Mechanical Potential of Adhesives Elaborated with the Gramineae Stem Lignin

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Abstract: The aim of this work is to valorize local materials and to replace synthetic resins in the wood industry with biodegradable resins made from renewable resources such as the dry stems of herbaceous plants. Klason extracted the gramineae stem's lignins of Andropogon gayanus and Sorghum bicolor and then Soda methods then characterized using attenuated total reflectance Fourier transform spectra in the 4000 and 400 cm^{-1} range. Their decompositions were studied using Thermogravimetric Analysis. Their yield from lignins extractions are respectively 19.26% and 24.9%. Guaiacyl, Syringyl, p-hydroxyphenylpropane, phenols and secondary alcohols are present in these lignins. The gel times of their adhesive using paraformaldehyde as hardener decreases as the pH increases. At pH=12, these gel time values are, respectively 6.6 and 7 minutes. These lignins begin to decompose at 291°C. The Modulus of elasticity was studied by thermomechanical analysis and wood particleboards were prepared bonded with these resins. The stiffness of Andropogon gayanus lignin resin is better than that of Sorghum bicolor (4339.08 > 3767.87MPa). The Internal Bond strength of Particleboards manufactured with 10% of total adhesive solids on dry wood particles are respectively 0.37 and 0.41 MPa. These two lignins are good for wood adhesives. The average MOR and MOE values for the manufactured Andropogon gayanus and Sorghum Bicolor particleboards are respectively 14.51MPa and 1850.6MPa and 16.5MPa and 2053.4MPa. The manufactured particleboards have a low resistance to humidity and that they can only be used in a dry environment.

Keywords: Andropogon Gayanus, Sorghum Bicolor, Lignin, Extract, Adhesives, Thermomechanical Analysis, Particleboards, Mechanical Characteristics

1. Introduction

In recent decades, the problem of environmental pollution has become a major concern for the habitants of the planet Earth because it generates several problems such as the rise of the average temperature on the surface of the globe considered as the first consequence of the massive emissions of gas greenhouse effects; the destruction of the ozone layer or damage to the atmosphere; the multiplication of diseases; Soil and water pollution.

Faced with the growing threat of this environmental scourge, the issue of the sustainable development of our society is paramount. In view of the indispensable contribution of human

activity in the protection of environment, technical solutions have been developed. Thus, around the year 2000, biodegradables resins used in the wood industry were introduced [1-3]. It is in the same idea that many works have been done, particularly the extraction and characterization of lignin from different biomass resources [4]; a comparative study of organosolv lignins from wheat straw [5] and a method for the analysis of cellulose microfibrils in biorefinery [6]. Many lignins have been used in the development of adhesives, such as miscanthus lignin [7], wheat straw [5] and sugar maple [8]. Miscanthus and wheat straw lignin were extracted by the organosolv method [5, 7, 9], while sugar maple lignin was extracted by Klason method [8, 10].

It is economically significant, especially for developing African nations, to upgrade native materials and replace all synthetic resins used in the wood industry with biodegradable resins manufactured from renewable resources like wood, grass, and bone. Reducing the impact of climate change in some regions of this continent (Sub-Saharan Africa) may be of significant significance.

It is in this context that this paper responds to this concern by studying two Gramineae lignins particularly those of Sorghum bicolor and Andropogon gayanus stems of the Poaceae family from the Far North Region of Cameroon.

Andropogon is a building material used in sub-Saharan Africa, particularly in the northern portion of Cameroon. While Sorghum bicolor stems are used in the construction of huts, fences, hangars, and roofs, these more or less leafless stems are woven into mats known as "secco" and sold in peri-urban marketplaces. They are also used in the manufacture of germ seed.

Despite the numerous advantages of Andropogon gayanus and Sorghum bicolor stems, these gramineae are rarely handled effectively. They are waste that is frequently dumped into the wild and occasionally burned and used as firewood in homes in Northern Cameroon. In particular, the Andropogon frequently causes bush fires, which is a source of environmental dangers. Since resins and biodegradable composite materials will be produced locally, the extraction of their lignin would represent a significant economic opportunity for these African nations [2, 11].

The aims of this article are to extract the lignins of Andropogon gayanus and Sorghum bicolor stems, determine their physicochemical characteristics using attenuated total reflectance Fourier transform (ATR- FTIR) spectroscopy and phytochemical tests, determine their potential to develop adhesives and to study the decompositions of these lignins using thermogravimetric analysis.

2. Materials and Methods

2.1. Samples Preparation

The Sorghum bicolor stems are recovered from the fields two weeks after harvesting the cobs, while the Andropogon gayanus straws are harvested when they look yellowish. These samples are first dried in the open air for two (02) weeks and

then crushed into very small particles. The crushed products are weighed, packed and labeled per 140-gram packet.

2.2. Gramineae Lignin Soda Extraction

In a 2 L reactor, 140 g of crushed dry stems of Andropogon or Sorghum are cooked in an oil bath with about 980 ml of 2M NaOH at a temperature of 170°C for 3 hours. After cooling, the mixture is removed from the bottom of the reactor and filtered in order to separate the fibrous material from the liquid (black liquor). To the black liquor, dilute sulfuric acid at 2.5M is added slowly with stirring at a pH of 5.5 to precipitate the lignin which will be recovered after filtering under vacuum. The lignin obtained is washed several times with hot water at 60°C. and dried at room temperature for 24 hours then placed in an oven at 45°C. for a period of 48 hours and conditioned.

2.3. Quantity of Lignins

1g of each crushed product was mixed with 15 ml of sulfuric acid (72%) in 1-liter flask, and stirred for 2 hours. The mixture was diluted by adding 560 ml of distilled water, refuxed for 4 hours, and allowed to settle for 4 hours. It is later filtered and thoroughly washed in warm water at 60°C to eliminate the trace of acid. The prepared lignin (insoluble Klason lignin) was dried in an oven at 105°C for 24 hours [12]. The formula (1) below makes it possible to obtain the level of Klason lignin (T_1).

$$T_l = \frac{a}{E} \times 100 \qquad (1)$$

Where (a), (E) represent respectively the weight of the lignin and sample

The lignin retained corresponds to the average of five samples.

2.4. Gramineae Lignins Characterization Using Attenuated Total Reflectance Fourier Transform (Atr-Ftir)

Powdered lignin's were characterized using the Perkin Elmer Frontier ATR-FT device coupled with a diamond crystal. About 2 mg grinded powder was placed on the diamond crystal and the contact was obtained by applying a manual force of about 150 N to the sample. Each spectrum was obtained with 32 scans with the resolution of 4 cm⁻¹ for 4000 and 400 cm⁻¹ wavelengths [1, 13].

2.5. Thermogravimetric Analysis (Tga)

About 10mg of each cured samples of lignins was placed in an aluminum crucible at a temperature rise of 20°C to 800°C at a rate of rise of 5°C/min, and an isotherm at 800°C. for 30 min under inert gas (argon). The NETZSCH STA 449F3 was used for TGA analyzes. For each formulation the weight gain (TG curves) and the rate of mass loss (DTG curves) were determined [11].

2.6. Adhesives Development

An aqueous solution containing 35% lignin extract and 5% paraformaldehyde powder is introduced into a beaker. The

entire sticky mixture is stirred using a magnetic stirrer for 10 minutes, the pH of the whole is adjusted to 10 by adding sodium hydroxide (NaOH). The process is stopped when the viscosity reaches 750 mPas using the Brookfield RV viscometer. Pin Nr, 27 to 25°C. These adhesives have been used to produce particle boards.

2.7. Gel Time

About 10 g of adhesive was introduced into a test tube and placed in a water bath boiling at 100°C. Gel time was taken since the moment the tube was introduced in water until reaching the gel point stirring with a wire spring. Sodium hydroxide solution ($NaOH$) was used to adjust different pH of the mixture (pH= 5; pH=8; pH= 10; pH = 12). The pH retained to develop the resin was pH = 10 [1]. Two resins formulations were developed with Andropogon gayanus lignin (LPA4055) and bicolor Sorghum lignin (LPS4055).

2.8. Thermomechanical Analysis of the Different Resins Developed

22 mg of each resin was put on beech wood plates (2 plates) of dimensions $17 \times 5 \times 1.1$ mm and then, the beech wood were bonded and placed in the furnace of the Thermomechanical Analyzer METTLER TOLEDO TMA 40 linked to a processor TC11 and a computer to register and interpret graphically the behavior of the resin to undergo tests. Samples were tested in bending in non-isothermal mode between 25 °C and 250 °C at a heating rate of 10°C /min. Deflection curves that allow MOE determination were obtained by the three-point bending TMA mode. The MOE of the wood joints bonded with different resin systems gave a good indication of the final strength of the adhesive system tested [1].

2.9. Particleboards Manufacture and Testing

Two particleboards of $350 \times 300 \times 14$ mm^3 dimension were prepared using particles of sorghum bicolor and Andropogon gayanus (moisture content = 2%) at 28 kg/cm^2 maximum pressure and 190°C–200°C press temperature during 7.5min. The total adhesive resin solids loaded on dry wood was 10% w/w of the total mix of different lignin. The particleboards were tested firstly for dry internal bond (IB) strength in accordance with the standard EN312. And secondary the thickness swelling ratio (TS) and the water absorption rate (TA) are determined according to standard NF-EN 317 [14] on 10 test specimens of dimensions 50mm×50mm×14mm. Finaly the Modulus of

elasticity (MOE) and bending strength (MOR) were tested according to European Norm EN 310 [15] using an INSTRON 4467 universal testing machine. Those characteristics were calculated using the formulas below, respectively:

$$\sigma_{IB} = \frac{F}{s} \ (MPa) \tag{2}$$

F: breaking strength in Newton
S: area solicited in millimeters

$$TS = \frac{e_f - e_i}{e_i} \times 100 \tag{3}$$

with

e_i : thickness of the specimen before immersion in millimeters;
e_f : thickness of the specimen after immersion in millimeters.

$$TA = \frac{m_f - m_i}{m_i} \times 100 \tag{4}$$

with

m_i: initial mass of the specimen before quenching in gram;
m_f: final mass of the test piece after quenching in gram.

$$MOE = \frac{L^3}{4 \times b \times e^3} \times \frac{F_2 - F_1}{a_2 - a_1} \ (MPa) \tag{5}$$

$$MOR = \frac{3 \times L \times F_{Rupture}}{2 \times b \times e^2} \ (MPa) \tag{6}$$

with

L: distance between centers of supports, in millimeters;
b: width of the test specimen, in millimeters;
e: thickness of the test specimen, in millimeters;
Fi: strength causing a displacement ai, i ¼ < 1, 2 >;
ai: displacement;
$F_{rupture}$: breaking strength.

3. Results and Discussion

3.1. Lignins Extracts

Table 1 shows the sample E1 (Sorghum bicolor) and the sample E2 (Andropogon gayanus) content. According to these results, the rigidity of E1 is greater than that of E2. This is justified and confirmed by the Internal Bond (IB) values of the particles boards manufactured with E1 and E2 adhesives. These values are 0.41 MPa (E1) and 0.37 MPa (E2).

Table 1. Klason and Soda lignin content of the different samples.

Name	Samples	Klason lignin yeild		Soda lignin yeild	
		mass of the sample (g)	Klason Lignin %	mass of the sample (g)	Soda Lignin %
E1	Sorghum bicolor	1	24.9	140	23.57
E2	Andropogon gayanus	1	19. 26	140	19.98

3.2. Fourier Transform Infrared Spectroscopy (FT-IR) of the Extracted Lignin

The analysis of LA and LS spectra presented in Figures 1

and 2 revealed tree units and various functional groups which are typical for lignins, namely G (gaiacyl), S (syringyl) and H (p-hydroxyphenylpropane) as well as those of the functional groups attributable to phenols and secondary alcohol *(Table 2)*.

The hydroxyl groups in the phenolic and aliphatic structures are attributed to the absorption band of 3500-3100 cm⁻¹ [16, 17]. These hydroxyl groups can be attributed to the basic elements of lignin G, H and S. The region between 3000-2800 cm⁻¹ correspond to the CH elongations of the methyl and methylene groups, so the peaks 2891 cm⁻¹ and 2916 cm⁻¹ correspond to the CH vibration of the methoxyl groups [17]. The aromatic skeleton vibration bands for all lignins regardless of their origin are observed at 1599, 1596, 1513 and 1509 cm⁻¹. Peaks 1379 and 1342 cm⁻¹ are associated to aliphatic C-H stretching in CH₃ [18]. The aromatic skeleton vibration bands for all lignins regardless of their origin are observed at 1599, 1596, 1513 and 1509 cm⁻¹. Peaks 1379 and 1342 cm⁻¹ are attributed to aliphatic C-H stretching in CH₃ [18]. In addition, the bands around 1200 and 844 cm⁻¹ peaks 1155, 1075, 1076, 1034, 1033) reflect the deformations and stretchings of the C-H and C = O aliphatic esters and alcohols attributed to lignin HGS. The 1155 cm⁻¹ peak indicates the presence of G, H and S units [5, 19, 20]. There is a similarity between these two lignins, as shown by their spectra, particularly in the fingerprint (1800 - 500 cm-1) (Figure 3). The LS bands in this area (1800 - 500 cm⁻¹) are more intense than those of Andropogon lignin, thus confirming the higher percentage of Sorghum lignin's (127.13% > 9.26%).
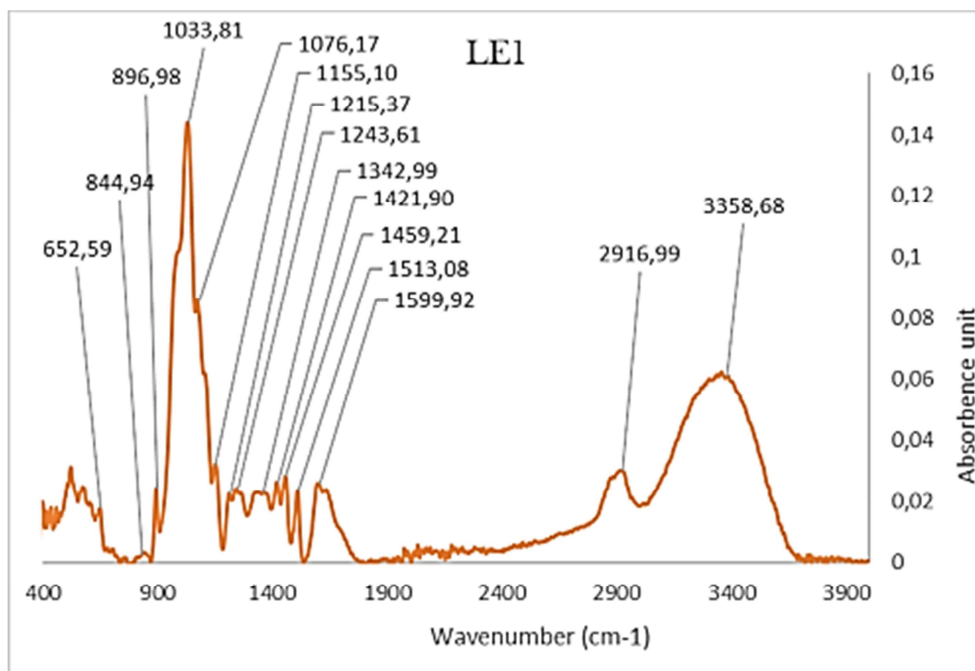

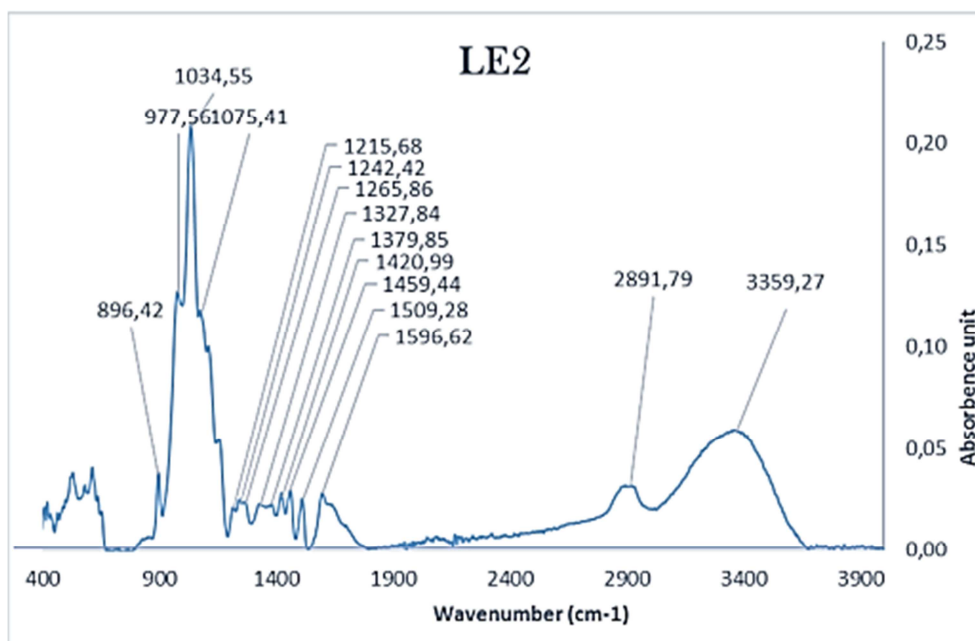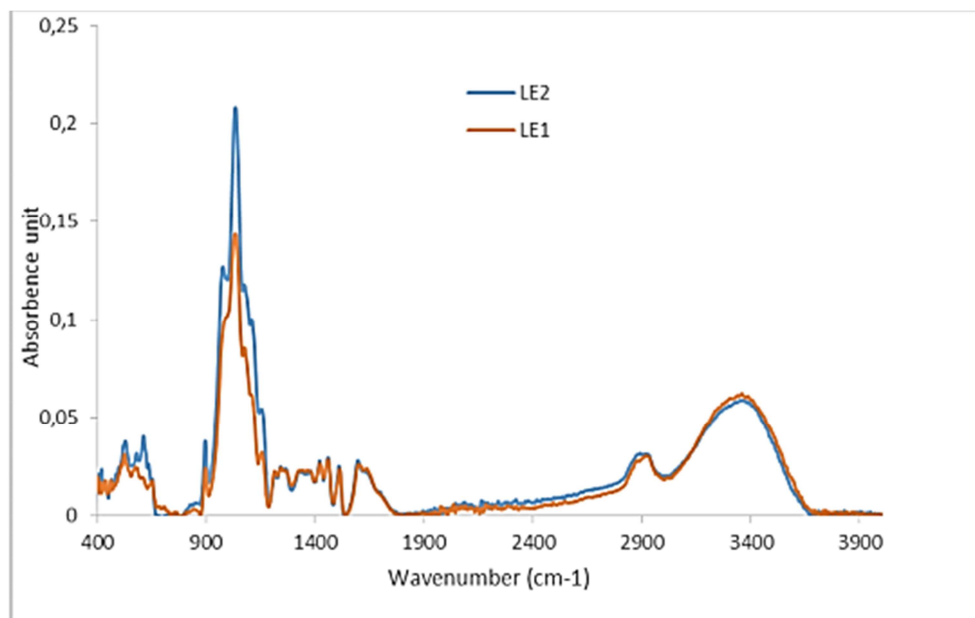**Figure 1.** *Infrared Spectrum of Sorghum Lignin (LE1).*

Figure 2. *Infrared Spectrum of Andropogon Lignin (LE2).*

Table 2. Assignments of FT-IR spectra of lignins from Andropogon and Sorghum.

Band of lignin Andropogon (cm⁻¹)	Band of Lignin Sorghum (cm⁻¹)	Assignments
3359	3358	O–H stretching
2891	2916	Aliphatic, CH stretching of methyl, methylene
1596	1599	Aromatic skeletal vibration and C = O stretching
1509	1513	Aromatic skeletal vibration
1459	1459	C-H deformation (methyl and methylene)
1420	1421	Aromatic vibration
1379	-	Aliphatic C–H stretching in CH_3
1327	1342	C-O of syringyl (S) ring
1265	1243	C-O of guaiacyl (G) ring
1215	1215	C- C + C-O stretch
-	1155	Guaiacyl C-H and syringyl C-H
1075	1076	C-O deformation of secondary alcohols and aliphatic ethers
1034	1033	Aromatic CH in plane deformation G + S
	844	syringyl (S) vibration

Figure 3. Superposition of infrared spectra of Andropogon (LE2) lignins in Sorghum (LE1).

3.3. Thermogravimetric Analysis (TGA) of Andropogon and Sorghum Lignin

As shown in the TGA and DSC curves of figures 4 and 5, the decomposition of these lignins covered temperature ranges from 200 to 700°C. Three main regions of mass loss are shown: The first weight loss step which occurs between 25–80°C (for LS) and 25–74°C (for LA) is due to the evaporation of absorbed water and some trace formation of volatile compounds such as CO_2 and CO released by the lignin. The second region appeared around 225–468°C for LS and 225–383°C for LA, their peak at 291°C is principally due to the degradation of the carbohydrate components of the lignins, which were converted to volatile gases including CO, CO_2 and CH_4. At the peak 468°C (for LS) and 383°C (for LA), the degradation volatile products derived from lignin such as phenolics, alcohols, aldehyde acids with the formation of gaseous products (CO, CO_2 and CH_4). The third region of mass loss of LA and LS occurred respectively around 381°C-700°C and 400°C-700°C. This third region is due to the decomposition of rigid segments in the lignin with a release of CO, CO_2, CH_4 and carbon formation. The decompositions, which occurs at temperatures greater than 500°C, are associated with aromatic rings [17]. It should be noted that the decomposition was not total, at 700°C, about 5% of nonvolatile lignin still remained in solid form and were not completely burned.

The TGA curve also demonstrates that materials only start to degrade thermally after absorbing a certain amount of heat energy. By triggering molecular chain rupture, heat starts the processes of degradation and breaks down the structure. The TGA data unambiguously demonstrate that lignin begins to break down at about 291°C, hence when making lignin-based blends, the working temperature shouldn't go above 200°C to 300°C.
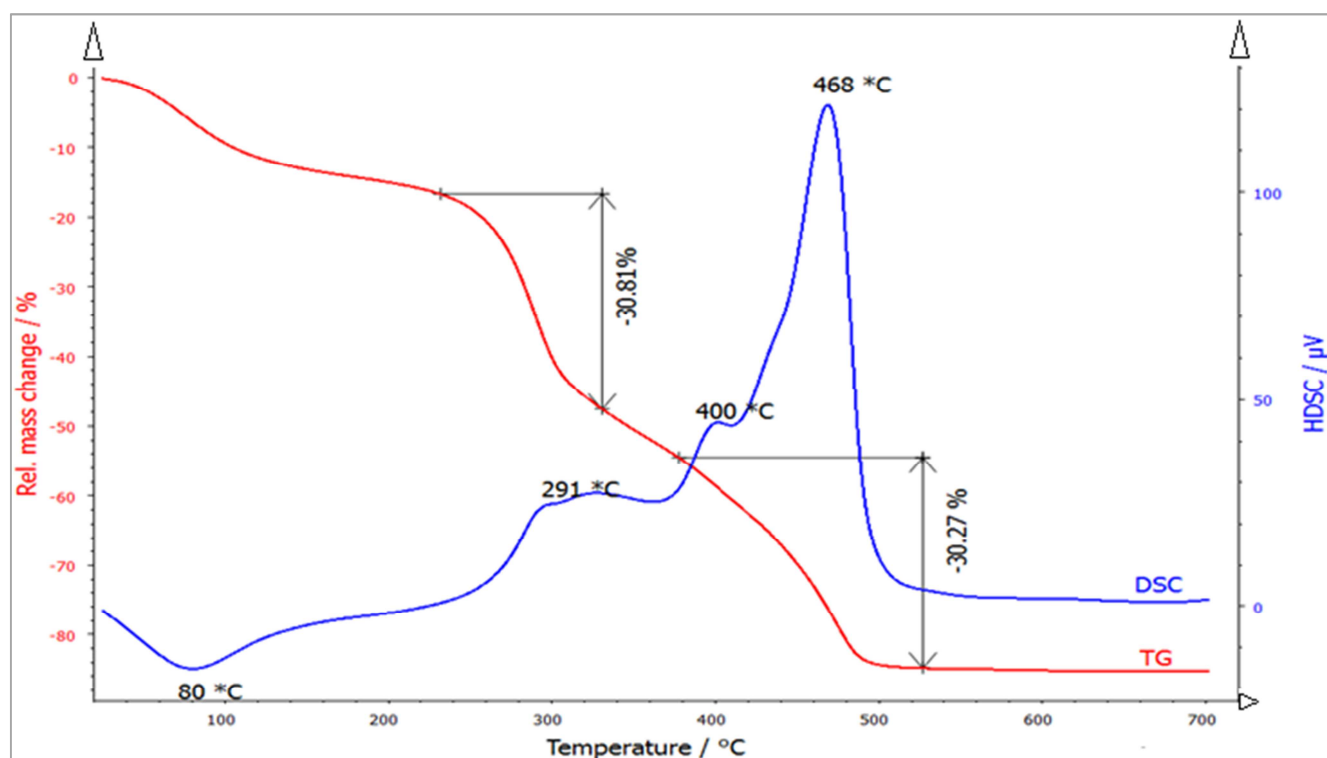
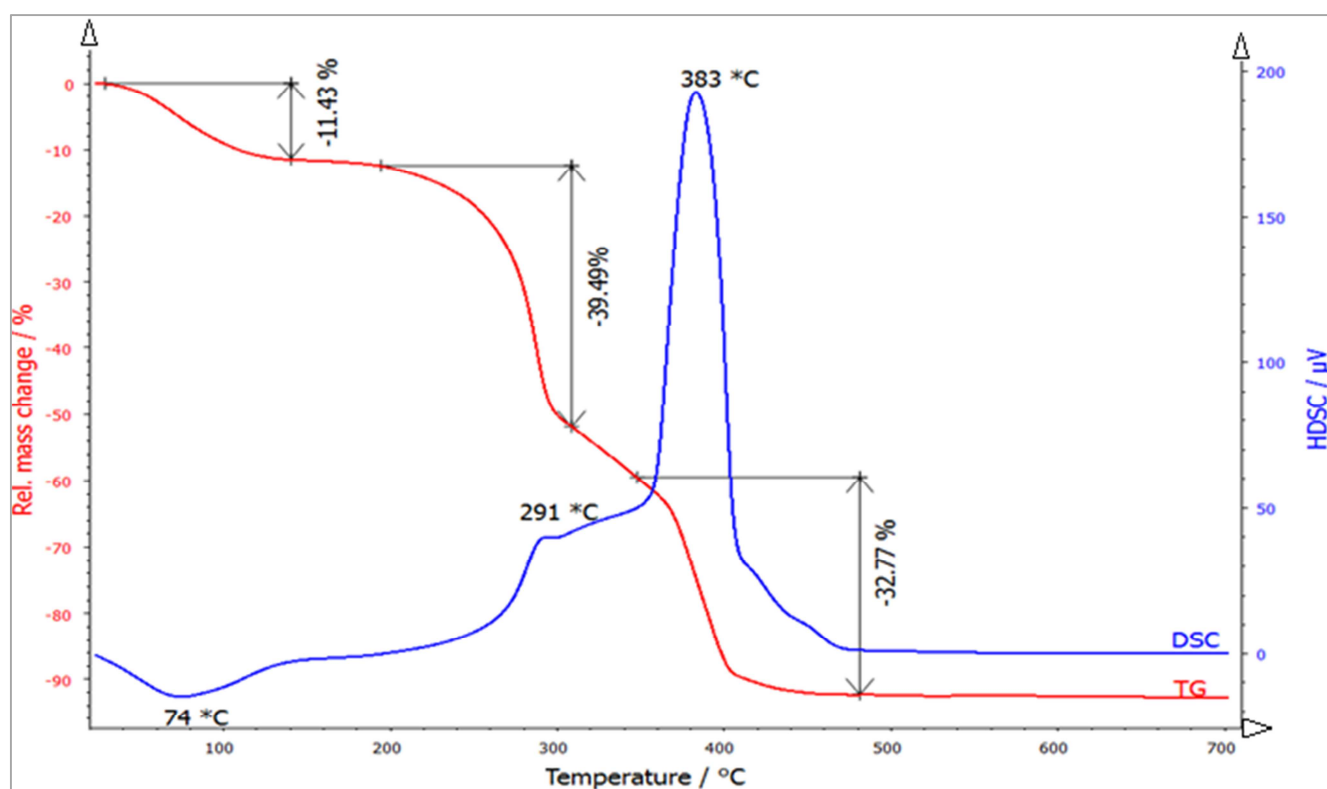**Figure 4.** *TGA and DTG curves of the Sorghum bicolor lignin (LS).*

Figure 5. *TGA and DTG curves of the Andropogon gayanus lignin (LA).*

3.4. Gel Time

Effect of pH on gel time (LPA4060 and LPS4060)
The study of the gel time of formulations (LPA4060 and LPS4060) as a function of pH is represented in Figure 6 below:
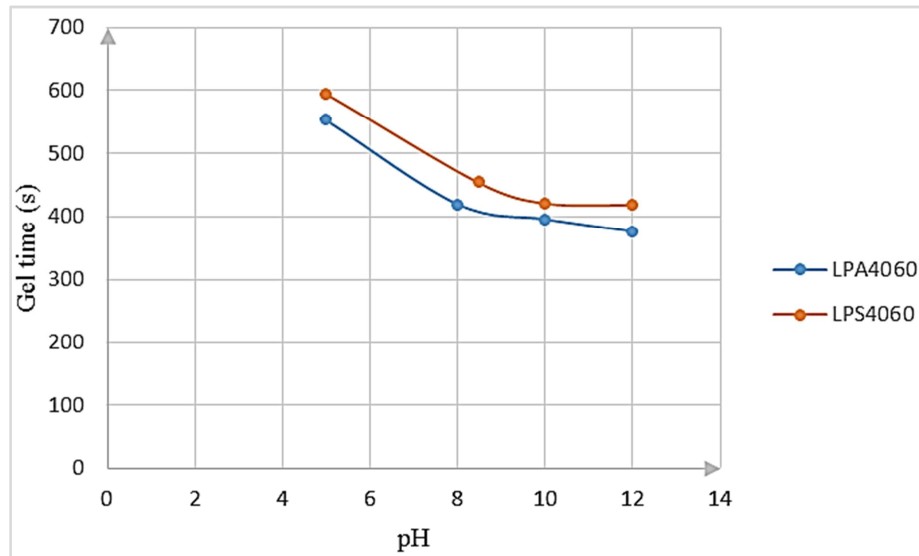
Figure 6. Gel time of formulations (LPA4060 and LPS4060) as a function of the pH.

According to Figure 6 above, the LPS4060 series represents the variation of the gel time of the bicolor Sorghum adhesive as a function of pH; the LPA4060 series represents the variation of gel time of Andropogon gayanus adhesive as a function of pH. The gel time of these formulations decreases as the pH increases. At pH=12, these gel time values are respectively 418 and 377 minutes. The gel time of formulation LPS4060 resin at pH = 12 is rather longer than the formulation LPA4060 resin. The gel times of the Andropogon lignin and Sorghum lignin resins corresponding to pH = 12 were adopted for the manufacture of particleboards.

3.5. Thermomechanical Analysis and Rigidity of Resins

The Figure 7 shows the thermomechanical analysis curves of Andropogon gayanus and Sorghum bicolor lignin resins using paraformaldehyde as hardener. The stiffness of Andropogon gayanus lignin resin is better than that of Sorghum bicolor (4339.08 >3767.87MPa). The MOE starts to decrease after 150°C due to the start of the degradation of resin constituents.
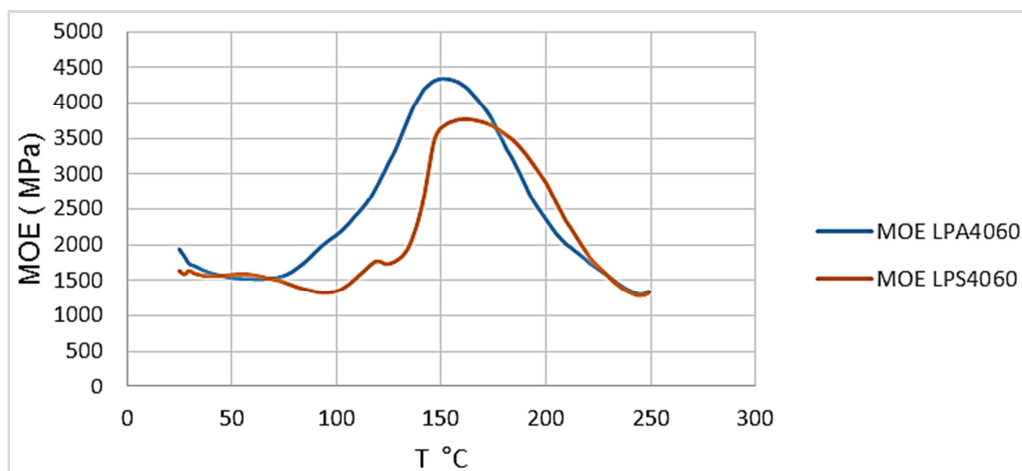

Figure 7. Thermomechanical analysis of Andropogon gayanus and Sorghum bicolor lignin adhesive.

3.6. Characterization of Manufactured Particleboards

Particleboards manufactured with the two formulations LPS4060 and LPA4060 containing paraformaldehyde powder as hardener had good IB strength. Results satisfied the dry IB strength requirement of the standard NF EN 312-2 (1996). Dry IB strength of particleboards manufactured with particles of Andropogon gayanus and the LPA4060 formulation was 0.37

MPa *(Figure 8)*, those manufactured with particles of Sorghum bicolor, and the LPS4060 formulation was 0.41 MPa *(Figure 9)*. These two IB values are higher than the standard Norm NF EN 312-2 (1996) (0.37>035 MPa and 0.41>0.35 MPa). These results are contrary to what we expected because the lignin resin of Andropogon was more rigid than that of Sorghum. This could be due to the quality of Andropogon gayanus particles. Although these results are above the norm NF EN 312-2, they remain below those

obtained by El-Mansouri (2006) [21] for wheat straw lignin. with a glyoxalated lignin /pMDI 60/40 formulation. Table 3 below illustrates the average values of the results of the determination of the Modulus of Elasticity (MOE) and the bending strength (MOR) of Andropogon gayanus (PLPA4060) and Sorghum Bicolor particleboards (PLPS4060) and their thickness in Swelling. The average MOR and MOE values for the manufactured Andropogon gayanus particleboards are 14.51MPa and 1850.6MPa. They are lower than those of Sorghum Bicolor16.5MPa and 2053.4MPa particleboard. These results are contrary to what we expected because the lignin resin of Andropogon was more rigid than that of Sorghum. This could be due to the quality of the reinforcement. According to EN 310, 11.5 and 13.0 MPa are the minimum requirements for MOR of particleboard for general purposes and interior fittings (including furniture), respectively, while the minimum MOE for interior fittings is 1600MPa. These performances confrmed that ours particleboards meets the requirements of standard NF-EN 310.

These results table 3 show that the thickness swelling rate and the absorption rate for 2 hours and 24 hours of the Andropogon particleboard are higher than those of Sorghum bicolor, in other words, the PLPS4060 particleboard have good resistance to humidity by compared to PLPA4060 particleboard. The greater the density of the material, the less the swelling in thickness. According to the European standard EN317, particleboard must have a maximum TS value of 23% for immersions of 2 and 24 hours. In general, the elaborate panels only resist a few minutes in boiling water (about 20 minutes), this deterioration is due either to the size of the particles, to the quality of the resin or to the hydrolysis of the chemical bonds which are responsible for resin cross-linking. This can also be explained by the fact that lignocellulosic materials are hygroscopic and contain high number of methoxyl and hydroxyl (O-H) groups that could absorb water from the surrounding atmosphere easily. This very hydrophilic nature of these panels could also be explained by the presence of the marrow of these rods in the various reinforcements. These high results compared to the requirements of the European standard EN317 (23% swelling in thickness), show that the manufactured particleboards have a low resistance to humidity and that they can only be used in a dry environment.

Table 3. *Bending strength (MOR) and Modulus of Elasticity (MOE) of Andropogon gayanus and Sorghum Bicolor particleboard and their thickness in Swelling.*

Type of particleboard	Thickness (mm)	MOR (MPa)	MOE (MPa)	Thickness in Swelling (%) 2h-24h
PLPA4060	14	14.51	1850.6	64.68-72.92
PLPS4060	14	16.5	2053.4	33.32-49.21

Figure 8. *Particleboard of Andropogon gayanus stems.*

Figure 9. *Particleboard of Sorghum bicolor stems.*

4. Conclusion

The LA and LS contain Gaiacyl (G), Syringyl (S) and p-hydroxyphenylpropane, phenols and secondary alcohols. They are very good for wood adhesive because IB for their particleboards are respectively 0.37and 0.41 MPa, their gel times at pH = 12 are 377 and 418 seconds, they begin to decompose at 291°C. The stiffness of Andropogon gayanus lignin resin is better than that of Sorghum bicolor. The average MOR and MOE values for the manufactured Andropogon gayanus particleboards are 14.51MPa and 1850.6MPa. They are lower than those of Sorghum Bicolor16.5MPa and 2053.4MPa particleboard. The manufactured particleboards have a low resistance to humidity and that they can only be used in a dry environment. These two very abundant and cultivable grasses in the Far-North region of Cameroon are to be encouraged in the manufacture of biodegradable composite materials and used as adhesives in wood industries.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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