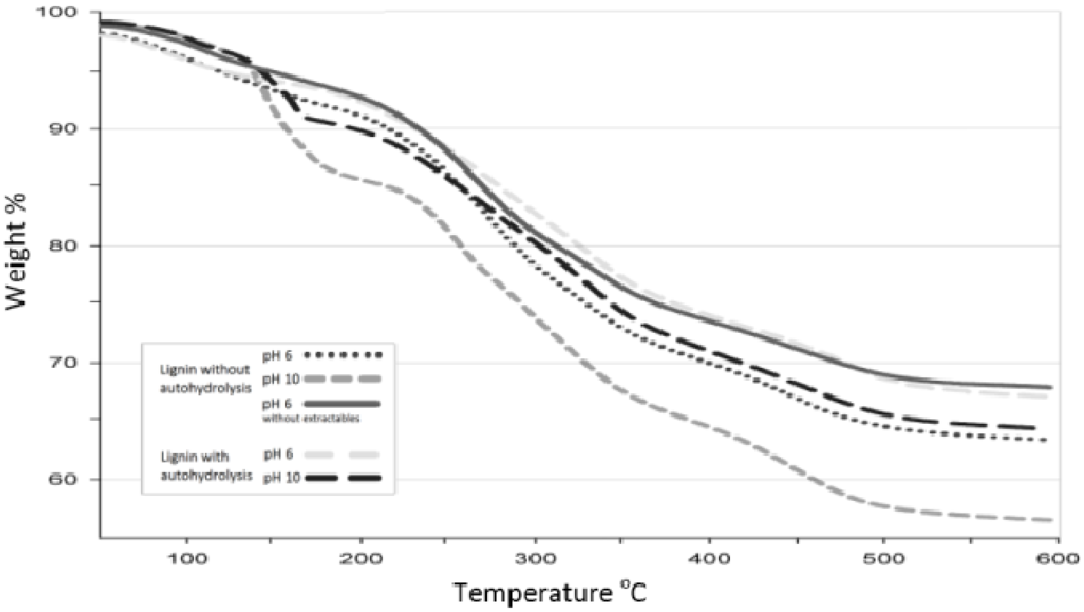
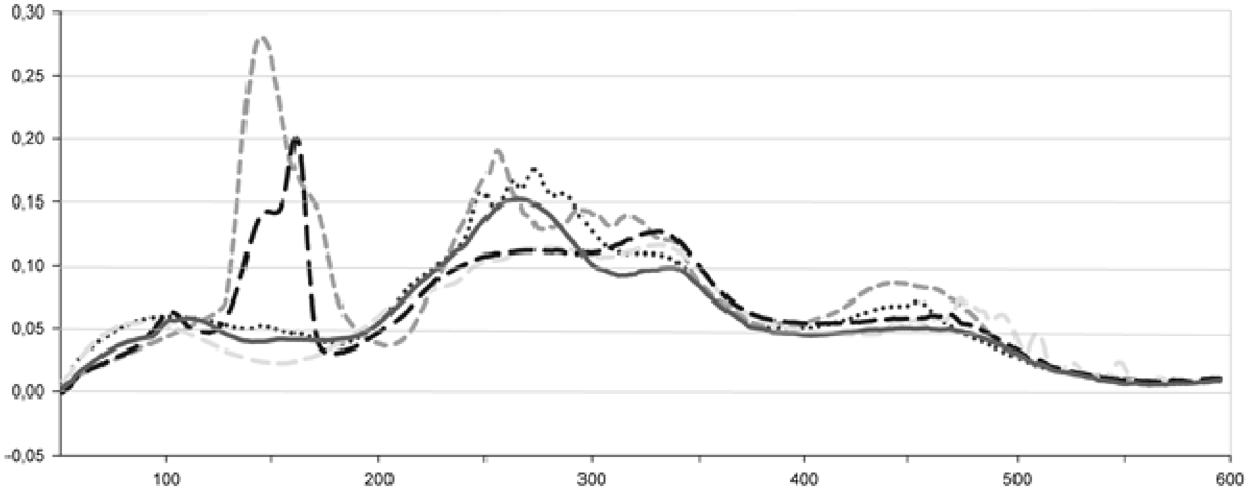
FIGURES

Figure 1. Thermogravimetric analysis of lignin obtained by alkaline delignification with and without prior autohydrolysis of Paulownia fortunei x tormentosa x elongata.



1 **Figure 2.** Derivative of the TGA curves of Figure 1 with respect to weight



2

Figure 3. Infrared spectra for Klason lignin contained in (A) soda-delignified pulp obtained with prior autohydrolysis and (B) black liquor extracted with H_2SO_4 at pH 6.

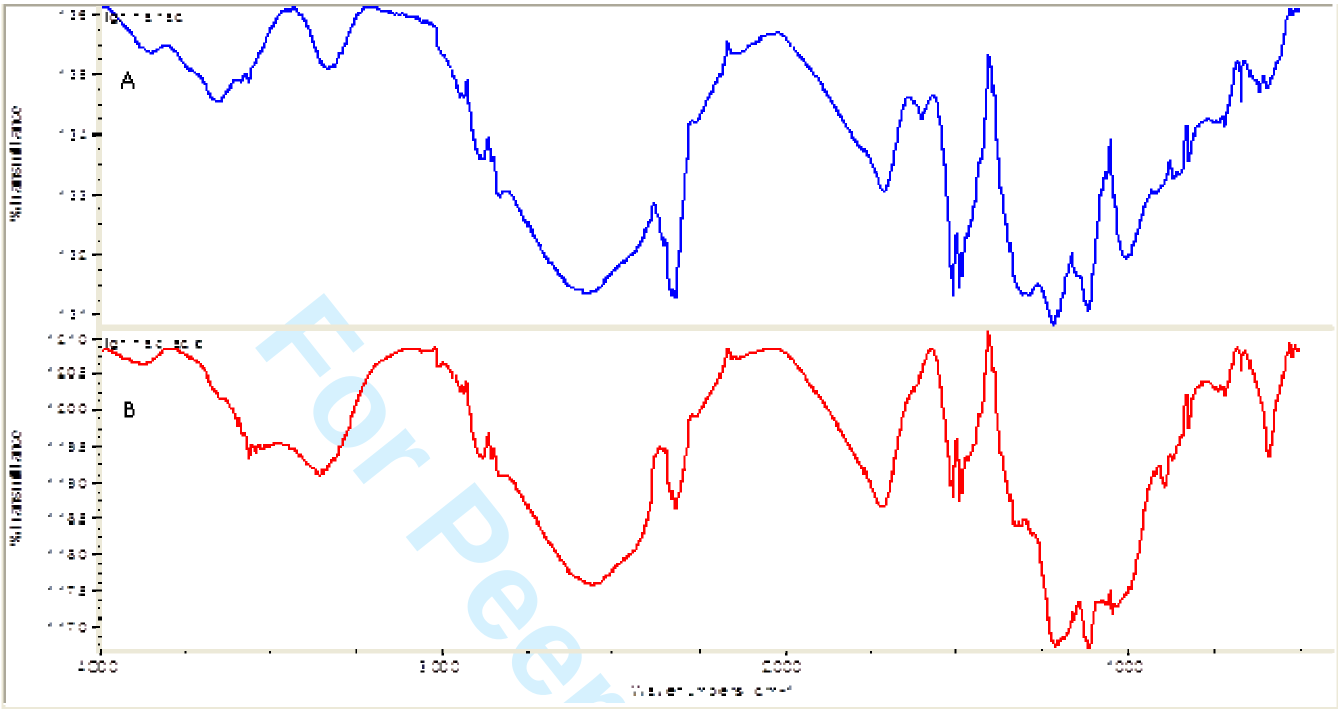


Figure 4. Infrared spectrum for soluble lignin contained in delignified pulp obtained with prior autohydrolysis.

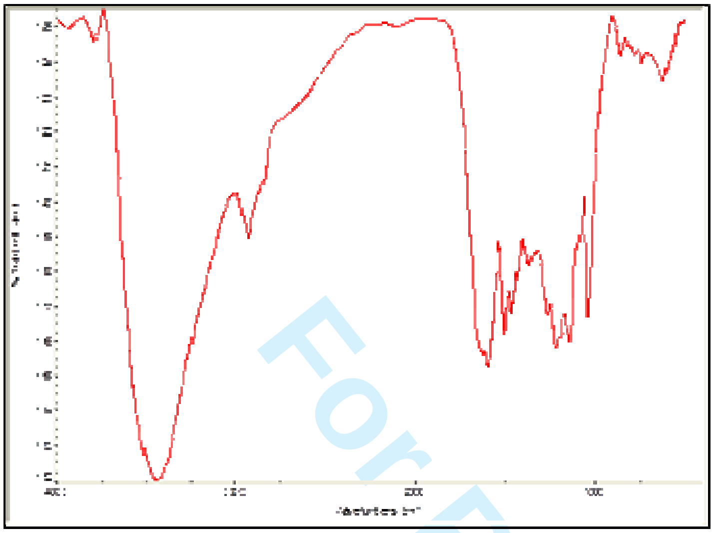


Figure 5. Scanning electron micrographs for lignin obtained with (1) and without (2) autohydrolysis. (pH 6). 50 µm.

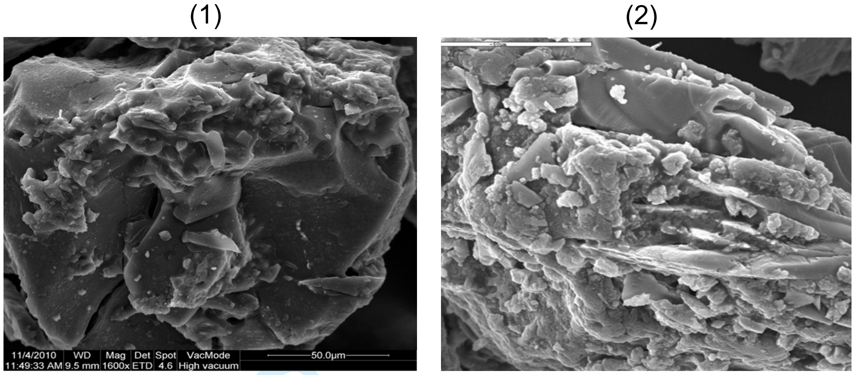

(1)
(2)

Figure 6. Scanning electron micrographs of lignin obtained with autohydrolysis and extracted at pH 10 (1) or pH 6 (2). 200 µm.

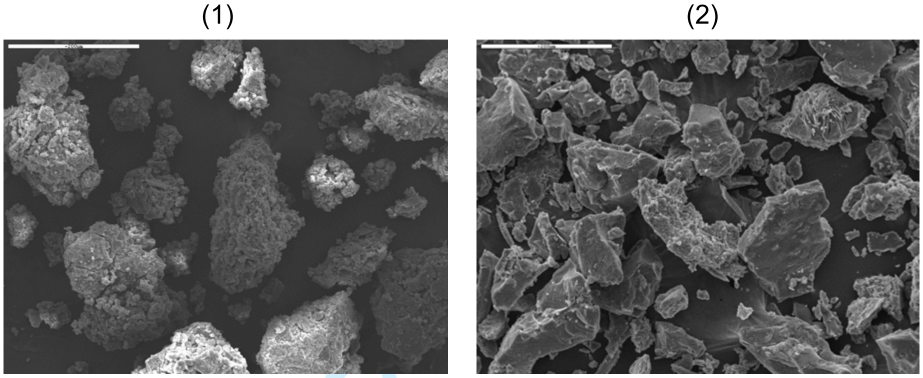


Figure 7. Magnification of a fragment of lignin obtained with autohydrolysis and extracted at pH 6. 10 µm.

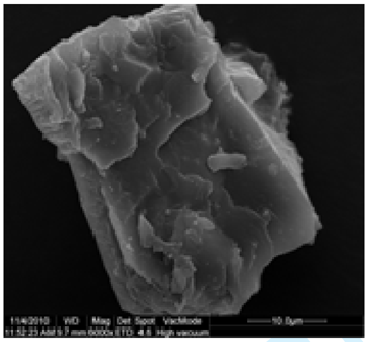


Figure 8. Elastic modulus of polylactic acid (PLA) composites containing variable amounts of lignin.

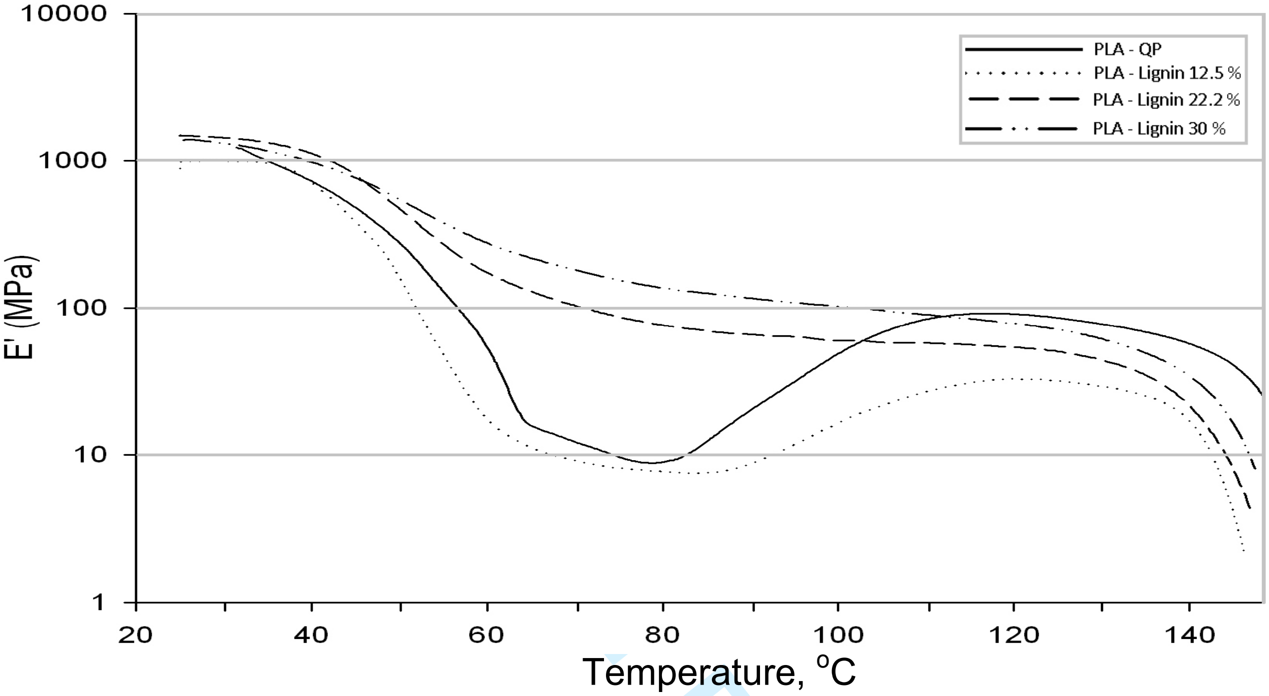


Figure 9. Delta tangent graph for polylactic acid composites with variable amounts of lignin.

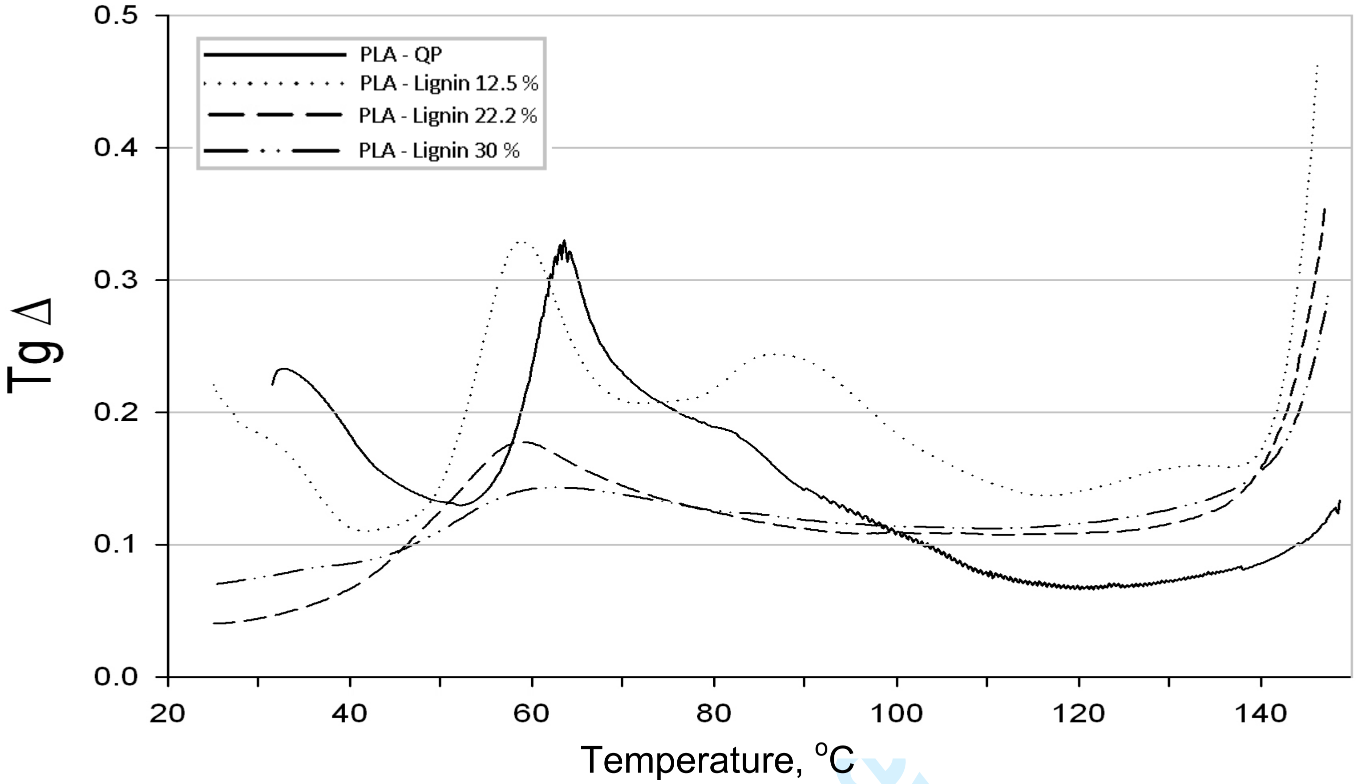
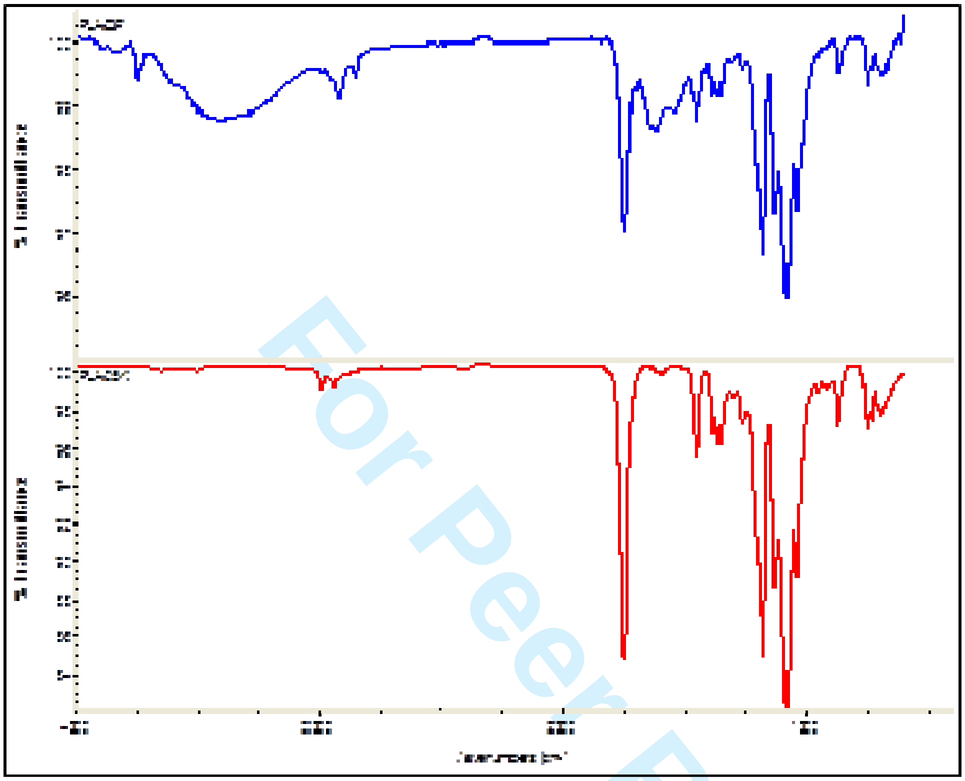


Figure 10. Infrared spectra for (A) chemically pure polylactic acid (PLA) and (B) a composite of PLA with Klason lignin extracted a pH 10.



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TABLES

Table 1. Klason and soluble lignin contents of the Paulownia trihybrid and of pulp obtained by delignification with soda in the presence and absence of a prior autohydrolysis reaction

Material	Lignina klason (%)	Lignina soluble (%)
Raw material	23.76 (0.85)	-
Pulp D (conventional alkaline delignification)	9.17 (0.03)	0.015 (0.002)
Pulp A+D (autohydrolysis + alkaline delignification)	7.20 (0.20)	0.0005 (0.00002)

Figure 1.

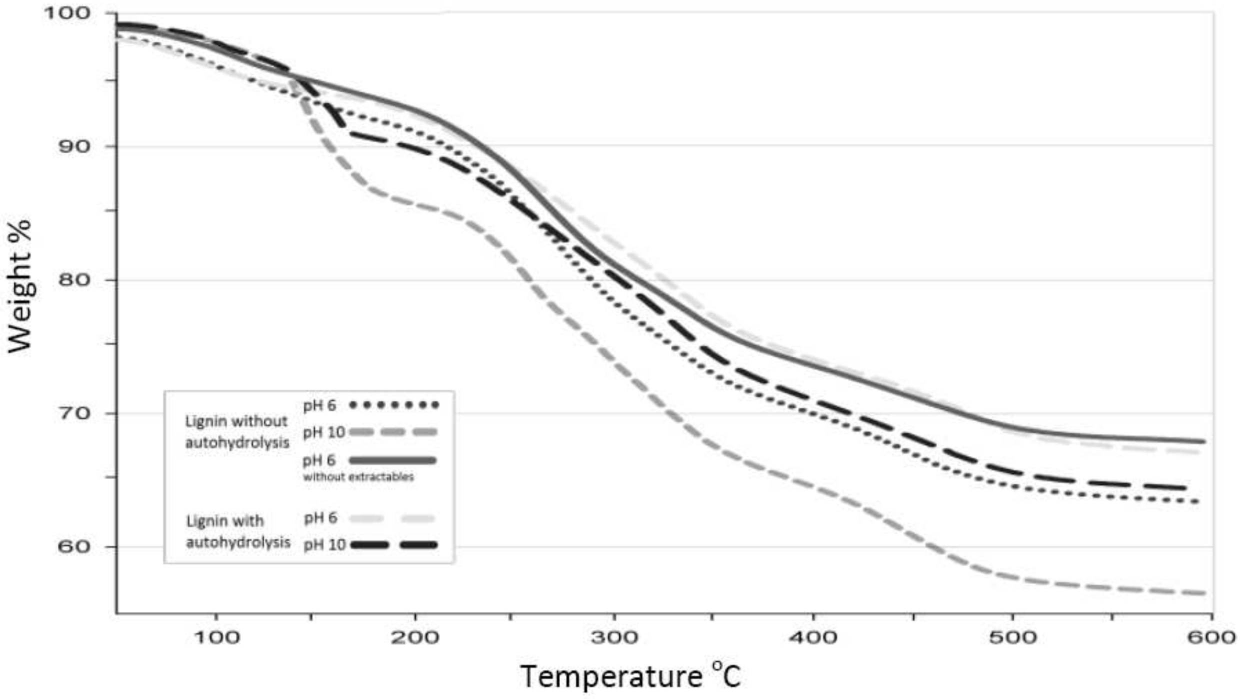

100
90
80
70
60
Weight %
100
200
300
400
500
600
Temperature °C
Lignin without autohydrolysis
pH 6
pH 10
pH 6 without extractables
Lignin with autohydrolysis
pH 6
pH 10

Figure 2

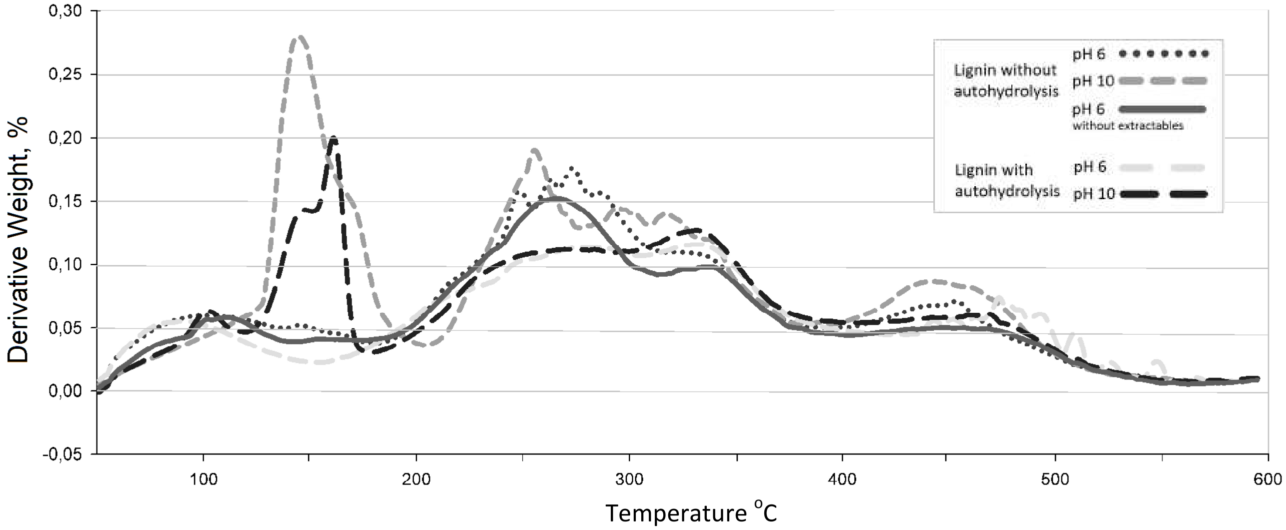

0,30
0,25
0,20
0,15
0,10
0,05
0,00
-0,05
Derivative Weight, %
100
200
300
400
500
600
Temperature °C
Lignin without autohydrolysis
pH 6
pH 10
pH 6 without extractables
Lignin with autohydrolysis
pH 6
pH 10

Figure.3

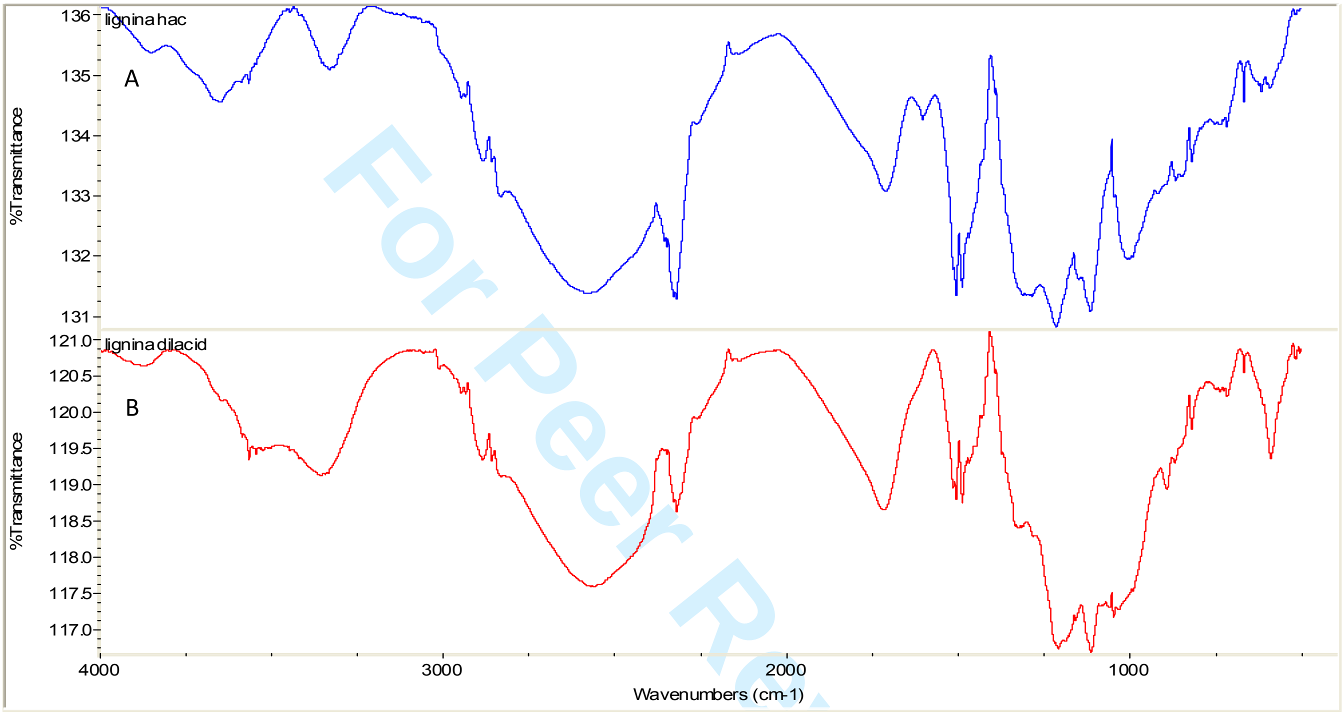

lignina hac
A
%Transmittance
136
135
134
133
132
131
lignina dil acid
B
%Transmittance
121.0
120.5
120.0
119.5
119.0
118.5
118.0
117.5
117.0
4000
3000
2000
1000
Wavenumbers (cm-1)

Figure 4.

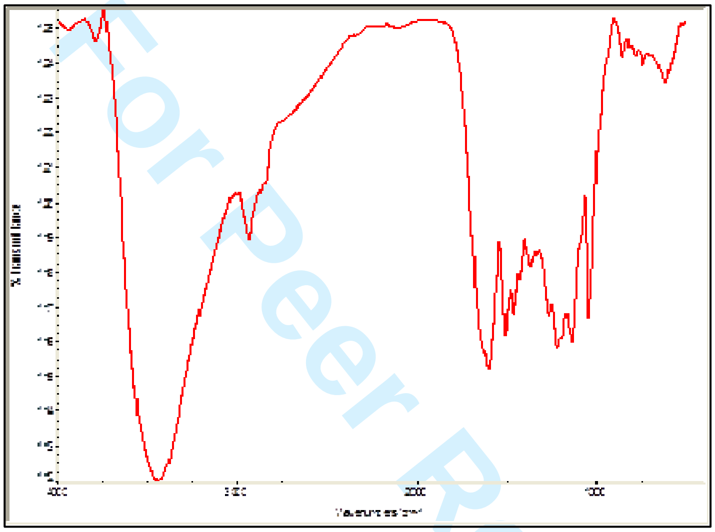
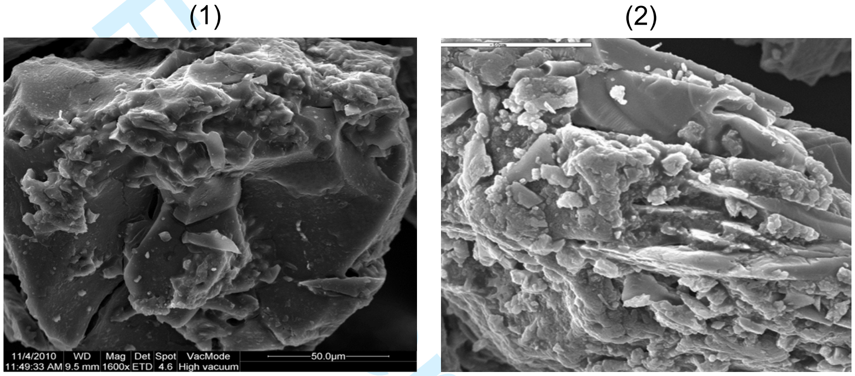


Figure 5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50.0μm

(1) (2)

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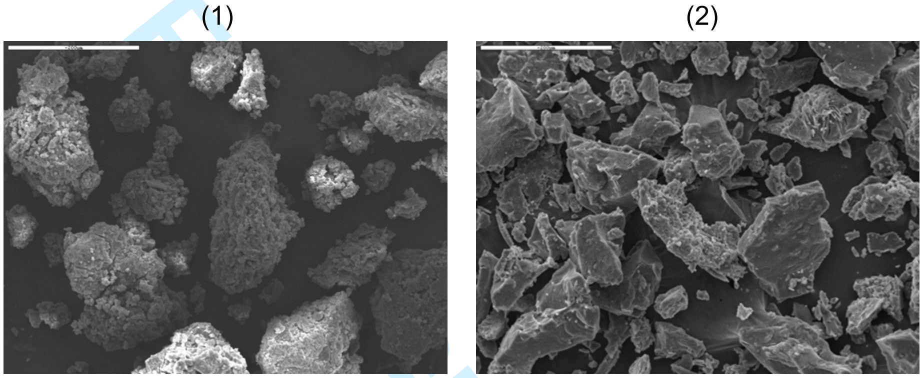

(1)
(2)

Figure 7.

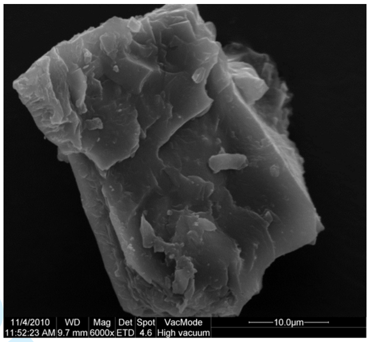

11/4/2010
WD
Mag
Det
Spot
VacMode
10.0µm
11:52:23 AM
9.7 mm
6000x
ETD
4.6
High vacuum

Figure 8.

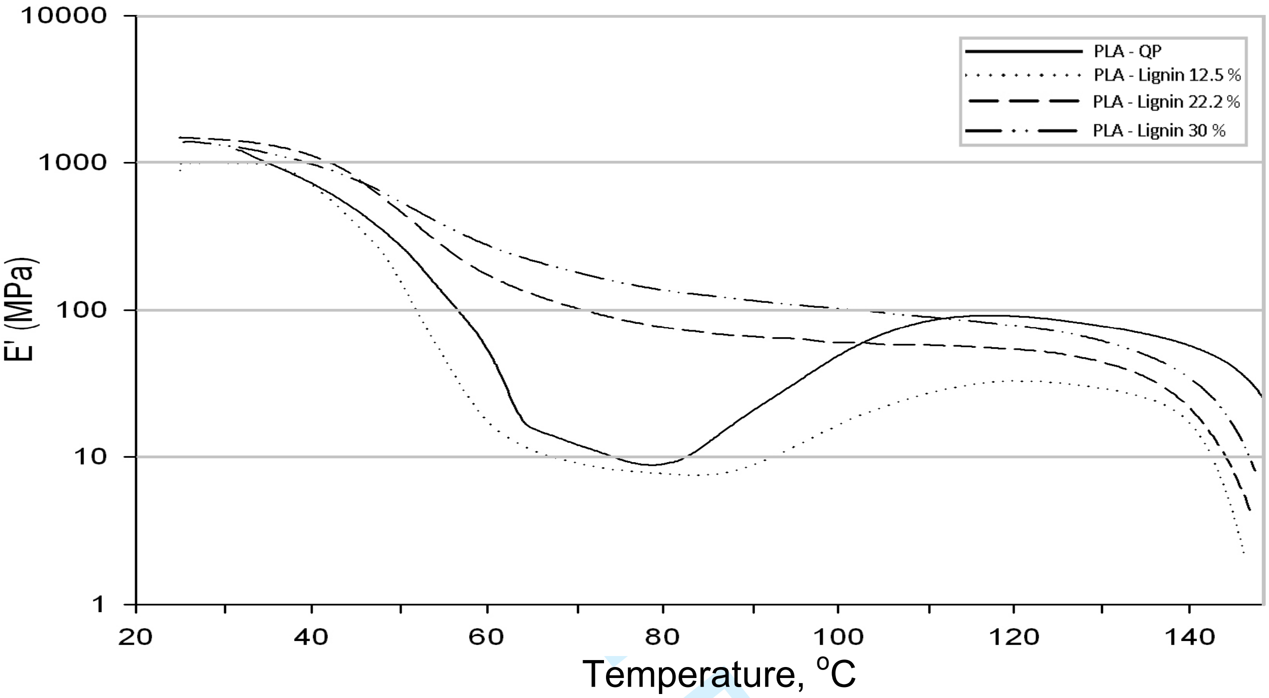

10000
1000
100
10
1
E' (MPa)
20
40
60
80
100
120
140
Temperature, °C
PLA - QP
PLA - Lignin 12.5 %
PLA - Lignin 22.2 %
PLA - Lignin 30 %

Figure 9.

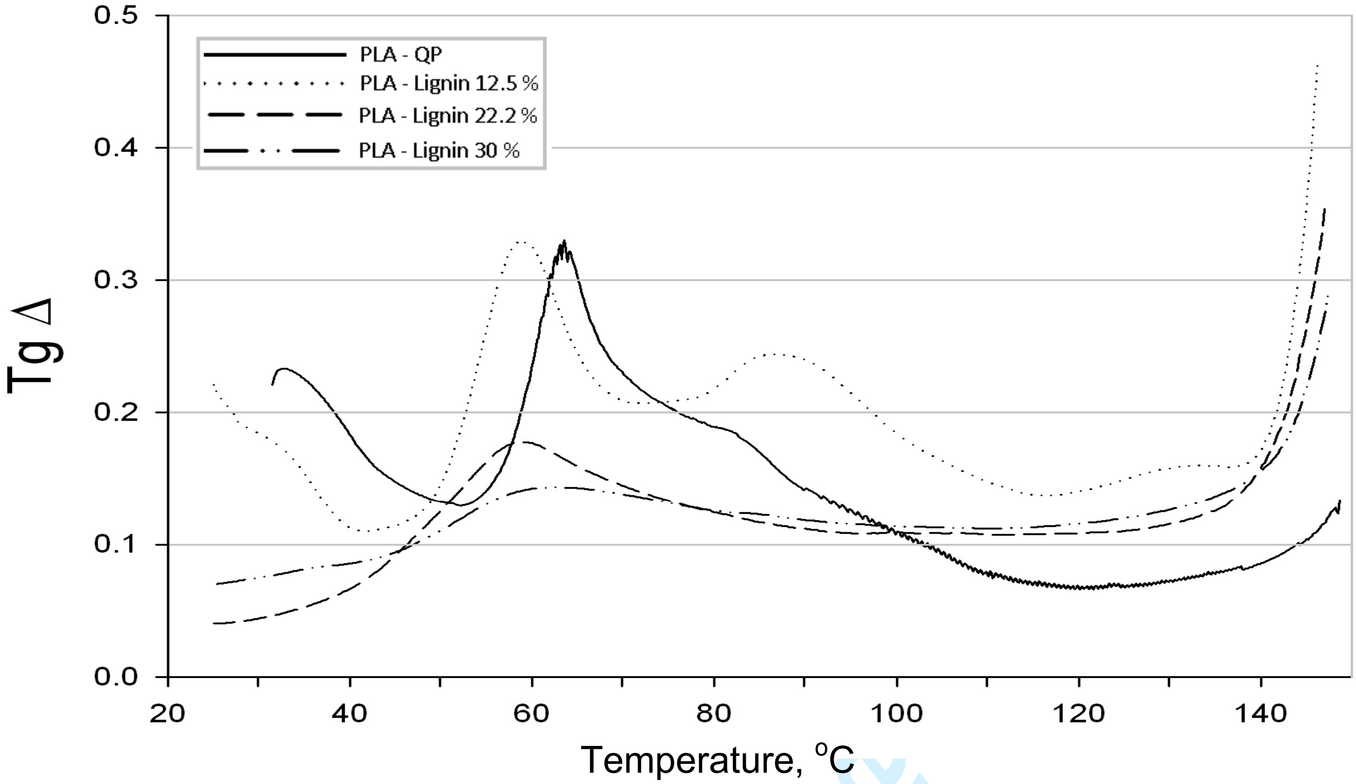
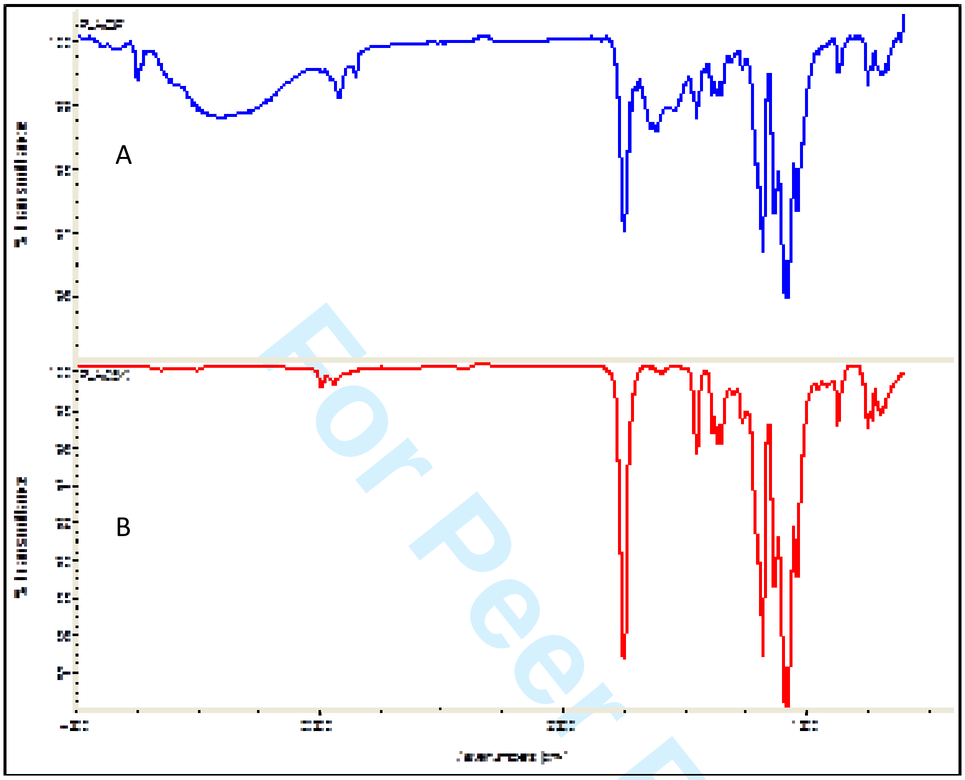

PLA - QP
PLA - Lignin 12.5 %
PLA - Lignin 22.2 %
PLA - Lignin 30 %
Tg Δ
0.5
0.4
0.3
0.2
0.1
0.0
20
40
60
80
100
120
140
Temperature, °C

Figure 10.



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