

# Characterization of Tannin-Based Resins from the Barks of *Ficus platyphylla* and of *Vitellaria paradoxa*: Composites' Performances and Applications

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# Abstract

This work investigates the physico-chemical and mechanical properties of tannins extracted from wood for composite materials manufacturing. Sustainable knowledge (in terms of physico-chemical properties and behaviours) of the material is needed to further enhance its applications. The condensed tannins extracted from the Bark of Ficus platyphylla (BFP) and the Bark of Vitellaria paradoxa (BVP) were analyzed using Matrix Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF), Mass Spectroscopy and Attenuated Total Reflectance Fourier Transform Mid-InfraRed (ATR-FT MIR) spectra in the ranges 1800 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, as well as using CP MAS <sup>13</sup>C-NMR. It was found that, these two tannins are procyanidin/prodelphinidin and made up of catechin/epicatechin, gallocatechin/epigallocatechin units, fisetinidin, galloyl and carbohydrates residues. Furthermore, BFP and BVP tannin bonded particleboard densities lie in the range recommended by NF EN 326-1994 standard. The resins also yielded good internal bond strength results of the panels, above relevant international standard specifications minimum requirements for interior-grade panels. The Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy Analysis (TEM/ EDXA) are showing the ultrastructure and reveal that most of the resin material appears to be in an amorphous phase mainly composed of carbon/oxygen with small amounts of K, Ca and Mg. These particles have a very irregular morphology.

## **Keywords**

Wood Condensed Tannins, Fibre/Matrix Bond, Mechanical Properties, Active Correlated Transmission Electron Microscopy (ACTEM), Matrix Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF)

# **1. Introduction**

The last decade has witnessed important development in biomaterials [1] [2] [3] [4]. As an alternative to their synthetic counterparts, biomaterials are known to cause no damaging effect to our living environment. The use of natural resources for industrial purposes generally appears to be a viable solution for a sustainable development. In the composite materials domain in particular, researchers are concerned with the implementation of novel binders having at least the same performances as synthetic ones. This opens an opportunity to use natural resources in structural applications. For instance, urea formaldehyde (UF) or phenol formaldehyde (PF) adhesives are, among other most used synthetic resins [5], known to cause formaldehyde emission (a substance harmful to human health) from the wood boards when used as a bonding agent. This work aims at obtaining a natural binder with mechanical properties comparable to those of UF or PF resins.

Polylactic Acid (PLA) and other bioresins derived from crops or vegetal plants are now actively applied in the packaging sector [6] [7] [8], and for interior lining in automotives and aeroplanes [9] [10]. Authors have reported on the development of biodegradable materials [6] [11]. Several other natural adhesives were developed using derivatives of plants and authors have analyzed the tannin structures used in the composition of adhesives [12]-[18]. Other authors have analyzed the use of tannin-based additives for thermal stabilization in bonding applications [19] [20] [21]. Yet, more studies need to be done for the derivation of bio-based resins for structural applications.

In the present work, tannin bioresins extracted from Barks of *Ficus platyphylla* (BFP) and Barks of *Vitellaria paradoxa* (BVP) are investigated as binders for vegetal powder fillers. The resultant composite material can prove valuable for the fabrication of panels for furniture and buildings. Continuous availability of *Ficus platyphylla* (FP) and *Vitellaria paradoxa* (VP) plants is guaranteed by their large diffusion, in the wild state, on the whole Soudano Sahelian zone including the Northern Cameroon, the Northern Nigeria, the Southern Chad, Central Africa Republic, Democratic Republic of Congo (DRC) and many others [22] [23]. However, sustainable knowledge (in terms of physico-chemical properties and behaviours) of the material is needed to further enhance its applications. To the best of our knowledge, such knowledge is yet to be established for most tannin binders. Despite their growing interest [22], BFP and BVP have not been investigated for tannin extraction. This paper contributes to filling that gap.

## 2. Materials and Samples Preparation

# 2.1. BFP and BVP

The Barks of *Ficus platyphylla* (moraceae family) and of *Vitellaria paradoxa* (sapotaceae family) were collected in the far North of Cameroon. After gathering, the bark was air dried at  $37^{\circ}$ C and reduced to a fine powder with a grinding apparatus. The sizes of the powder particles as observed through various sieves were between 20 to 100 µm.

# 2.2. Extraction of Tannin

The BFP and BVP powders were mixed with water (ratio 1:6 by weight) at ambient temperature during 48 hours. The solution was agitated and filtered to obtain purple red or black liquid. Finally, the purple red or black liquid was extracted using a mix of acetone and ethyl acetate resin on the ratio (1:1:1). The solvents were evaporated using a rotary evaporator. After evaporation, we obtained tannin in solution or solid tannin after lyophilization. The formulation of the resin was done using a water solution containing 40% for each tannin. These tannins were mixed with 5% of hexamethylenetetramine (hexamine) as hardener and their pH was adjusted to 11 adding 30% sodium hydroxide solution (NaOH). The high pH hardener was chosen as it performs well at such conditions [19]. Mixing is continued until a viscous solution is obtained, with its viscosity being estimated at 750 mPa.s.

# 2.3. Particleboards Manufacturing

Particleboards were prepared adding 10% of total resin solids on Palm Kernel Shell (PKS) powder particles and with PKS powder particles being at 2% moisture content. PKS powders were chosen as their good structural characteristics [24] and their physical properties, being actually used as concrete reinforcement aggregates and ceramics [13] [25]. Particleboards were manufactured in a 3-step pressure sequence during 8 min 30 s: the first step with a pressure of 28 kg/cm<sup>2</sup> during 3 min, the second with a pressure of 12 kg/cm<sup>2</sup> during 2 min and the third with a pressure of 5.8 kg/cm<sup>2</sup>, during 2 min 30 s. The temperature of the two pressing plates was set at 220°C. Rectangular particleboards with thickness of 14 mm and 350 × 300 mm<sup>2</sup> were manufactured, each particleboard weighing 1000 g. Particleboards were eventually cut into  $50 \times 50 \times 14$  mm<sup>3</sup> samples for testing according to EN 312 (NF EN 312-2, 1996) Standard.

# **3. Experiments**

# **3.1. ATR-FT MIR Analysis**

The BFP and BVP were analyzed using the PerkinElmer Frontier ATR device equipped with a Diamond/ZnSe crystal. A quantity of 2 mg of grinded powder was put on the crystal device and the contact was established by applying a 150 N force. Each spectrum was obtained with 32 scans with the resolution of  $4 \text{ cm}^{-1}$  from 4000 to 600 cm<sup>-1</sup>. The samples were scanned five times and the average of these spectra was studied in the fingerprint region between 1800 and 600 cm<sup>-1</sup>.

## **3.2. MALDI-TOF Analysis**

The samples were dissolved in acetone (4 mg/ml, 50/50% volume). The sample solutions were mixed with an acetone solution (10 mg/ml in acetone) of the matrix. The 2,5-dihydroxy benzoic acid was used as the matrix. For the enhancement of ions formation sodium chloride (NaCl) was added to the matrix (10 mg/ml in water). The solution and the matrix were mixed in the proportions of 3 parts for the matrix solution and 3 parts for the polymer solution and 1 part of NaCl solution, and 0.5 to 1  $\mu$ l of the resulting was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer [26].

## 3.3. CP MAS <sup>13</sup>C-NMR Spectroscopy Analysis

The dried powder samples of BFP and BVP tannins were analyzed by Cross-polarization/Magic Angle Spinning spectroscopy instrument (CP MAS <sup>13</sup>C-NMR). The spectra were recorded in a Bruker AVANCE l J 400 MHz spectrometer operating at a frequency of 100.6 MHz and a sample spin of 12 kHz, using a recycling delay of 1 s and a contact time of 1 ms. Number of spectra was about 15,000, and a 53 kHz decoupling field.

# 3.4. Resin Modulus of Elasticity

A thermo mechanical analyzer METTLER TOLEDO TMA 40 was used to study the hardening reaction of single resin systems and determine the resins modulus of elasticity (MOE) as a function of temperature. The TOLEDO TMA40 was linked to a processor TC11 and a computer to register and interpret graphically the behavior of the resin. The software used for data treatment was STARe 6.10 [27].

# 3.5. Board Density Profile

A StenOgraph of GreCon X-ray device was used to study the density profile of the particleboards specimen prepared according to the NF EN 326-1 international standard (1994).

## 3.6. Bonding Behavior

An INSTRON 4467 universal testing machine was used to determine the Internal Bond (IB) strength of the particleboards (following to the International standard NF EN 312-2, 1996). Dry IB test was done on 10 specimens and 10 additional specimens were IB-tested after immersion in boiling water during 2 h (NF B 51-262, 1972).

## 3.7. TEM of the BFP/BVP Resins

#### **3.7.1. TEM Specimen Preparation**

TEM specimens were made with the as-received powder as follows: powder was sonicated for 5 minutes in distilled water then dropped onto a lacey copper (Cu) coated grid.

## 3.7.2. TEM/EDX Analysis

A JEOL TEM, with a JSX-1000S Fluorescence Spectrometer X-ray analyzer controlled by automated analysis software was used for the ultrastructure characterization. With the addition of energy dispersive X-ray analysis (EDXA) or energy loss spectrometry (EELS), the TEM can also be used as an elemental analysis tool, capable of identifying the elements in areas less than 0.5  $\mu$ m in diameter from carbon to uranium. The Aberration Corrected TEM (ACTEM) ensures the highest image resolution. Low voltage increases image contrast which is especially important for the biological specimens used herein. A Low-Voltage Electron Microscope (LVEM) was operated at relatively low electron accelerating voltage between 5 - 25 kV. This increase in voltage significantly reduced the contrast, or even eliminated the need to stain.

# 4. Results and Discussion

# 4.1. BFP Characterization

## 4.1.1. ATR-FTMIR Analysis

**Figure 1** shows the FT-MIR spectrum of BFP tannin extract, and several peaks proper to condensed and hydrolysable tannins can be observed. Indeed, the peak at 1607 cm<sup>-1</sup> is attributed to the vibrational motions of C=C in the aromatic rings [25]. The peaks at 1371 cm<sup>-1</sup>, 1233 cm<sup>-1</sup>, 1144 cm<sup>-1</sup>, and 1030 cm<sup>-1</sup> describe the presence of ring substitutions. These ring substitutions may belong to both tannins (condensed and hydrolysable). The 821 cm<sup>-1</sup> and the 779 cm<sup>-1</sup> peaks



Figure 1. Pattern of BFP.

describe both OH wagging of aromatic alcohols and out of plane bending of aromatic CH. These observations are consistent with previous results reported in the literature [28] [29] [30]. Moreover, the peaks at 1445 cm<sup>-1</sup>, 1371 cm<sup>-1</sup>, 1316 cm<sup>-1</sup>, 1233 cm<sup>-1</sup> and 1144 cm<sup>-1</sup> indicate the presence of proanthocyanidin and particularly the gallocatechin in the BFP tannin extract, while the 1516 cm<sup>-1</sup> peak shows evidence of the presence of condensed tannins, as reported in previous studies [7] [29] [30] [31] [32]. The peak around 1316 cm<sup>-1</sup> is attributed to the symmetric stretching of the C-O bond of the ester group, while the peak 1233 cm<sup>-1</sup> indicates stretching and bending of groups which can represent some residues of esters [33]. Such residues are not new in the structures of condensed tannins, as already highlighted by Navarrete *et al.* [10]. C-O stretching modes are assigned to the peak 1144 cm<sup>-1</sup> for symmetric elongation of the C-O-C groups in the pyran ring of condensed tannins, consistent with the work reported by Chen *et al.* [34]. The peaks 1030 cm<sup>-1</sup>, 1144 cm<sup>-1</sup>, and 1233 cm<sup>-1</sup>, enable the distinction of procyanidins and prodelphinidins [35].

#### 4.1.2. MALDI-TOF Analysis

**Figure 2** shows the MALDI-TOF Spectra of BFP, indicating four monomers in the formation of the oligomers in the BFP tannin extract: A, B, C and D, for which the structural formulas of each unit mass is shown in **Figure 3**. To mass A correspond two structures: Catechin or robinetinidin; B stands for gallocatechin, C stands for catechin gallate and D for fisetinidin. The molecular weight of all these three structures must be increased by 23 Da to obtain the value of their characteristic peaks of the MALDI spectrum due to the Na<sup>+</sup> matrix enhancer used. Their real masses are: 290.3 Da, 306.3 Da 442.4 Da and 273.4 Da for A, B, C and D respectively. Many monomers can lose or gain some hydrogens. Their masses (including or not the Na<sup>+</sup> one) are summarized in **Table 1**, showing that BFP tannin extract is a predominantly procyanidin/prodelphinidin composed of catechin/robinetinidin, gallocatechin, catechin gallate and fisetinidin. There are some carbohydrates residues in this extract [10].



Figure 2. MALDI-TOF of BFP tannin in the 200 - 1500 Da range.



Figure 3. Structural formula of the mass of units (a) (b) (c) and (d).

Table 1. Monomers and oligomer structures	present in BFP tannin extract.
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M + Na <sup>+</sup> (exp.) Da	Species
290	Catechin/robinetinidin without + Na <sup>+</sup>
311	Catechin + Na <sup>+</sup>
326	Gallocatechin + Na <sup>+</sup> which lost 3H
467	Catechin gallate deprotonated + Na <sup>+</sup>
481	Galloylated catechin + Na <sup>+</sup> which lost H
494	Catechin + glucose protonated+ Na <sup>+</sup>
495	Catechin + glucose deprotonated + $Na^+$
496	Catechin + glucose triprotonated + Na <sup>+</sup>
640	Catechin gallate + glucose + Na <sup>+</sup> which lost 5H
670	Gallocatechin + glucose dimer tetraprotonated (without $\mathrm{Na}^{\scriptscriptstyle +})$
730	Galloylated catechin + fisetinidin which lost 2H (without Na <sup>+</sup> )
813	Fisetinidin trimer which lost 6H (without Na <sup>+</sup> )

# 4.2. BVP Characterization

### 4.2.1. ATR-FTMIR Analysis

**Figure 4** shows the FT-MIR analysis of BVP tannin extracted, indicating many peaks ascribed to condensed and hydrolysable tannins (**Table 2**). Indeed, the peaks 1734.8 cm<sup>-1</sup>, 1605 cm<sup>-1</sup>, 1518 cm<sup>-1</sup>, 1442 cm<sup>-1</sup>, 1367 cm<sup>-1</sup>, 1315 cm<sup>-1</sup>, 1282 cm<sup>-1</sup>, 1244 cm<sup>-1</sup>, 1200 cm<sup>-1</sup>, 1102 cm<sup>-1</sup>, 1048 cm<sup>-1</sup>, 867 cm<sup>-1</sup>, 817 cm<sup>-1</sup>, 778 cm<sup>-1</sup> have been reported in previous studies [8] [36]-[51]. The peaks at 1605 cm<sup>-1</sup>, 1518 cm<sup>-1</sup> and 1442 cm<sup>-1</sup> are attributed to vibrational motions of C=C in the aromatic rings [28]. The peaks at 1367 cm<sup>-1</sup>, 1315 cm<sup>-1</sup>, 1282 cm<sup>-1</sup>, 1244 cm<sup>-1</sup>, 1200 cm<sup>-1</sup>, 1040 cm<sup>-1</sup>, 867 cm<sup>-1</sup>, 817 cm<sup>-1</sup>, and 778 cm<sup>-1</sup> stand for the

ring substitution. Peaks 867 cm<sup>-1</sup>; 817 cm<sup>-1</sup>; 778 cm<sup>-1</sup> belonging to 900 - 740 cm<sup>-1</sup> regions are attributed to both –OH wagging of aromatic alcohols and out of plane bending of aromatic CH [28] [31]. Many peaks of the spectrum in **Figure 4** describe the presence of condensed tannins in this extract. Specifically, the peak at 1734 cm<sup>-1</sup> stretching belongs to flavonols; the peaks at 1518 cm<sup>-1</sup> and 1442 cm<sup>-1</sup> are typical to condensed tannins; the 1200 cm<sup>-1</sup> peak is attributed to C-OH aliphatic stretching of condensed tannin as reported by Jensen *et al.* [29] and Ragupathi *et al.* [30]. Many peaks describe the presence of proanthocyanidins in the BFP tannins extract, such as those at 1605 cm<sup>-1</sup>, 1442 cm<sup>-1</sup>, 1282 cm<sup>-1</sup>, 1244 cm<sup>-1</sup> and 1102 cm<sup>-1</sup> [26]. The 1282 cm<sup>-1</sup>, 1244 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> peaks are attributed to the presence of gallocatechin. The presence of hydrolysable tannin in this extract can be justified by the peaks at 1282 cm<sup>-1</sup>, 1244 cm<sup>-1</sup>.

### 4.2.2. MALDI-TOF Analysis

**Figure 5** shows the MALDI-TOF Spectra of BVP, indicating three monomers in the formation of the oligomers: A, B and C. To the mass A correspond two ures: Catechin or robinetinidin; B stands for gallocatechin and C for catechin gallate.









The molecular weight of all these three structures must be increased by 23 Da to obtain the value of their characteristic peaks of the MALDI spectra due to the Na<sup>+</sup> matrix used. Their real masses are: 290.3, 306.3 and 442.4 and respectively for A, B and C. Several monomers lost or gained some hydrogens, and their masses are summarized in Table 2.

# 4.3. CP MAS <sup>13</sup>C-NMR Spectra Analysis of BFP and BVP

Determining to which site of the flavonoids the carbohydrate residues are linked in the structure is of great interest. Figure 6 and Figure 7 show the <sup>13</sup>C NMR spectra, indicating that the variations of the structure on the standard procyanidin pattern are present in the BFP and BVP tannins. The peak at 182 (183) ppm could be ascribed to a quinone coming from the open air oxidization of phenol hydroxyl groups. The peak at 176 ppm is in the low range of a quinone band [10]. Likewise, this peak indicates the presence of a gallic acid residues linked in C3 to the heterocycle ring of a flavonoid structure, thus the presence of galloylated flavonoid monomers participating to oligomers formation. Afterward, the peak at 170 - 172 ppm indicates the presence of acid residues, hydroxy phenolic acids linked to C3 in proantho-cyanidins [47]. Specifically, the C5, C7 and C8a carbons of procyanidins appear between 160 ppm and 150 ppm [52]. Thus, the signals appearing at 157 and 156 ppm belong to the C5, C7 carrying OH groups and C8a of procyanidins [53]. Resonances around 146 ppm correspond to the C3 and C4 in B-ring sites of procyanidins, as reported by Santiago-Medina et al. [15]. In addition, signals at 132 (131) and 117 (116) ppm are assignable to C1 and C5 of procyanidin units respectively, consistent with the

M + Na <sup>+</sup> (exp.) Da	Species
269	Fisetinidin (without Na <sup>+</sup> ) which lost 4H
303	Gallocatechin (without Na <sup>+</sup> ) which lost 3H
311	Catechin + Na <sup>+</sup> which lost 1H
326	Gallocatechin + Na <sup>+</sup> which lost 3H
325	Gallocatechin + Na <sup>+</sup> which lost 4H
468	Catechin gallate triprotonated + Na <sup>+</sup>
480	Catechin galloylated + Na <sup>+</sup> which lost 2H
481	Catechingalloylated + Na <sup>+</sup> which lost H
495	Catechin + glucose deprotonated + Na <sup>+</sup>
494	Catechin + glucose protonated + Na <sup>+</sup>
497	Catechin + glucose tetraprotonated + Na <sup>+</sup>
640	Catechin gallate + glucose + Na <sup>+</sup> which lost 5H
669	Gallocatechin deprotonated digalloylated + Na $^{+}$
728	Galloylated catechin+ fisetinidin which lost 4H
843	Galloylated catechin gallate + gallocatechin + Na $^{+}$ which lost 3H

Table 2. Monomers and oligomer structures present in BVP tannin extract.



Figure 6. CP MAS <sup>13</sup>C NMR Spectrum of BFP tannin.



Figure 7. CP MAS <sup>13</sup>C NMR Spectrum of BVP tannin.

work reported by Davis et al. [54]. Around 120 ppm, signals are due to the C6 sites. Often, if the C6 and the C8 were linked to C4, their chemical shifts increased to 106 ppm. This peak could be recognized in the BFP and BVP tannin extract, most likely attributable to the interflavonoid C4-C8 and C4-C6 linkages [15]. The peak at 99 (100) ppm could be associated with C6, C8 and C10. The peaks at 74 and 76 ppm indicate the presence of acid residues, hydroxyl phenolic acid like molecules. In addition, 63 and 76 ppm peaks assigned to carbohydrate residues often joined on flavonoids. The shifts between 70 and 90 ppm can be attributed to the stereochemistry of the heterocycle C-ring of procyanidins. Thus, the peak around 76 ppm indicate C2 in cis form while the C2 in transform gives a peak at 82 (83) ppm [55]. The shifts around 65 ppm (64, 66) indicate the presence of catechinic acid like molecules. Likewise, the C4 sites involved in the interflavonoid bonds (C4-C6 or C4-C8) have a chemical shift at around 38 (37) ppm, as reported by Zhang et al. [55] and earlier by Cui et al. [56]. However, when the C3 is bearing a hydroxyl group alone the neighbouring C4 of the catechin gives the signal around 32 (31) ppm [15].

From these observations, BFP and BVP tannin extracts are procyani-

din/prodelphinidin types composed of catechin/robinetinidin, gallocatechin and catechingallate. There are some carbohydrates residues in these extracts.

## 4.4. Resin Mechanical and Thermal Behaviours

## 4.4.1. Board Density Profile

**Figure 8** and **Figure 9** show the density profile of the particleboards bonded with BFP and BVP tannins. The results imply good bending properties of the prepared particleboards. Indeed, average density values for all samples are in good agreement with international standards (630 - 700 kg/m<sup>3</sup>). These curves show a constant and linear density profile, that allows good internal bond strength.

# 4.4.2. Internal Bond (IB)

Particleboards manufactured with the tannin/NaOH/PKS and hexamine as hardener have exhibited good IB strength. Results of the dry IB strength are



Figure 8. Density profile of BFP tannin bonded particleboard.





consistent with the NF EN 312-2 (1996) standard. These formulations give  $[IB_{(BFP)} = 0.92 \text{ MPa} \text{ and } IB_{(BVP)} = 0.71 \text{ MPa}] 0.35 \text{ MPa}$  (EN 312). The values were obtained at 210°C during 8.5 min. This means that tannin developed from barks of *Ficus platyphylla* and *Vitellaria paradoxa* have good adhesive performances using PKS powders in particleboards.

### 4.4.3. Thermo Mechanical Analysis (TMA)

The results of the TMA analysis were obtained by preparing and testing specimens of PKS/BVP and PKS/BFP particleboards panels. The maximum value obtained for the Modulus of Elasticity for PKS/BFP and PKS/BVP panels is definitely encouraging. Indeed, the TMA results for these specimens presented the maximal values of 2091 MPa for PKS/BFP and 1989 MPa for PKS/BVP (**Figure 10**), in comparison with the value of 2450 MPa of wood/UF panels [57]. The MOE of the PKS/BVP and CKS/BFP particleboards give a good indication of the final strength of the tested adhesive and the possible final performance of the tested adhesives for the targeted application.

#### 4.5. TEM Analysis: Majority Phase and EDS spectra

**Figure 11(a)** and **Figure 11(b)** of Particle 1 shows typical morphology with irregular, somewhat layered shape but with inhomogeneity. Despite the thermochemical treatment underwent by the barks used herein, the TEM-observed ultrastructure of BVP is vegetal-like, containing a very tinny cell wall of 25 - 50 nm. Spot X-ray microanalyses were taken from five location-particles (arrows in **Figure 11(a)**; they show quite a range in composition. **Figure 11(b)**, for example shows location 1 mostly composed of C, O with Si and some K, Mg. **Figure 11(c)** shows location 2 that mostly contains silicon oxide with Al, Ca and K likely in C matrix. **Figure 11(d)** of location 3 mostly has silicon oxide with Al,



Figure 10. TMA analysis of PKS/BVP and PKS/BFP coupons MoE versus temperature.





**Figure 11.** (a) Particle 1 majority phase; (b) X-ray spot spectrum of location 1; (c) X-ray spot spectrum of location 2; (d) X-ray spot spectrum of location 3; (e) X-ray spot spectrum of location 4; (f) X-ray spot spectrum of location 5.

Ca and K likely in C matrix. Figure 11(e) of location 4 mainly has calcium oxide or carbonate. Figure 11(f) of location 5 shows that this region largely contains silicon oxide.

As would be expected, the particle appears to be a composite of several components. Note that Cu is from the support grid. To sum up, most of the material appears to be an amorphous phase composed mainly of carbon/oxygen with small amounts of K, Ca and Mg. These particles have a very irregular morphology. Secondary phases or contaminants appear to be mainly silicon oxides and calcium oxide or carbonate. These secondary phases can be found as separate particles or agglomerated with the primary phase. Also detected were various other materials in small amounts, e.g. graphite.

# **5.** Conclusion

This paper reports a comprehensive tannin extraction method for preparation and application of tannin-based resins. Structures of tannin from BFP and BVP were elucidated on the one hand by MALDI-TOF and FT-MIR mass spectrometry, as well as by CP MAS <sup>13</sup>C-NMR analysis. Analyses showed that these tannins investigated in this study are procyanidin types and indicated the presence of robinetinidin, fisetinidin, catechin, gallocatechin and flavonoid units as well as some galloyl residues linked to the C3 sites of the flavonoids. Applying this method to BFP and BVP has permitted to highlight the required components to be used in a resin formulation process. Chemical analyses have shown that BFP and BVP tannins are made up of oligomers corresponding to monoflavonoid units. It also contains proanthocyanidins having epicatechin monomers. The content of fisetinidin units has been reported to be negligible. The presence of these chemical constituents confirms that BFP and BVP tannins are condensed and could then be readily used as adhesive materials. This observation was confirmed in the manufacturing of PKS based particleboards as well as the subsequent IB and TMA tests carried out. The test results are close to those of the wood/UF particleboards. Moreover, ACTEM with the addition of energy dispersive X-ray analysis was carried out. The results show a vegetal-like ultrastructure having a very tinny cell wall. In addition, most of the BVP tannin resin appears to be an amorphous phase mainly composed of carbon/oxygen with small amounts of K, Ca and Magnesium Mg. These particles have an irregular morphology. Secondary phases or contaminants appear to be mainly silicon oxides and calcium oxide or carbonate.

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