Biobased Adhesives from African Mahogany Tannins: Characterization by ^{1}H and ^{13}C NMR and Physicochemical Properties

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Abstract: The study of the development of tannin-based adhesives from the African mahogany *Khaya ivorensis* A. Chev tannins condensed hexamine was carried out. Tannins from the bark, sapwood, and heartwood were extracted employing the industrial method ($NaOH/Na_2SO_3/NaHSO_3$) and they were used to synthesize different formulations of biobased adhesives. Tannins/hexamine/water adhesives obtained were characterized by differential scanning analysis (DSC) to know their physical changes under heat action. Polymerization temperatures were between 90°C and 153°C. These adhesives heat resistance was studied by thermogravimetric analysis (TGA). Results showed good thermal stabilities properties for adhesives with degradation temperatures between 225°C and 250°C. Besides, a thermomechanical analysis (TMA) shows a high value of elasticity modulus for these adhesives. Finally, 2D HSQC NMR analysis was performed to confirm the good reactivity between African mahogany tannins and hexamine linked with strong bounds.

Keywords: Bark, Sapwood, Heartwood, *Khaya ivorensis*, Tannins, Thermal stability.

INTRODUCTION

Due to their phenolic nature, tannins are used or have been used for the production of biobased adhesives and leather goods (Pizzi and Stephanou, 1994; Navarrete *et al*., 2010). They are important components of wood just as much as cellulose, hemicellulose, and lignin (Pizzi and Cameron, 1986). In this respect, there has been lately a significant interest in the synthesis of tannin-based resins. Tannins are the renewable resource, which is most widely used in the adhesives production, they could be provided from different species such as of mimosa (*Acacia dealbata*), quebracho (*Schinopsis lorentzii*), tsuga (*Tsuga mertensiana*), rhus (*Rhus typhina*), pine (*Pinus radiata* and *Pinus pinaster*) (Kim and Kim, 2003; Li *et al*., 2016;Ping *et al*., 2011). Concerning the type, the most commonly used tannins for adhesives are condensed tannins. They are characterized by a single highly active site (C6), while the other part is engaged in an inter flavonoid bond (C8).

In the formulation of tannins-based adhesives an agent to initiate polymerization is normally added (Moubarik *et al*., 2009). In this sense formaldehyde (Pizzi, 1980), hexamethylenetetramine (Saayman *et al*., 1971), furfurilic alcohol, glyoxal, etc are widely used. Hexamine is a compound whose chemistry has been known in the field of resins and adhesives for a long time. It is rather moderately unstable in acid conditions but becomes rather stable in basic conditions (pH ≈ 8-10). Thus, in an alkaline medium, only three formaldehyde molecules are released with the corresponding formation of trimethylamine. Accordingly, it has been reported that formulations of adhesives with tannins and hexamine used for

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particleboards, present very low formaldehyde emission (Pichelin *et al*., 1999).

The importance of tannins in the industrial environment has already been proven. Particleboard adhesives based on acacia tannins had been used in several countries. For instance, in South Africa, the totality of the panels used in interior furnishings are made with these adhesives. Their performance is superior to that of synthetic adhesives derived from petroleum derivatives (Pizzi *et al*., 1981; Scharfetter and Pizzi, 1981). However, it should be noted that the quantities of tannins available commercially are less important than those synthetic derived from petroleum. It is therefore important to research other sources of tannins as important as those currently used to extract these compounds. It is within this framework that this study was carried out namely, the elaboration bio-based adhesives with tannins extracted from mahogany wood (Taiwo and Ogunbodede, 1995; Bikoro Bi Athomo *et al*., 2018; Bikoro *et al*., 2019). Besides that, mahogany wood (*K. ivorensis*), which is one of the most exploited species in Gabon, is mainly sawn and the by-products of its transformation are mainly burnt. It is therefore interesting to evaluate the properties of the tannins extracted (Anris *et al*., 2020; Péguy *et al*., 2020) from its residues to valorize (Wang *et al*., 2016) into bio-based adhesives.

MATERIAL AND METHODS

Materials

Chemicals

All the chemicals used in this study were purchased from Fisher Scientific, Across Organic, and Sigma Aldrich. Deionized water (IPREM), sodium carbonate decahydrate (>98%, Fisher), sodium bisulfite for analysis Across Organic), sodium hydroxide (98.5%, Across Organic), sodium sulfite (anhydrous, Fisher).

Wood Sampling

Bark, sapwood, and heartwood from a *K. ivorensis* were collected *and* sampled with a section disk of 10 cm of thickness and 85 cm (*AMG1*), 80 cm (*AMG2*), and 75 cm (*AMG3*) of diameter. The wood was harvested at Mitzic in the North of Gabon by the SNBG (Société Nationale des Bois du Gabon) during the period between 2016 and 2017. The fresh samples were put in sterilized bags, air-dried for one week in the laboratory, and oven-dried (105°C) for 48h. The dried samples were ground to pass through 60 mesh (≈1 mm diameter) with a rotative knife grinder (Retsch SK1).

Methods

Alkaline Extraction of Tannins

According to a previous optimization of alkaline extractions developed by (Chupin *et al*., 2013), African mahogany bark, sapwood, and heartwood tannins were extracted by water solution containing 0.25 % of NaOH, 0.25 % of Na_2SO_3, and 0.25% of $NaHSO_3$. The sample/water ratio was 1: 9. NaOH was used in the extraction to ensure high alkaline conditions (pH≈9) and to increase the extraction yield. Na_2SO_3 and $NaHSO_3$ were added to lessen the viscosity and to stabilize the extracts. The grounded samples were immersed in water under continuous magnetic stirring for 2h at 80±5°C. The supernatant was filtered through whatman paper n^o 3 and the residue was rinsed with water. The filtrates were dried in an oven at 40°C. Then, the samples were frozen at -20°C, and then they were lyophilized by using an Alpha 1-4 LO plus Martin Christ. After 24h the lyophilized samples were crushed in a mortar and the powder was recovered.

Adhesive Formulation

Different formulations of the biobased adhesives were synthesized by using different tannins, namely tannins from bark (TB), sapwood (TS), and heartwood (TH) of mahogany. The composition of the different formulations was as described next: 1.52 g of mahogany tannins, 2.16 g of water, and 0.32 g of hexamine (solution 99%). Three replicates were obtained for each formulation (Saad *et al*., 2014).

Thermogravimetric Analysis (TGA)

Thermal decomposition was performed using a TA Instrument (TGA Q50 instrument). The temperature program was set from 24 to 600°C at a heating rate of 10°C/min. The measurements were conducted under air (60 mL/min) and nitrogen (40 mL/min).

This analysis was performed in a TA Instruments TGA Q5000 IR equipment, under dynamic nitrogen flow with a flow rate of 40 mL/min. Samples of the biobased adhesives of 12 mg were placed in a platinum crucible and heated in a temperature range of 24 to 600 ºC at a constant heating rate of 10 ºC/min under air atmosphere. For the quantitative calculations, the response factors between the weight gain (TG) and the mass loss rate (DTG) were determined.

Differential Scanning Calorimetry (DSC)

A TA instrument (DSC Q500) was used for this test and was run simultaneously with TGA Q50. The mass sample used was between 5 and 22 mg. The analysis was performed under a nitrogen atmosphere

(60ml/min) from 25ºC to 200ºC. For the tests two different ramps of temperature were used, one of 5°C/ min and another one of 10°C/min.

Fourier Transformed Infrared Spectroscopy Analysis (FTIR)

Tannins extracted from *K. ivorensis* sapwood and heartwood by the acetone/water solvent method (7:3, v/v) were analyzed by FTIR spectroscopy. The samples were oven-dried at 105°C for 24h and then, 5 mg of the dried powders were placed on the crystal device and the contact was obtained by applying a strength of 150 N on the sample. The analyses were performed with 32 scans, a resolution of 4 cm^{-1}, and in the range 4000 to 600 cm^{-1}. All the experiments were carried out in ATR (attenuated total reflection) mode with a PerkinElmer Frontier spectrophotometer equipped with a diamond/ZnSe crystal.

Thermomechanical Analysis (TMA)

For this test, the samples were prepared with two plywood sheets (14 mm x 5 mm x 1 mm) and a resin film of 120g/m^2. The analyses were performed from 25ºC to 150ºC at a heating rate of 10ºC/min, and the applied force was 0.5N. Three replicates were done for all samples.

2D HSQC NMN Analysis

In this analysis, around 50 mg of tannin-based adhesive was dissolved in 0.5 mL of DMSO d_6. The 2D HSQC NMR spectra were recorded at 25 °C in a Bruker AVANCE 500 MHz equipped with a z-gradient double-resonance probe. The spectral widths were 5000 and 12,300 Hz for the ^{1}H and ^{13}C dimensions, respectively. The number of collected complex points was 1024 for the ^{1}H dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256-time increments were always recorded in the ^{13}C dimension. The $^{1}J_{CH}$ used was 145 Hz. Prior to Fourier transformation, the data matrices were zero filled to 2048 points in the ^{13}C dimension. Data processing was performed using MestReNova software. The central solvent (DMSO) peak was used as an internal chemical shift reference point ($\delta C/\delta_H$ 39.5/2.49).

Results and Discussion

FTIR-ATR Spectroscopy Analysis

This analysis was carried out for assessing the structure, main functional groups, and the bonds formed during the reaction of polymerization of the adhesives. Thereby, in Figure **1**, we show the flavonoid base structure numbered. Then Figures **2** and **3**, the spectrum of mahogany tannins and adhesive with TB, TS, and TH are shown. The formation of tannin based adhesive is based on the reaction between the tannin and formaldehyde (Kim and Kim, 2003). Previous studies have shown that mahogany tannins are condensed and that the presence of free monomer fragments is rare (Bikoro Bi Athomo *et al*., 2018). Consequently, this assumes that the C8 (Figure **1**) sites are more involved in the auto condensation reactions.

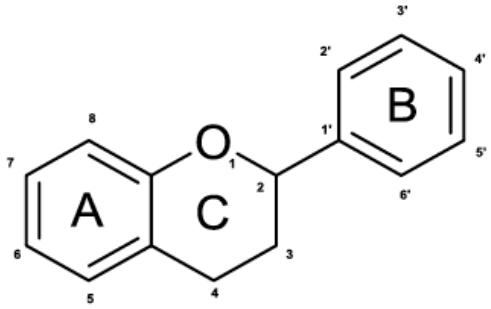

Figure 1: Flavonoid structure.

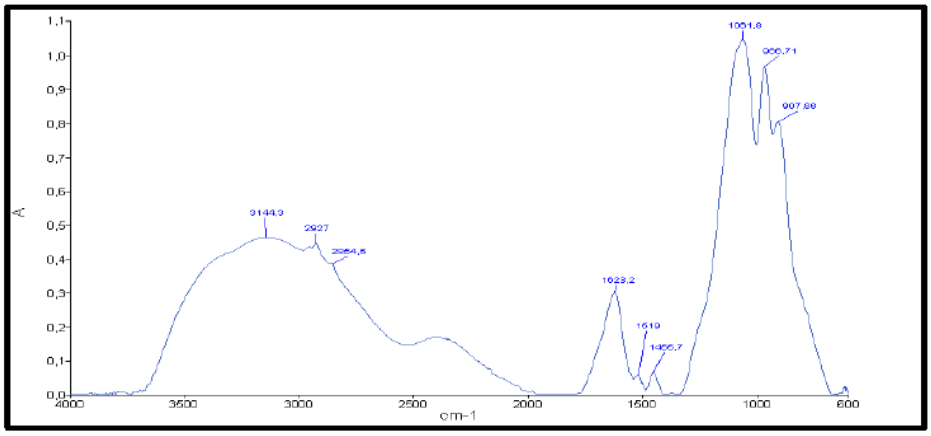

Figure 2: FTIR analysis spectra (measured using a spectrophotometer equipped with a diamond/ZnSe Crystal) of bark tannins extracted from Khaya ivorensis.

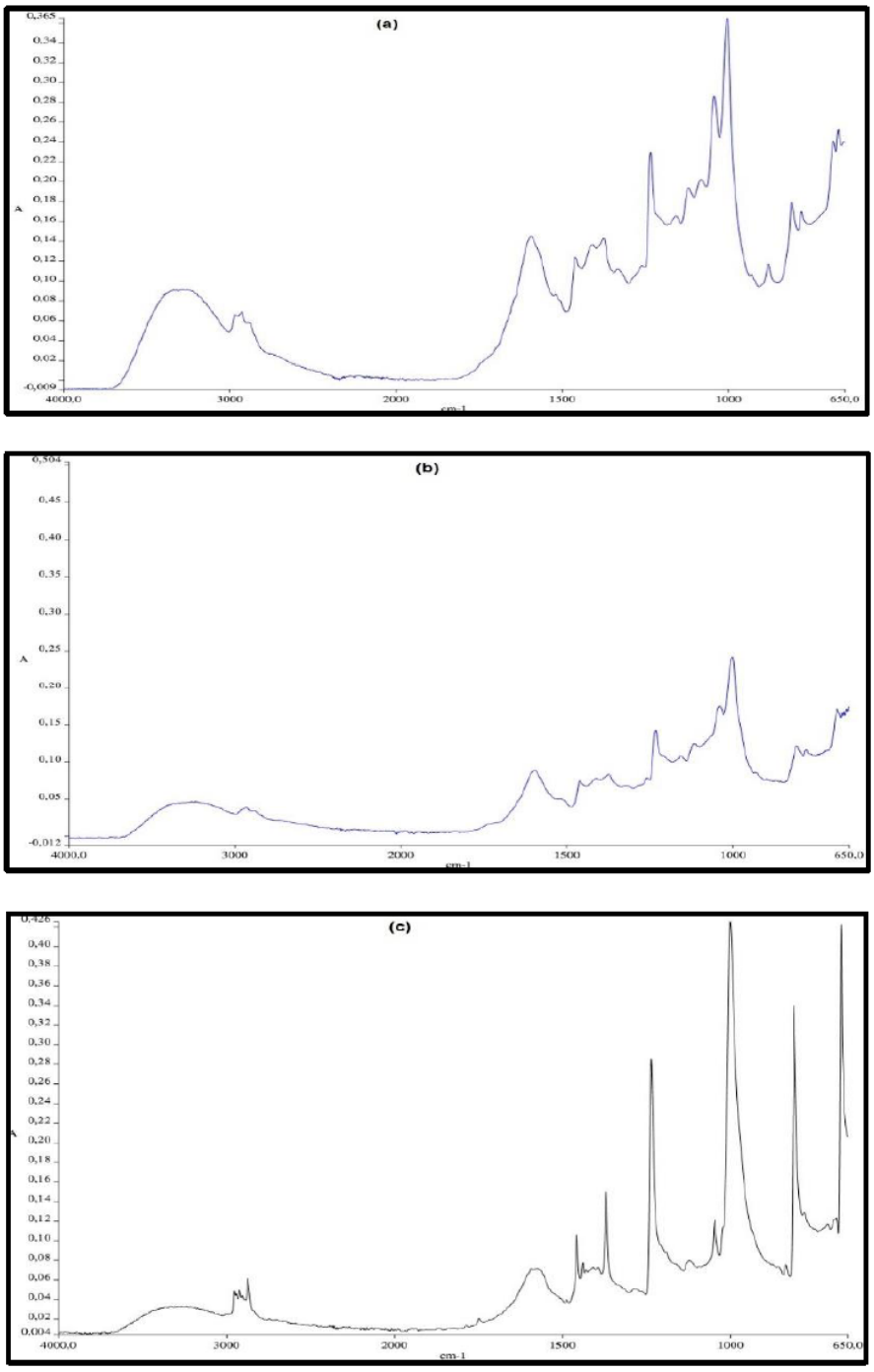

Figure 3: FTIR spectrums (measured using a spectrophotometer equipped with a diamond/ZnSe Crystal) of tannin-based adhesives TB (**a**), TS (**b**), and TH (**c**) of African mahogany.

The C6 site of A ring remaining therefore the most active for tannin's reaction of polymerization with formaldehyde, the main product derived from hexamethylenetetramine decomposition. However, at basic pH (≈10), the highly reactive amino-immine intermediates resulting from hexamine decomposition are at the origin of reactions with phenolic species present as condensed tannins, without passing through the formation of formaldehyde (Kammoun and Pizzi, 2000 a; Kammoun and Pizzi, 2000 b).

In respect to the spectra shown in Figures **2**-**3**, the broad peak in the 3700-3000 cm^{-1} region was characteristic of the benzene nucleus –OH stretching and tannin's methylol group. This region intensity was much lower in TH resins (0.03A) than in TS resins (0.05A) and TB resins (0.09A). This indicates that the hydroxyl sites of condensed tannins in mahogany heartwood were more reactive with hexamine than the bark and sapwood. The low peak intensity at 2905 cm^{-1} was assigned to benzene nucleus –CH stretching,

methylene (-CH_2-) and dimethylene ether (-CH_2OCH_2-) bridges present within the structure of the tannin-based adhesives.

The peak at 1595 cm^{-1} was assigned to elongation ring' double bond elongation. The signals at 1443-1452 cm^{-1} were related to the deformation-vibration of carbon-carbon bonds in the phenolic groups (Nuopponen *et al*., 2006). However, this group does not participate in the chemical reaction during the polymerization. The peak at 1238 cm^{-1} was assigned to –CO stretching of the benzene ring and the dimethylene ether bridges formed by reaction with hexamine. Signals between 1028 cm^{-1} to 1000 cm^{-1} were characteristic of the C-O bond in mahogany condensed tannin. The bands at 767 cm^{-1} and 850 cm^{-1} were assigned to the C-H deformation vibration of phenolic rings (C5, C6, C2', C3' and C6'). This group can indicate the degree of polymerization because it disappeared during the reaction between tannins and hardener (Figure **4**). Indeed, the intermediates methylene aminoimino as CH_2=N-CH_2^+, resulting from hexamine decomposition will react wit,h the C6, C6' and C3' sites of condensed tannins during the crosslinking process, knowing that C4 and C8 sites are involved in autocondensation mechanisms.

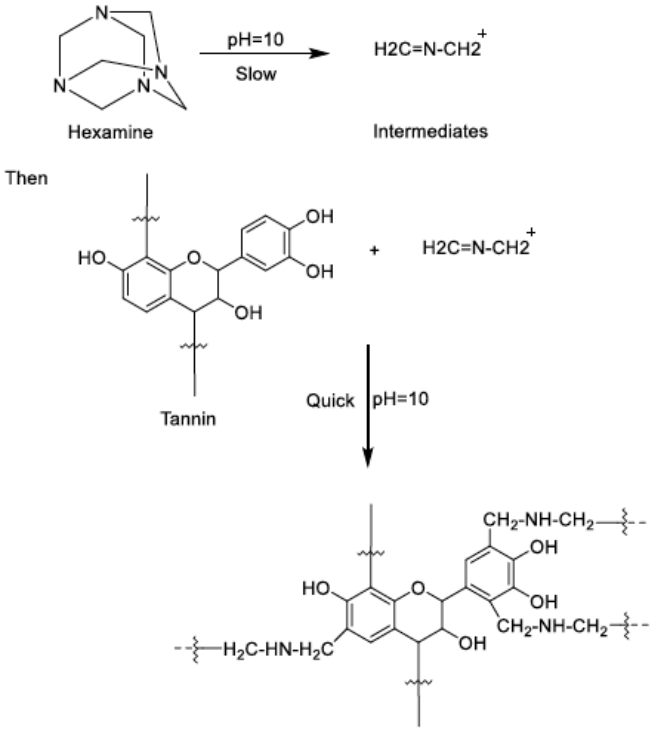

Figure 4: Crosslinking between tannins and hexamine (Pichelin *et al*, 2006).

TMA Analysis

The results of TMA analysis corresponding to the different formulations of mahogany tannin-base adhesives are shown in Table **1**. The elasticity modulus (MOE) was given as a function of temperature for the formulated resins. MOE was obtained for the same formulation at 150°C for different parts of the wood. Thus, it was confirmed that the Mahogany tannin-based adhesives obtained in this work displayed a higher MOE (Table **1**) compared to the ones from mimosa, Aleppo pine, and quebarcho reported in previous work (Saad *et al*., 2014). However, in TMA, the MOE depends on the thickness of the lamiae used for the sandwich. In this study, we used laminae of 1 mm thickness while the values in literature were using laminae of 0.6 mm. It means that the sandwich of this study was at minimum 67% thicker (without considering the adhesive that is probably more) than those in literature. We used a force of 0.5 N while in the literature the alternating force used was of 0.6 N, this can too impinge a lot on the MOE measure of another 20%.

Regarding the comparison between the different formulations of the mahogany tannin-based adhesives, the MOE values were significantly higher in the tannin-based adhesive from sapwood and heartwood. The other formulation from the bark was similar compared to that was found by Zanetti and Pizzi (2002; Zanetti *et al*., 2002; Gfeller *et al*., 2003).

Table 1: Elasticity Modulus of Tannin-Adhesives from K. Ivorensis. Each Curve is one Means of Three Analyses

Tannin-Based Adhesive	Temperature (°C)	MOE (MPa)
Bark	101± 0.32*	4393 ± 1691*
Sapwood	101± 1.3*	10341± 2827*
Heartwood	95 ± 0.42*	12360 ± 4328*

Temperatures corresponding to the maximum values of MOE were around 100°C. TB and TS temperatures were approximately the same while TH resin temperature was weaker. It was assigned to the temperatures of the polymerization reaction. These behaviors were attributed to the disappearance or not of OH in tannins/hexamine reaction. This reaction is significantly dependent from the nature of bridges between the condensed tannins units, from the availability of reactive sites and nucleus A and B (Yazaki and Collins, 1994; Pizzi, 2000; Pizzi, 2003; Moubarik *et al*., 2009; Basso *et al*., 2017). It appears that the MOE of mahogany tannin-based adhesives were stable after 150°C (MOE was around 9000 MPa) and these temperatures values were higher than the urea-formaldehyde resin (Moubarik *et al*., 2013). This

temperature was low compared to the required conditions for producing particleboards by hot pressure. The results of this study highlighted that the three African mahogany tannin-based adhesives are comparable to quebracho tannins ones, but *K. ivorensis*' sapwood and heartwood displayed higher MOE values.

Thermal Analysis of the Adhesives

DSC and TGA analysis are shown in Figure **5** and Figure **6** and show the thermogram (derivative DTG) obtained under nitrogen from the African mahogany tannin-based adhesives (TB, TS, and TH) were superimposed. The thermal decomposition and thermal stability of formulations checked by TGA (Moubarik *et al*., 2009) allowed observing two peaks (evaporation and degradation) for each formulation analyzed. The first was between 130 and 140°C for sapwood and heartwood, while bark first peak was around 70°C. The second degradation peaks were found between 225°C and 250°C for the different formulations. 228.5°C for the sapwood, 236.9°C for the heartwood, and around

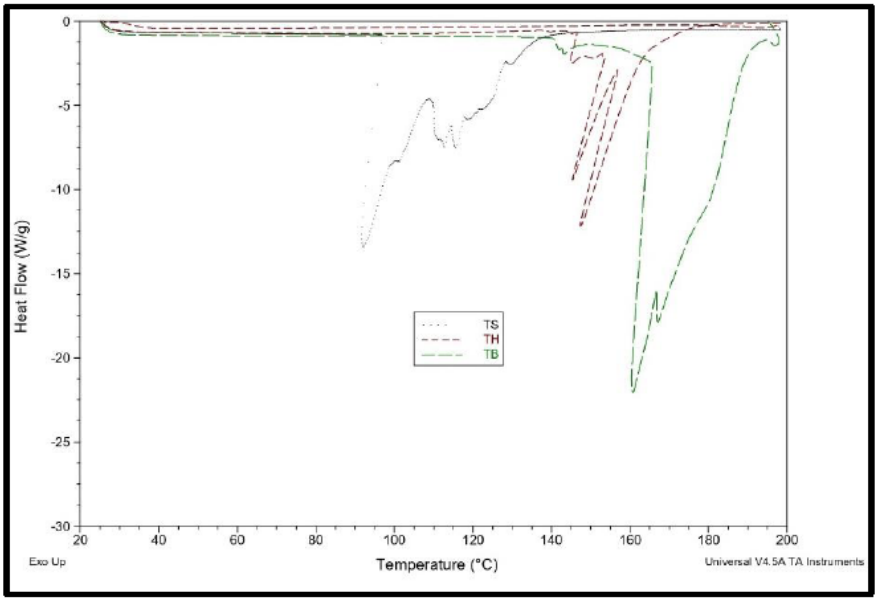

Figure 5: DSC spectrum of tannin-based adhesives from *K. ivorensis*. Each curve is a mean of three samples.

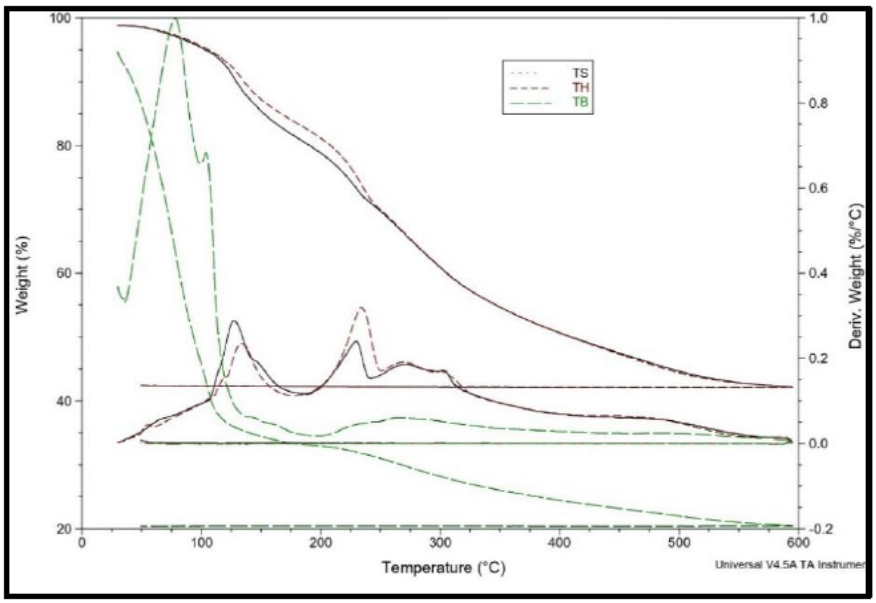

Figure 6: TGA spectrum of tannin-based adhesives from *K. ivorensis.* Each curve is a mean of three samples.

250°C for the bark. These results showed that sapwood and heartwood tannin-based adhesives had the same thermal behavior as those tannins from the same parts of wood (≈ 118 °C).

This is in agreement with what was previously published by Bikoro *et al* (2018 and 2019). However, the first temperature of degradation of tannin-based adhesive (≈109°C) from the bark was low compared to

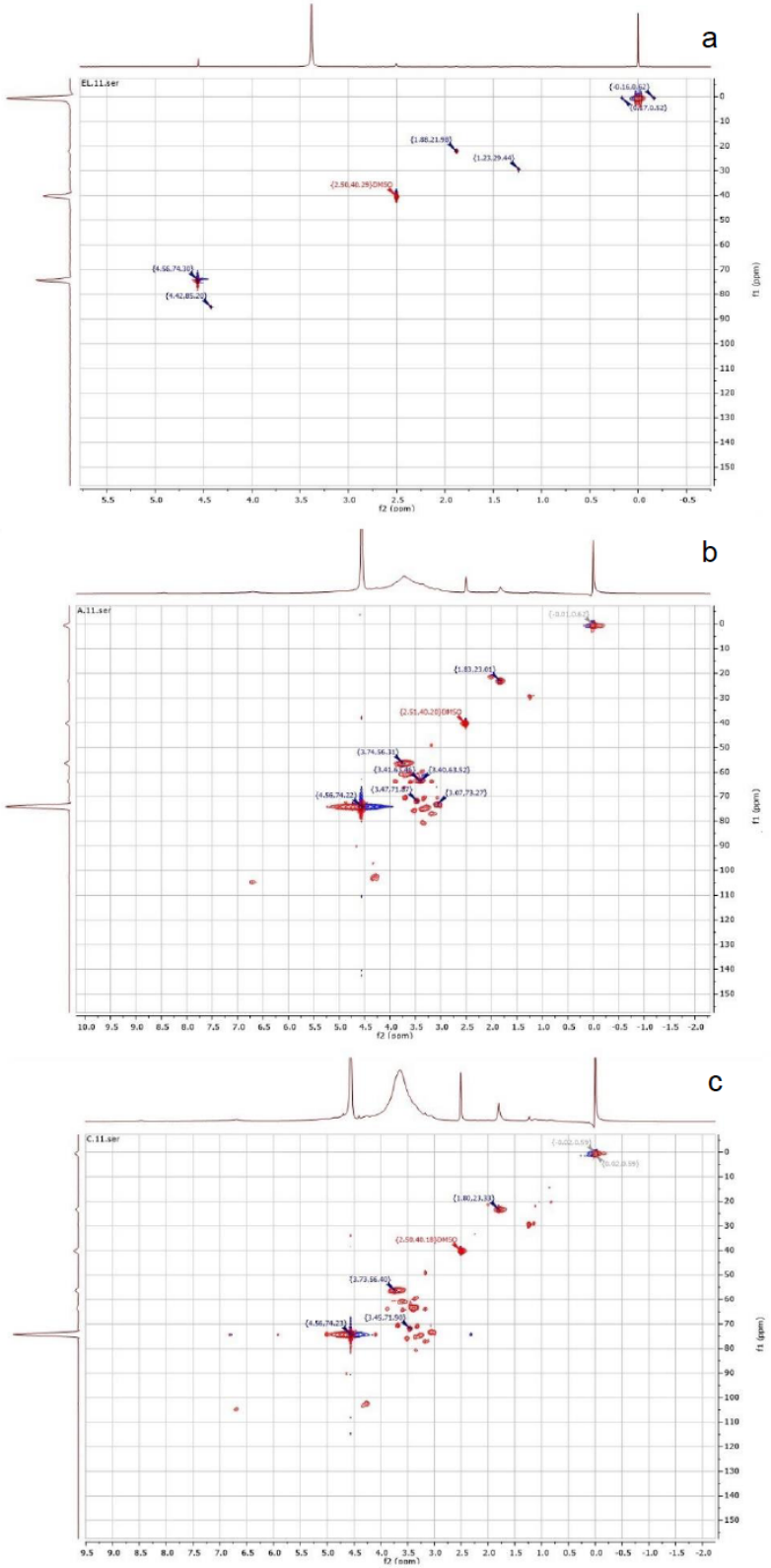

Figure 7: 2D HSQC NMR ^{13}C (f1) and ^{1}H (f2) spectra of mahogany tannin-based adhesive of bark (**a**), sapwood (**b**) and heartwood (**c**).

tannins-based adhesives from sapwood and heartwood. The first degradation was assigned to the moisture and volatiles evaporation such as H_2O, H_2 (Gaugler and Grigsby, 2009; Basso *et al*., 2017). That suggests the degradation of simple sugars and organic acids. Further, the degradation of all tannins-based adhesives was beginning around 200°C. These were assigned to the thermal degradation of the intermolecular C-O bond of condensed tannins or intermolecular C-C bond during auto condensation and polymerization reaction. DSC analysis showed one major domain for bark and heartwood. Each curve of the curing process passed one exothermic peak. However, for sapwood, the analysis showed two majors domains (Figure **5**). The most prominent peaks for the adhesives of each part of wood used depicted between 105°C and 153°C. The values were 92°C, 115°C, and 153°C respectively for sapwood, bark, and heartwood. These peaks were assigned to the crosslinking reaction between the extracted tannins and hexamine present in the adhesives (Zhang *et al*., 2017). The higher peak in the heartwood tannin-based adhesives suggested that heartwood tannins acquired more bonding with hexamine compared to bark and sapwood.

Furthermore, a study about the production of tannins adhesives with the bark of Nigerian trees showed that tannin from *K. ivorensis* could be used and replaced the best commercially available synthetic adhesives (Taiwo and Ogunbodede, 1995). However, it was with aqueous extracts (yield of 23%) and the hardener used as paraformaldehyde.

NMR ^{13}C and ^{1}analysis

The 2D HSQC NMR measurements were undertaken to give additional and complementary information on the chemical structure of tannin-based adhesives from *K. ivorensis*. Spectra and peaks intensity of tannin-based adhesive are shown in Figure **7** $H/C_{n\ or\ n'}$ (f1, f2). It has been observed a greater number of points in the sapwood and the heartwood compared to the bark. Sapwood and heartwood showed identical ^{13}C and ^{1}H NMR spectra. However, bonds with high intensity were observed in tannin-based adhesives from sapwood and heartwood. The reaction has been shown that higher peaks characteristics to C-C bonds were more abundant in the heartwood (Figure **7**) tannin-based adhesive of African mahogany compared to bark and sapwood adhesives.

Previous studies investigated by Grabber (Grabber *et al*., 2013) on acetone extracts, showed $^{1}H(f1)$-$^{13}C(f2)$ HSGC NMR spectrum of condensed tannins in *Lotus species*. According these studies, peaks assignment for condensed tannins (^{13}C and ^{1}H chemical shifts in ppm) were: H/C_4 (35.7, 4.78), H/C_3 (71.1, 3.98), H/C_2 (75.0, 5.27), H/C_8 (95.8, 5.93), $H/C_{2'}$ (prodelphinidin) (105.6, 6.58), $H/C_{2'/5'}$ (procyanidin) (115.0, 6.76) and $H/C_{6'}$ (procyanidin) (117.3, 6.77). Signals at (71.8, 3.47) and (71.9, 3.45) ppm, were mainly present in sapwood and heartwood adhesives respectively. Those peaks were assigned to the H/C_3 of condensed tannins of African mahogany. However, signals at (74.3, 4.56), (74.2, 4.56) and (74.2, 4.56) ppm were present in the three parts analyze and have been assigned to the H/C_2 of condensed tannins. It was observed the absence of characteristic peaks for prodelphinidin and procyanidins. Furthermore, this could indicate also that these carbons were involved in bonds other than $H/C_{n\ or\ n'}$, formed during the polymerization process of tannins and hexamine.

The reaction between tannins and hexamine is formed with oligomeric, ionized iminomethylene bases, and tannin. The signal at 63.4.6 ppm was assigned to benzylamine bridges.

CONCLUSION

This study has concerned the development of a tannin-based adhesive with mahogany tannin extract from bark, sapwood, and heartwood. Their thermal characterizations have shown that adhesives assigned heat resistance temperatures up to 250°C. A high degradation step under 100°C was observed for adhesives produced from the bark tannins, attributed to the elimination of volatile compounds and moisture. The thermomechanical analysis showed that the adhesives had elasticity modulus comparable to those of adhesives used for the production of particleboards. These results are encouraging for possible industrial production, however, it would be necessary to carry out rheology analysis to better characterize the viscosity of this type of formulation. Furthermore, it could be interesting to study NMR analysis on these adhesives to observe all chemical modifications, which could explain the behavior of the adhesives.

AUTHOR CONTRIBUTION

Authors' contribution: Dr. Arsène Bikoro Bi Athomo was the principal investigator of the subject. Dr. Peguy Starlin Engozogho participated as a worker in a related field of tropical wood chemistry. Dr. Rodrigue Safou Tchiama contributed actively as a wood scientist and

Ph.D. committee member; he criticized and corrected the final manuscript. Pr. Florent Eyma and Pr. Bertrand Charrier acted as scientific directors.

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CONFLICTS OF INTEREST

The authors declare that they have no competing interests.

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