# Value-Added Derivatives of Soda Lignin from Alfa Grass (*Stipa tenacissima*). I. Modification and Characterization

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**ABSTRACT:** Alfa grass (*Stipa tenacissima*) is the only raw material for manufacturing paper pulp in Algeria, Tunisia, and Morocco. Soda lignin (SL) is obtained from black liquor (BL), a byproduct of manufacturing paper from alfa grass. This work was aimed at modifying SL and using it as a polymer lubricant. Modified SL was obtained in two steps: the precipitation of BL at pH 4 with sulfuric acid (2*N*) followed by the modification of SL by esterification using stearic anhydride (SA) dissolved in dioxane at 50°C for 8 h. The effects of different contents of SA on the hydrophobic properties and heat stability of modified SL were evaluated with contact angle analysis and thermogravimetric analysis. A commercial stearate used in plastic processing was chosen as the reference. Its thermal properties were ascertained with thermogravimetry, and its behavior was similar to that of the modified lignins. A structural comparison study was performed with Fourier transform infrared (FTIR) spectroscopy and solid-state $^{13}$C-NMR. The FTIR and $^{13}$C-NMR results showed that there were significant differences between the main structures of SL samples reacted with 10, 30, or 100% (w/w) SA. The main part of the work consisted of modifying SL, evaluating the properties of the obtained products with respect to their use as lubricants, and comparing them to industrial lubricants. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1546–1554, 2010

**Key words:** esterification; FT-IR; NMR; thermogravimetric analysis (TGA)

## INTRODUCTION

In Algeria, alfa grass (*Stipa tenacissima*) is found primarily on high steppe plains. It is regarded as the last rampart against the ingress of the desert because of its very developed root system, which allows the fixation and protection of the ground. In industry, the importance of this fiber, also called esparto, lies in the use of its fibrils in manufacturing paper pulp.[1] The black liquor (BL) contains almost 40 g of soda lignin (SL) per liter (as measured when it is precipitated at pH 4).[2]

Before its applications can be considered, knowledge of the structure of SL from alfa grass is required; this study presents such an approach.

Lignin is an amorphous polyphenolic material arising from the polymerization of three major phenylpropanoid monomers: coniferyl, sinapyl, and coumaryl alcohols.[3] The lignin structural elements are linked by carbon–carbon and ether bonds to form a three-dimensional network associated with the hemicellulose polysaccharides inside the cell wall. Lignin is usually insoluble in all solvents and can be degraded only by physical or chemical treatments.[4] During the chemical pulping process at high temperatures and high pressures, the degradation of lignin occurs, and it dissolves into the spent liquor. The delignification reactions involve the cleavage of the phenolic β-O-4 linkage and α-O-4 linkage and release from the associated polysaccharides. The alfa fibers contain about 21.2% lignin; this is relatively significant in comparison with hardwood and softwood materials.[4]

SL is a chemically degraded technical lignin produced in large quantities in the soda pulping process. It is presently used almost exclusively as fuel in the recovery system of soda mills. SL and SL derivatives have, however, the potential to be used in other applications.

The esterification of wood by fatty acids or their acid chlorides containing long hydrophobic chains can provide a water-repellent adduct. A direct reaction between fatty acids and wood has low practical probability and a low chemical yield. Thiebaud and Borredon[5] developed an esterification method using fatty acid chlorides and no solvents. The good hydrophobicity of the modified wood was even

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better with long-chain fatty acid chlorides.[6] The thermal stability of the modified wood was also improved. The thermoplasticity of wood is increased by the esterification of its hydroxyl groups with fatty acid chlorides in a dinitrogen tetroxide/dimethylformamide pyridine medium or with fatty acids combined with trifluoroacetic anhydride in benzene.[7] The explanation for this is that the bulky substituents weaken and dilute the hydrogen bonds, increase the flexibility of the molecular chains, and lubricate and plastify the macromolecular layers. Fatty acid chlorides [$CH_3$—$(CH_2)_n$—COCl, where $n$ is 6, 8, 10, 12, 14, or 16] have been used for wood modification.[8]

Thielmans and Wool[9] studied the kinetics and stoichiometry of kraft lignin esterification with anhydrides of several different sizes. They found that to compensate for the weak reactive rate of the hydroxides, it is necessary to use a 10-fold excess of anhydride in comparison with kraft lignin, and this is relatively expensive; therefore, they used methylimidazole as the catalyst (preferred over pyridine) with dioxane as the reaction solvent. In this work, the main objective was to develop a synthetic lubricant allowing BL from industrial papermaking to be substituted for industrial lubricants in certain markets (e.g., TPW104 and Optipak 100) at a comparable cost with equivalent or nearly equivalent specifications. The comparison of the modified SL with industrial lubricants was done with Fourier transform infrared (FTIR) spectroscopy, $^{13}$C-NMR, thermogravimetric analysis (TGA), and contact angle analysis.

## EXPERIMENTAL

### Raw materials

Alfa SL was isolated from industrial soda BL by acid precipitation.

The pH of the BL was 12.3, and its density was 1.02 g/mL. The SL was precipitated from the concentrated BL by acidification to pH 4 with sulfuric acid at 72% (w/w). The precipitated lignin was then centrifuged and washed with water that was adjusted to pH 2 with the corresponding acid used in the earlier step. The SL was then dried in a vacuum oven at 50°C for 24 h before further analysis. A detailed description of the isolation procedure has been presented elsewhere.[2]

The comparative or reference product was TPW104 (an industrial lubricant). TPW104, a commercial lubricant, was provided by Struktol Co. of America (Stow, OH). This compound is based on zinc stearate. The products used in this work were stearic anhydride (SA; 98% w/w), which was used as a comonomer; 1-methylimidazole (1MIM; Aldrich, Ontario, Canada), which was used as a catalyst; cyclohexane (99% w/w; Laboratoire Mat, Quebec, Canada), which was used as a precipitating agent; 1,4-dioxane (99% w/w; Fisher, Strasbourg, France), which was used as a solvent; and anhydrous ethyl ether (Fisher), which was used as a quencher.

### Esterification and separation

The esterification reactions were performed with the catalyst 1MIM (liquid state). SA (solid state) was chosen as the reactant because stearates are widely used in the plastic processing industry as lubricants. 1,4-Dioxane was used as the solvent for SL with the pure stearic compound SA. As the modification reaction progressed, all derivatized lignins remained completely soluble in the reaction mixture with 1,4-dioxane as the solvent. The lignin functionalities and extent of reaction were determined with FTIR and $^{13}$C-NMR spectroscopy.

All chemical modifications were performed at 50°C in a closed nitrogen atmosphere with vigorous stirring. Although there is evidence that reactions went to completion within 2 h, they were left to react overnight to ensure complete conversion.

The reaction mixture was made of 1 g of 1MIM and 20 mL of 1,4-dioxane per gram of SL added. A total of 5 mL of 1MIM in 100 mL of a 1,4-dioxane mixture was added to catalyze the reaction.

Ethyl ether addition quenched the reaction. This mixture was then washed three times with twice distilled water. The aqueous phase was drained, and this removed all 1MIM. Some derivatized lignins formed a granular sediment in the ethyl ether phase because of limited solubility. Cyclohexane was subsequently added to the ether phase to precipitate the derivatized SL. The SL granular precipitate was recovered by filtration and dried *in vacuo* for 24 h. The quantities used in the extraction process per 100 mL of the reaction mixture were 200 mL of ethyl ether, 3 × 200 mL of water, and 200 mL of cyclohexane.

Stearic acid modified SL was recovered by the addition of a 10-fold amount of water to the reaction mixture, which was followed by centrifugation, filtration, and vacuum drying for 24 h. All modified SLs [reacted with 10 (LM1), 30 (LM2), and 100% (LM3) SA], esterified by SA (10, 30, and 100%, respectively), were analyzed.[10]

### Elemental analyses

Lignin samples were analyzed for carbon, hydrogen, and nitrogen, and sulfur was determined from the difference between the total and CHNS contents. Because the SL was an industrial lignin, the amount of ash was rather high[2] and had to be taken into

account to calculate the percentage of oxygen from the difference in the elemental analysis, the amount of ash being 14.05%.[10]

### Solid-state $^{13}$C-NMR

The $^{13}$C-NMR analyses were run on solid samples with a Bruker Avance 300 spectrometer (Toronto, Canada) with a field of 75 MHz. All spectra were recorded with the technique of cross-polarization and rotation with magic angle spinning with 7-mm tubes. The samples were spun at 4000 Hz. The time of contact for cross-polarization was adjusted to 1 ms, and 3000 scans were recorded.

### FTIR spectroscopy

The lignins were measured on a Nicolet (Menlo Park, CA) Omnic 560 FTIR spectrometer. Pellets for IR analysis were prepared by trituration with a mortar and pestle of approximately 5 mg of each sample with about 250 mg of potassium bromide (KBr) and the subsequent pressing of the mixture in a die. FTIR was used to investigate reactive compatibilization and showed that hydroxyls of SL reacted with SA to yield an SL–SA copolymer.

### TGA

A Mettler–Toledo TGA/SDTA851e thermogravimetric analyzer was used to study the thermal properties of lignins. The heating rate was set at 10°C/min over a temperature range of 25–325°C. Measurements were carried out in a air atmosphere with a rate of flow of 50 cm$^3$/min. For each measurement, 7 mg of the oven-dried sample was used to determine the weight loss of the material as a function of temperature or time. The results obtained by TGA were useful for studying the applicability of different lignin samples in various composite materials.

### Contact angle measurements

Static contact angles were measured with a KSV CAM 200 (Quebec, Canada) computer-controlled, video-based instrument (KSV Instruments, Ltd., Finland). The instrument included a charged coupling device video camera, a frame grabber, an adjustable sample stage, and a light-emitting diode light source. A water drop (14 μL ± 7%) was allowed to fall onto the solid (a compressed SL powder pellet) from a syringe tip to produce a sessile drop. Images were captured at a rate of 3 per second for 0.25 min.

The contact angles were calculated by curve fitting of the captured drop profile to the theoretical shape predicted by the Young–Laplace equation. The software (CAM200) fitted the Young–Laplace equation to the shape of the drop with all points on the drop profile. The tangent to the curve was assigned where the curve intersected the baseline. The angle between this tangent and the baseline was the contact angle. The angle between this tangent and the baseline was the contact angle within ±0.1°; each measure was repeated twice.

**TABLE I**
**Lignins Modified by the Mixture of SA with 5 g of SL and 5 ml of 1MIM as Catalyser**

| Lignin modified | SA added (% w/w) | Amount recovered (g) | Relative yield for SL (% w/w) |
|---|---|---|---|
| LM1 | 10 | 0.4450 | 8.90 |
| LM2 | 30 | 1.2595 | 25.19 |
| LM3 | 100 | 2.7737 | 55.47 |

## RESULTS AND DISCUSSION

### Isolation of SL from BL

The weight of SL obtained from 1 L of BL is 40 g/L; in our work, all the analyses were based on SL obtained at pH 4. To avoid any biological breakdown during storage, it was necessary to subject our samples to drying in a drying oven at 70°C or *in vacuo* at 40°C, and this occurred just after the last stage of washing.

### Esterification

The results of esterification are shown in Table I; we note that because the esterification was partial, the recovered quantities were lower than the starting quantity of SL, and the method of liquid–liquid separation recovered only modified lignins (LMs).[8]

### Elemental analysis

Table II presents the carbon, hydrogen, oxygen, nitrogen, and sulfur contents of SL and modified SL and the formula from phenylpropanoid (C9). LM3 had the lowest oxygen and highest carbon contents. LM1 had the highest oxygen and lowest carbon contents. Nitrogen was detected in the lignins, and it came from protein bound to the lignins. A comparison of the first and last reactions (LM3) showed that the nitrogen content of each lignin was slightly increased; this implied that the protein was chemically combined with the lignins,[11] and there was difficulty in removing it by purification with liquid–liquid extraction. The same was true for the sulfur content resulting from acid precipitation.

The elemental analysis allowed us to determine the molecular formula weight of the lignin expressed in phenylpropanoid (C9) units. In our case, the molecular formulas are presented in Table II. The

**TABLE II**
**Content of Each Sample and the Formula from Phenylpropanoid (C9) Units**

| Sample | Carbon (%) | Hydrogen (%) | Oxygen (%) | Nitrogen (%) | Sulfur (%) | $C_9$ formula ($C_9H_YO_Z$)[14,19] |
|---|---|---|---|---|---|---|
| SL | 45.5 | 5.2 | 35.25 | 1.26 | 2.29 | $C_9H_{12.34}O_{5.23}$ |
| LM1 | 41.2 | 6.7 | 38.05 | 0.85 | 0.13 | $C_9H_{17.56}O_{6.23}$ |
| LM2 | 44.3 | 5.1 | 36.55 | 1.07 | 0.18 | $C_9H_{12.43}O_{5.57}$ |
| LM3 | 57.2 | 5.3 | 23.45 | 1.57 | 0.26 | $C_9H_{10.01}O_{2.77}$ |

carbon content increased significantly for LM3 only because of the large amount of grafted anhydride. For LM1 and LM2, the amount of carbon was lower, although anhydride was clearly grafted, because the anhydride, being a strong oxidizing agent, degraded or oxidized the lignins. Thus, elemental analysis cannot be used for determining the amount of grafting.

The $^{13}$C-NMR spectra of the SL and modified SL samples (LM1, LM2, and LM3) are presented in Figure 1. Table III presents the assignments of the important signals as proposed in the literature.[10,12,13]

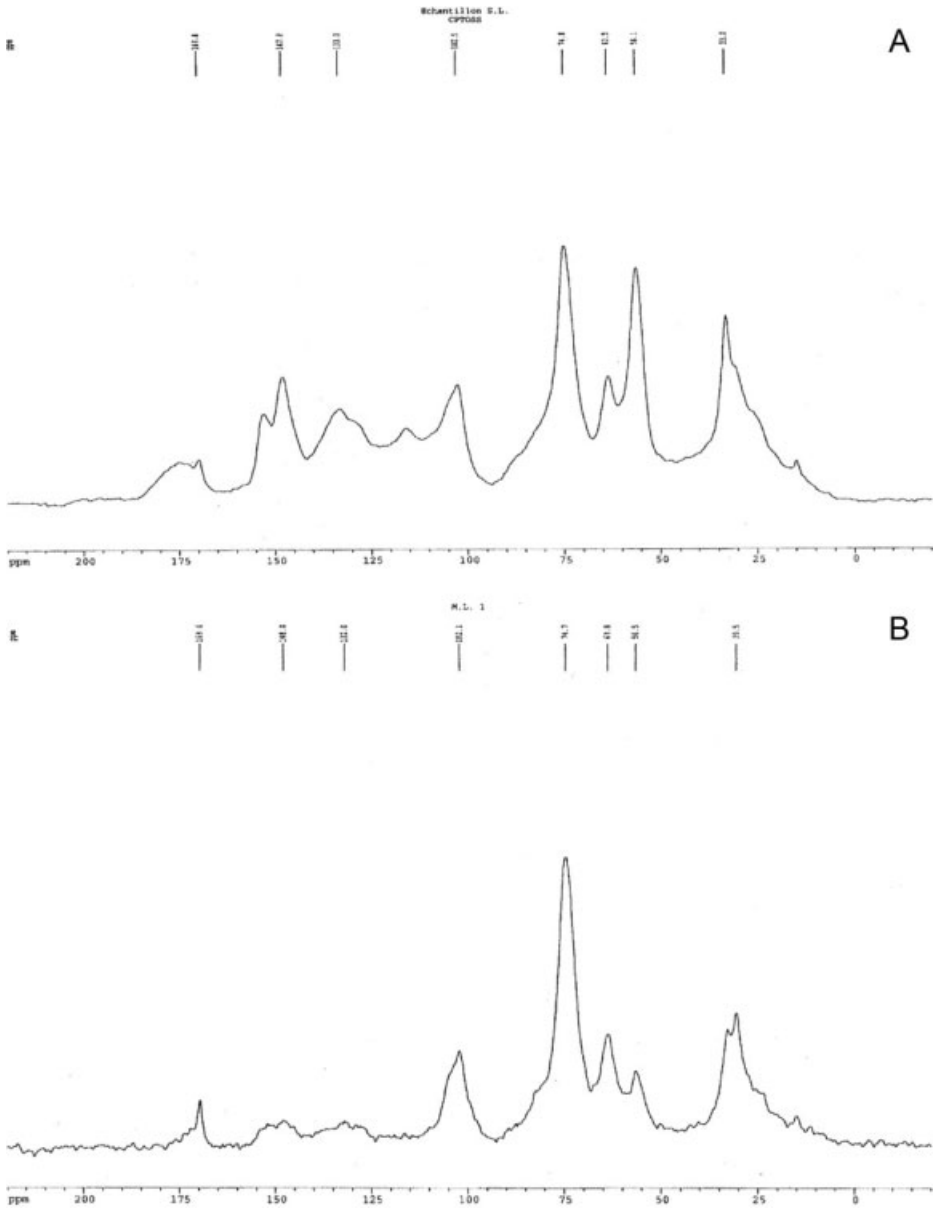


**Figure 1** A: Solid state $^{13}$C-NMR of SL; B: Solid state $^{13}$C-NMR of LM1; C: Solid state $^{13}$C-NMR of LM2; D: Solid state $^{13}$C-NMR of LM3.

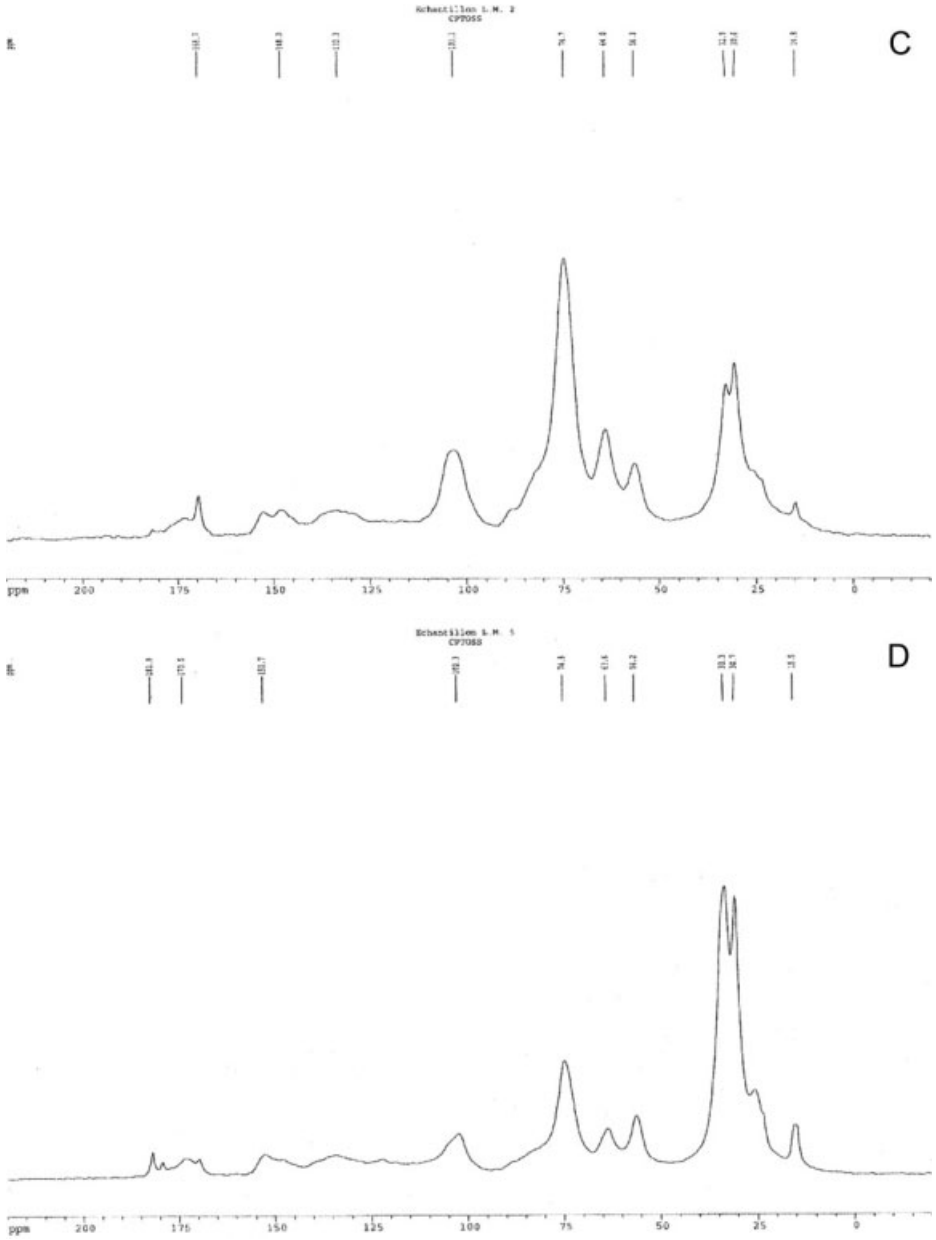


**Figure 1** (*Continued from the previous page*).

From SL to LM1, LM2, and LM3, the spectra of these products have been identified differently. This explains why SL reacted with SA.

The peak at 169.6 ppm in the spectrum of SL corresponded to a carboxylic acid moiety that was always present in the spectra of LM1 and LM2 with a light increase in the intensity, but it disappeared in the spectrum of LM3 [Fig. 1(C)]. In the latter case, there was an increase in the concentration of the stearic acid resulting from the esterification of SL by SA. This same peak disappeared and reappeared at 173 ppm (aliphatic ester C=O), and a peak appeared at 181 ppm that corresponded to a carbonyl function bonded to an aromatic cycle[14] [Fig. 1(D)].

Generally, these two peaks present in the spectra of LM3 at 181.9 and 173.5 ppm are assigned to carbonyl and carbonyl–carbon. The presence of these functional groups in lignin preparations has generally been interpreted as a sign of oxidation.[10]

The peak at 152.7 ppm corresponded to C4 in etherified G units with α-C=O. A decrease was observed in the signal at 147 ppm, which also corresponded to C4 in etherified G units. The decrease at 133 ppm corresponded to C1 in the G unit. Some authors assigned this peak to C3/C5 in the G unit, a confirmation of the change after the reaction with SA. The peak at 102.5 ppm, corresponding to C2/C6, was always present with a decrease in the

**TABLE III**
**Assignments of $^{13}$C-NMR, Solid State for SL, LM1, LM2, and LM3**

| Signal[a] | Chemical shift (ppm) | Assignment |
|---|---|---|
| 4 | 181.7 | C=O in Ar—CHO units |
| 4 | 173.5 | Aliphatic ester C=O |
| 1, 2, 3 | 169.6 | Aromatic ester or acid C=O |
| 4 | 152.7 | C4 in etherified G units with α-C=O |
| 1, 2, 3 | 147–148 | C3 in nonetherified G units |
| 1 | 132–133.5 | C1 in nonetherified G units |
| 1, 2, 3, 4 | 102–104 | C2/C6 in S units |
| 1, 2, 3, 4 | 74–75 | Cβ in β-O-4 units |
| 1, 2, 3, 4 | 63–64 | Cγ in β-5 units |
| 1, 2, 3, 4 | 55–56.6 | Aromatic $OCH_3$ in S and G units |
| 1, 2, 3, 4 | 33 | $CH_2$ |
| 1, 2, 3 | 30 | Saturated aliphatic side chain carbons |
| 3, 4 | 14–16 | β/γ-Methyl |

[a] 1 = SL; 2 = LM1; 3 = LM2; 4 = LM3.[13,15].

intensity from SL to LM1, LM2, and LM3. This confirmed that the methoxyl groups in syringyl units at positions 3 and 5 were attacked by the stearic acid consumed in the esterification reaction.

The peak at 74.7 ppm was always present with a decrease in the intensity in the spectrum of LM3. It corresponded to $C_\beta$ in the β-O-4 linkage. The stearic acid resulting from the reaction of the anhydride was at the origin of the cleavage of this linkage.[15]

The peak at 63.5 ppm corresponded to Cγ in β-5 and β-1 units. The peaks at 56.1 ppm were those of methoxyl groups in syringyl and guaiacyl units.[13,14]

In the spectrum of LM1, the peak at 56 ppm (methoxyls) was lower than those at 74.7 ($C_\beta$) and 63.5 ppm (Cγ), except in the spectrum of LM3, in which it exceeded that at 63.5 ppm. These three peaks were in regression in LM3; the stearic acid continued to hydrolyze C β-O-4 and β-5 bonds with more hydrolysis in the case of β-5. The intensity of the peaks at 30 and 33 ppm increased from LM1 to LM2 and LM3, and this confirmed that lignin esterification by SA took place because these two peaks corresponded to $CH_3$ and $CH_2$, respectively. The peak at 15 ppm, corresponding to β/γ-methyl, progressed slightly while passing from the spectrum of SL to those of LM1, LM2, and LM3.[12,13]

## IR spectroscopy

Figure 2 shows the IR spectra obtained for the SL, LM1, LM2, and LM3 samples. Table IV presents the assignments of the important signals as proposed in the literature. The clearest difference occurred in the 1590–1730-cm$^{-1}$ region, the 1400–1500-cm$^{-1}$ region, and the 1030–1200-cm$^{-1}$ region. In LM3, the peaks at 1469 cm$^{-1}$ corresponding to the CH in methyl and methylene groups[16,17] and the peak at 1462 cm$^{-1}$ corresponding to the methoxyl groups were strongly affected by the presence of carbonyl groups.

The 1589–1698-cm$^{-1}$ absorption was assigned to conjugated carbonyl groups with the aromatic ring, but the small peak at 1731 cm$^{-1}$ was assigned to unconjugated carbonyl and ester groups.[18–20]

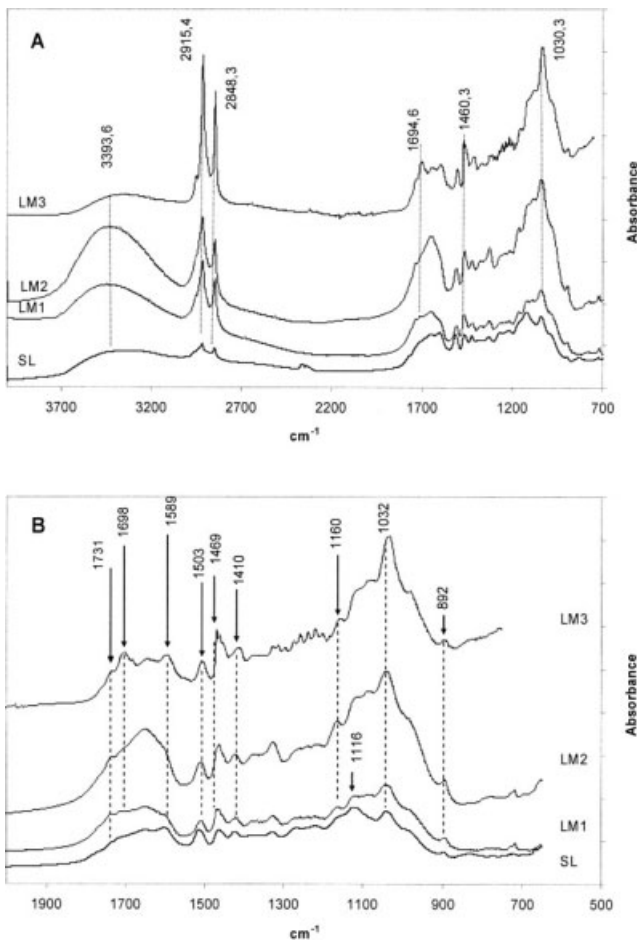


**Figure 2** FTIR spectra of SL and modified SL, A: between 4000–700 cm$^{-1}$; B: between 700–2000 cm$^{-1}$.

**TABLE IV**
**Band Assignment for the Lignin in the Infrared Region**

| $cm^{-1}$ | Assignment | References |
|---|---|---|
| 3357–3455 | Bonded O—H stretching vibration | Braun et al. (2005)[19] |
| 2916 | C—H aliphatic stretching in $CH_2$ and $CH_3$ | Terron et al. (1996)[25] |
| 2848 | C—H in O—$CH_3$ | Naveau (1968)[26] |
| 1731 | β-C=O aliphatic stretching vibration (unconjugated) | Prakash et al. (2006)[8] |
| 1698 | α-C=O aliphatic stretching vibration (conjugated) | Nadji et al. (2006)[2] |
| 1639 | C=O conjugated para-substituted aryl ketones | Nadji et al. (2006)[2] |
| 1589 | C=C vibration in aromatic ring | Terron et al. (1996)[25] |
| 1500–1520 | C=C vibration in aromatic ring | Tejado et al. (2007)[27] |
| 1454–1469 | C—H aliphatic stretching in $CH_2$ and $CH_3$ | Braun et al. (2005)[19] |
| 1406–1414 | C—H in methoxyls (G, S) and R—O—aryl ether | Jairo and Morris (1980)[20] |
| 1319–1323 | Syringyl ring breathing | Mohammad Ibrahim and Chuah (2004)[3] |
| 1275 | C—$OCH_3$ in guaiacyl rings | Mohammad Ibrahim and Chuah (2004)[3] |
| 1160 | Asymmetrical C—O—C stretching | Naveau (1968)[26] |
| 1116 | C—O stretching in secondary alcohols | Bonini et al. (2005)[18] |
| 1030 | C—O stretching in primary alcohols | Bonini et al. (2005)[18] |
| 889 | Aromatic C—H bending out of plane | Bonini et al. (2005)[18] |

The 2800–3100-$cm^{-1}$ peaks were attributed to the C—H stretching of aliphatic carbons in methyl and methylene groups. A comparison of the OH stretching region of 3600–3000 $cm^{-1}$ for each sample indicated enhanced hydroxyl formation. This may have been due to hydrogen-atom transfer and phenol formation from the phenoxy radical produced from the initial β-O-4 ether bond homolysis.[19]

The strong band at 3490 $cm^{-1}$ was characteristic of OH group, aliphatic, and phenolic compounds. The band at 1323 $cm^{-1}$ was assigned to the bending vibration in the phenolic OH group, whereas the band at 1030 $cm^{-1}$ was characteristic of primary alcohol.[21] The clear shoulder at 2848–2915 $cm^{-1}$ and the band at 1469 $cm^{-1}$ were assigned to CH stretching of methyl and methylene groups.

The band at 1116 $cm^{-1}$ was due to ether stretching. The band at 892 $cm^{-1}$ was assigned to C—H deformation and ring vibration.

The small band at 716 $cm^{-1}$, which was present in the spectra of all lignins precipitated from sulfuric acid, was due to C—S stretching.[3] The band at 1160 $cm^{-1}$ corresponded to C—O—C stretching,[22] whereas the IR spectrum showed absorption at 1123 $cm^{-1}$ corresponding to C—H bending in syringyl units and C—O stretching in secondary alcohol and absorption at 1030 $cm^{-1}$ corresponding to the C—H bending in plane in guaiacyl units and C—O stretching in primary alcohols.[18]

Bands at 1330, 1220, and 1115–1120 $cm^{-1}$ corresponded to syringyl units, whereas small bands at 1275 and 1160 $cm^{-1}$ and high bands at 1032 $cm^{-1}$ were assigned to guaiacyl units of lignin molecules.[23] In our product, the stearic acid resulting from SA was an agent for chemical cleavage and may have changed the syringyl form to the guaiacyl form.[3]

The IR spectra of the lignins showed the same peak intensity at 1503 $cm^{-1}$ due to the aromatic units in lignin. Therefore, the peak at 1503 $cm^{-1}$ was used as a constant standard to derive the relative absorbance of all residues and extractives. The peak shown around 1698 $cm^{-1}$ was derived from the C=O stretching vibration of the conjugated carbonyl compound.

A small peak was observed around 1635 $cm^{-1}$ for the LM3 sample, indicating that carbonyl compounds were free or present as low-molecular-weight compounds and were easily extracted with methanol.[20]

The only IR bands that could inform us well about the rate of esterification of our samples without any interferences with other bands were the peaks of CH at 2915 and 2848 $cm^{-1}$ (Fig. 2).

We can say that esterification is always partial and never complete because O—H bands are always present. The remaining peaks due to O—H slip toward the higher frequency zone, and this means that LM has fewer hydrogen bonds; this results in higher expandability and lower density.[8] This assumption was confirmed at the time of the weighing of the products.

When comparing the spectra of all lignins, we noticed the variation of the band at 3490 $cm^{-1}$, which is characteristic of hydroxyl groups. Also, the increase in the intensity of the bands at 2915–2848 $cm^{-1}$ was due to the presence of alkyl chains and the presence of new bands around 1640–1730 $cm^{-1}$, which were characteristic for carbonyl groups.

The objective of our work consisted of increasing the hydrophobic character of lignin so that it could play the role of an external lubricant for an extrusion machine.

## TGA

In Figure 3(A), dynamic TGA curves in an air environment for each sample exhibit two mass-loss steps. The initial mass loss below 105°C [Fig. 3(B)] was due to the gradual evaporation of absorbed moisture. The second mass loss from approximately 150 to 325°C was due to the decomposition of the major constituents of the lignin and the LMs. Natural fillers are composed of cellulose, hemicellulose, and lignin. Our results were in good agreement with the theoretical stoichiometric values, which are based on the fact that lignocellulosic materials are chemically active and decompose thermochemically between 150 and 500°C: hemicellulose mainly between 150 and 350°C, cellulose between 275 and 350°C, and lignin between 250 and 500°C.[24]

At 200°C, LM3 was the most stable sample, but at 220°C, LM2 was the most stable. In our work, we were interested in the behavior under 220°C because the maximum thermal composite working temperature used was 160°C.

Figure 3(B) shows isothermal TGA curves, also in an air environment. LM2 showed higher stability for all the treatments. However, LM3 was more stable than LM1 for only 450 s (7.5mn). After this time, LM3 was less stable than LM1.

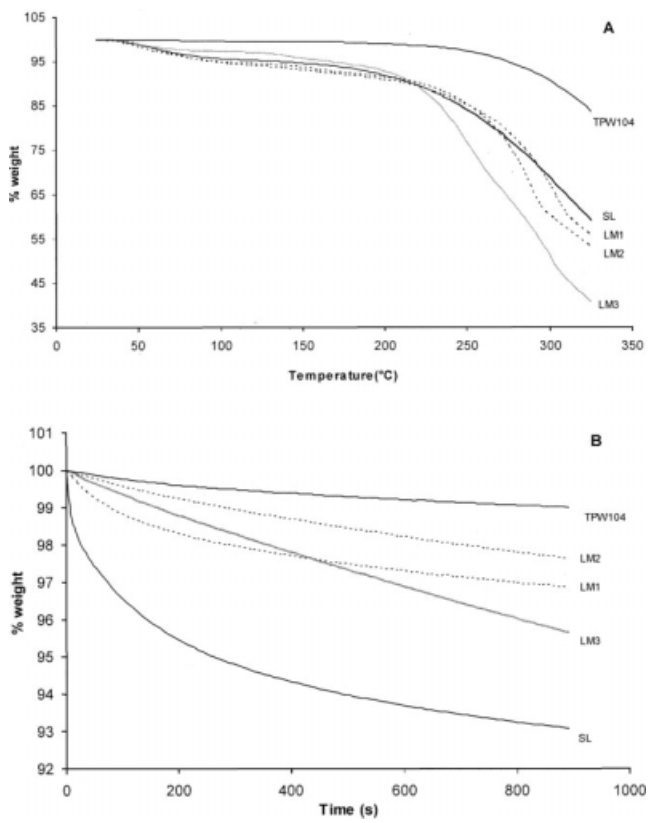


**Figure 3** Behaviour of lignins in: A: Dynamic mode at 10°C/mn.; B: Isothermal mode at 180°C.

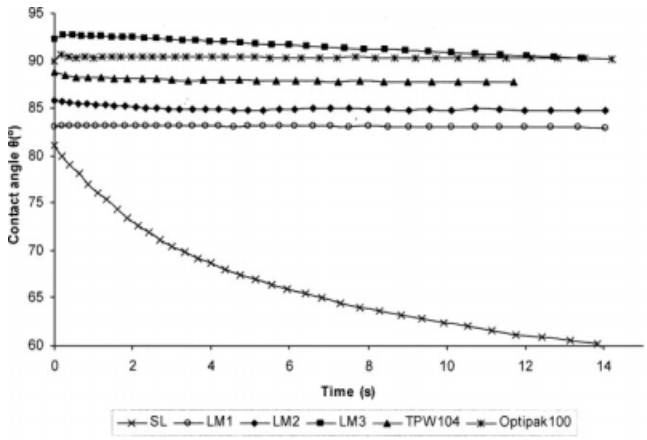


**Figure 4** Contact angle of SL, SL modified & industrial lubricants (Tpw104 & Optipak100).

## Contact angle

From the graph in Figure 4, we can say that the LMs fulfilled our aim, which was to increase the hydrophobicity of SL in the hope of replacing industrial lubricants such as TPW104 and Optipac100.

The hydrophobicity, as characterized by the contact angle with water, increased along with the percentage of reacted SA on the lignin. Indeed, the contact angle of LM3 exceeded that of TPW104 and coincided with that of Optipak 100 (after a 12-s contact time; Fig. 4).

The average contact angles of the water with the treated lignins are shown in Figure 4.

However, there is a clear trend of the contact angle increasing with the weight of SA increasing in the mixture. This could be expected because the grafting of SA chains ($C_{18}$—) onto lignin is known to result in a more hydrophobic material.[16] The contact angle of LM3 exceeded those of both industrial products (Fig. 4).

## CONCLUSIONS

The objectives of our work were reached: partial esterification was confirmed by IR and $^{13}$C-NMR methods. This was evidenced by FTIR through the reduction in the bands of peaks corresponding to —OH at 3400 cm$^{-1}$ and the increases in the peaks at 2915 and 2848 cm$^{-1}$ as well as the appearance of the peaks at 1698 and 1731 cm$^{-1}$, which were characteristic of conjugated carbonyls and esters and unconjugated carbonyls, respectively. Solid-state $^{13}$C-NMR clearly showed aliphatic lengthening of the esterified sites, as shown in the peaks at 25 ppm in the spectra of the LMs.

This esterification remarkably increased the hydrophobicity of the LMs. The hydrophobicity of LM3 exceeded that of TPW104, which is already used as

an industrial external lubricant. Thus, partial esterification concretized the awaited results: an increase in the hydrophobic SL byproduct for its development as a lubricant in thermoplastic processing.

The treatment of SL in the presence of SA and 1MIM as a catalyst appears to be an interesting environmentally benign method for the operating environment in synthesis and for modifying lignin properties to achieve less hydrophilic and thermally more stable products.

These results are very encouraging because they point to a possible promotion to an industrial spin-off. This will be the object of proposals for possible applications.

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