

Thermomechanical performance of rigid bio-foams elaborated with African resources

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Abstract

Rigid bio-foams were developed using local natural resources and particularly the Vitellaria paradoxa tannin, furfuryl alcohol from sugar cane bagasse, Vachelia nilotica bio-hardener extracts reinforced with Androgon particles fibers. The tannin extract obtained is a condensed type with a predominance of quercetin and chalcone monomers associated to some residues of furan. The compressive strength, thermal conductivity and thermal resistance of the best rigid bio-foam obtained were respectively 0.4 MPa; 0.021 W/m.K and 0.714 m². K/W. The Andropogon particles fibers used improve the thermomechanical characteristics of the rigid bio-foams developed. This tannin can be used as a lignocellulosic adhesive. These rigid bio-foams can be used as insulating materials in the building industry.

Keywords: *Rigid bio-foams, Vitellaria paradoxa tannin, sugar cane bagasse furfuryl alcohol, Vachelia nilotica bio-hardener, thermomechanical.*

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I. Introduction

Faced during the last decades by the numerous environmental problems, scientists interest focused all over the world on the fragility of ecosystems that could lead to catastrophic, harmful scenarios. Thus, various research teams in the world, and particularly in Africa, have begun to work on the use of natural resources to replace oil-derived synthetics one. Then the valorization of local materials has been integrated into various applications, and the derived insulating materials used in the construction industry were so born. This is the case of new materials elaborated by various researchers around the world [1, 2, 3]. In addition, tannin rigid foams have also emerged from the early work of Meikleham and Pizzi [4]. Following this initial research, studies on behavior control of tannin-based foams have become of interest from an ecological viewpoint [5, 6]. Most materials developed during these last decades and usable in the building sector were elaborated with synthetic hardeners such as formaldehyde, glyoxal and hexamine [6, 7]. New types of foaming systems have been used to elaborate foams based on tannins, such as chemical foaming by reaction with isocyanate and water [8] or using mechanical agitation with a nonionic surfactant having an influence on properties [9,10,11]. The versatility of polyurethane foams and their susceptibility to modification allows them to replace several synthetic materials previously used (PVC, rubber, polystyrene), and of natural origin (leather) [12, 13]. Many researchers have proposed works synthesizing rigid polyurethanes [14, 15]. In the same ideas, rigid polyurethane foams

containing lignin oxyalkylated with ethylene carbonate and polyethylene glycol [16] and others foams using palm oil-based polyester polyol [17] were elaborated. In general, tannin-based foams are formed mainly in an acidic medium but also in a basic medium [4; 18]. These foams so prepared are of growing interest in the building industry.

It is in this perspective of developing performant foams, limiting unnecessary energy losses, to add value to local materials and reduce the importation of raw materials usable in the development of composites materials that a rigid foam based on African resources such as *Vitellaria paradoxa* tannin extract, furfuryl alcohol from sugar cane bagasse, *Vachellia nilotica* locally extracted exudate as bio-hardener and reinforced with *Andropogon* particles fibers has been developed.

The plants mentioned above have a considerable importance in Africa. The *Vitellaria paradoxa* nuts almonds are used to make shea butter and as traditional medicine. It grows in the central and western savannah of Africa. The *Andropogon* is recognized in sub-Saharan Africa for its ornamentals values. The *Vachellia nilotica* is recognized for the use of their leaves, pods, seeds, wood, bark, etc... It is also used as livestock fodder, for reforestation of areas undergoing desertification, for the production of gum arabic, tannins, dyes, firewood, as well as for its medicinal properties and the sugarcane is cultivated mainly for the production of the sugar extracted from their stems.

II. Materials and methods

2.1. Extraction of sugar cane bagasse furfuryl alcohol

The sugar cane bagasse powder and the diluted sulphuric acid were mixed in the beaker using a manual stirrer. After a few minutes, the sulphuric acid and distilled water (according to the distribution of table 1) were added to the mixture to obtain the hemicelluloses to be then hydrolyzed in xylose. The complete mixture was then transferred to a round-bottom flask containing glass beads, to proceed to the distillation, increasing the substrate temperature to 168°C using a cottonseed oil bath to collect the distillate fractions. Next, we decanted. The extracted product was then decanted and a colourless or yellow oily product was obtained with an almond-like odour that became brown/black when in contact with the air: it was the furfural. Finally, the collected furfural and a microscopic fungus (*Saccharomyces cerevisiae*) were mixed in a jar (respecting the proportions mentioned in table 2) and stored at ambient temperature (37 °C) for 24 hours. At the end of the process furfuryl alcohol was obtained. Its extraction procedure is summarized in figure 1.

Table 1: Different constituents used for furfural

Constituents	Quantities
Dry powder (g)	50
H ₂ SO ₄ (ml)	500
H ₂ O (ml)	50
N _a Cl (g)	40
Temperature (°C)	165

Table 2: Ferment (*saccharomyces cerevisiae*) mass as function of the volume of furfuraldehyde

Samples	<i>Vitellaria paradoxa</i> Tannin(g)	sugar cane bagasse Furfuryl alcohol (g)	Water (g)	Diethyl ether (g)	Paratoluene sulfonic acid at 65 % (g)	<i>V. nilotica</i>	<i>Andropogon</i> fibers (g)
M ₁	25	20	23	4	5	13	10
M ₂	25	17	23	4	6	11.5	13.5
M ₃	25	15	2	4	5	13.5	0

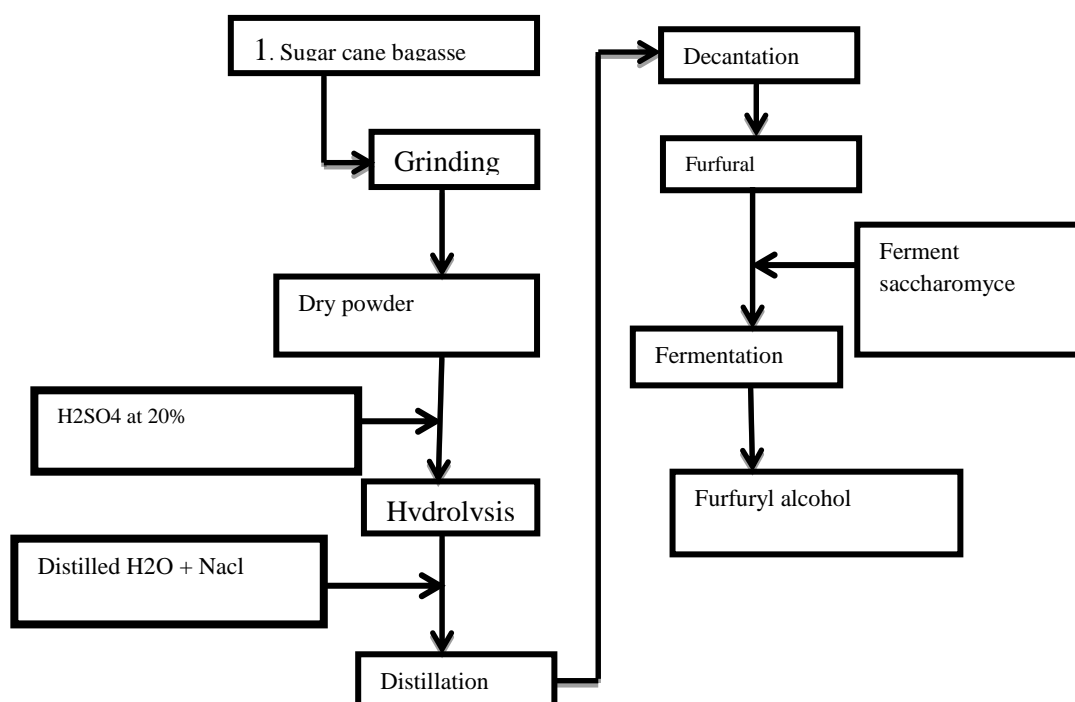


Figure 1: Schematic sequence of the extraction of furfuryl alcohol from sugar cane bagasse

2.2. *Andropogon* stems fibers extraction

The dry *Andropogon* stems extract from the far north of Cameroon were crushed in particles of 1-2 mm dimensions.

2.3. *Vitellaria paradoxa* bark tannin extraction

Crushed *Vitellaria paradoxa* bark was introduced into a bath containing hot water (in a 1:6 ratio) and a solution containing 0.4% sodium bicarbonate and 2% sodium bisulfite. The mixture was continuously stirred mechanically at 60° C during 4 hours. The mixture was then filtered and concentrated by rotary evaporator. After these steps, a tannin powder was obtained by freezing the liquid fraction using liquid nitrogen and a laboratory freeze-drier [1].

2.4. MALDI TOF analysis of tannins extract

The sample was dissolved in acetone (4 mg/ml), this solution was next mixed in a 50:50 proportion with a matrix solution of 2, 5-dihydroxybenzoic acid and acetone (10 mg/ml acetone). This was then mixed with NaCl. Finally, the mixed solution was placed on the MALDI sample MALDI target and evaporated before placing it in the spectrometer. The spectra were recorded on a KRATOS compact MALDI AXIMA PERFORMANCE TOF 2 instruments [1, 7].

2.5. *Vachelia nilotica* hardener extraction

The *Vachelia nilotica* tree trunk was injured at several places at 1 cm depth and after a few minutes, an organic liquid of high viscosity started oozing out. This liquid was covered with a plastic sheet and left to dry for two days. The exudates were then collected and dried at ambient temperature during three weeks. Finally, the dried exudates were powdered easily to stock and use as hardener [2]. The *Vachelia nilotica* tree used came from the forest of Zidim in the far north region of Cameroon.

2.6. Rigid bio-foams elaboration

2.6.1. Materials

The *Vitellaria paradoxa* tannin powder extracted according to the method described above was used for the preparation of the foams. The chemicals used to prepare the foams were: sugar cane bagasse furfuryl alcohol used as heat generator and strengthener, the *Vachelia nilotica* bio-hardener used as crosslinker, water used as solvent, diethyl ether used as blowing agent, and para-toluene-4-sulphonic acid (pTSA, 65 wt.% aqueous solution) used as catalyst.

2.6.2. Foams preparation

Three types of rigid bio-foams (M_1 , M_2 and M_3) were elaborated at 120 °C according the components shown in Table 3.

The furfuryl alcohol, the diethyl ether and the bio-hardener were mixed in an aqueous solution contained in a beaker at room temperature. Then, the tannin extract was added to the solution followed by the addition of the *Andropogon* stems fibers in the proportions shown in Table 3 under continuous vigorous stirring. After homogenisation, the whole solution was mixed with *para*-toluen sulfonic acid for 20 s and placed in a ventilated oven preheated at 35°C. After an induction time of around 30 s, foaming occurred spontaneously in the oven. Once fully hardened, some minute later, the foams was left drying at room temperature for 24 hours and extracted from their molds. The materials were placed again in the oven at 35°C during 4 additional hours in order to remove the remaining traces of blowing agent. At the end of the process, the samples M_1 , M_2 and M_3 were cut off the foam blocks in samples of 3 cm x 3 cm x 1.5 cm size to be characterized.

2.7. Thermomechanical characterization of rigids bio-foams

The following rigid bio-foams characteristics were determined at a density of 0.05 g/cm³:

- Compressive strength

The compression strength was measured using an INSTRON 4467 universal testing machine according to the NF EN 13164 Norm [19]. The samples size of 1.5 cm x 3 cm x 3 cm x were compressed towards the direction of growth, at a rate of 2 mm/min, and the compression strength of the samples was measured considering the maximal resistance end of the elastic region, when the first layer of the foam breaks.

- Thermal conductivity

The measurements were done by applying three different temperature ranges 3 to 18 °C; 18 to 32.5 °C, and 32 to 47°C on 3 cm × 3 cm × 1.5 cm samples using a λ -Meter Lambda-Messtechnik EP500e (Dresden, Germany) equipment according to the ASTM C 518-85 relevant standard [20]. The formula used to determine the thermal conductivity λ was:

$$\lambda = \Phi \times \Delta X / \Delta T$$

where: λ : Thermal conductivity in W/m K.; Φ : Heat flux flowing through the sample, W/m² . ΔX : sample Thickness in m.

ΔT : The difference in temperature between the hot and cold surfaces of samples in K.

- Thermal resistance

The thermal resistance R (m². K /W) value was considered as the ratio of the samples thickness (expressed in meter) and the thermal conductivity (λ).

2.8. Rigid bio-foams thermogravimetric analysis

100 mg of powdered rigid bio-foams was placed on a balance located in the furnace of a thermogravimetric analyzer TGA NETZSCH STA 449F3 Jupiter (Selb, Germany) and heat was applied in the 20 and 900°C temperature range for 30 min at a heating rate of 5°C/min under argon gas.

III. Results and discussions

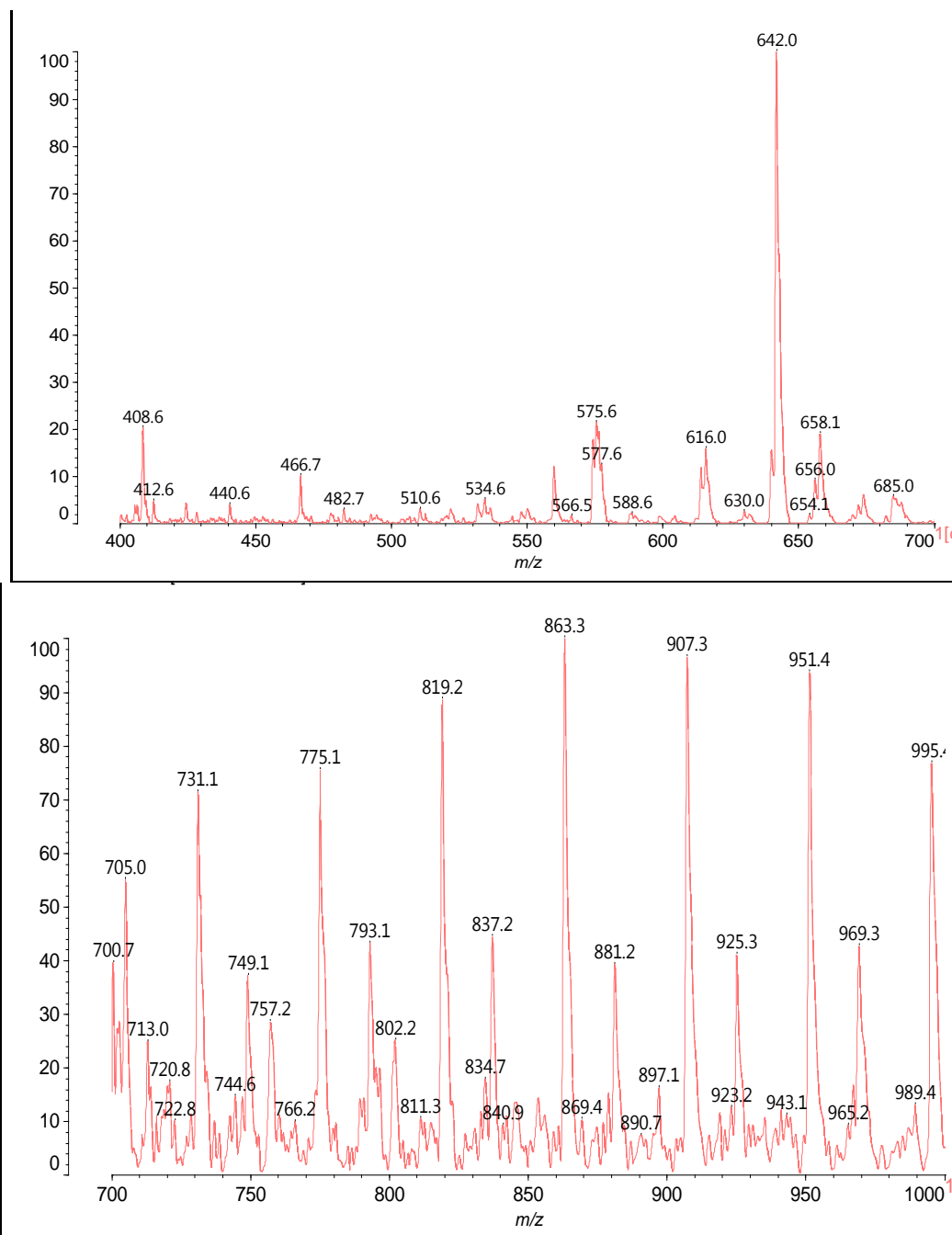
3.1. Furfuryl alcohol extraction

The furfuryl alcohol from cane bagasse was extracted locally at 24% yield. It is a light orange-yellow liquid, soluble in water, of low molecular weight alcohols and soluble in most organic solvents.

3.2. MALDI-TOF analysis of *Vitellaria paradoxa* tannin extract

The examination of different peaks of the MALDI TOF analysis spectra (Figure 2) in the range tested showed the presence of several oligomers in the *Vitellaria paradoxa* tannin extract. They consist of some monomer units such as catechin gallate, myricetin, galocatechin, quercetin, cyanidin, fisetinidin, apigenin chalcone and some furan residues. The molecular weight of these monomers is shown in Table 4 and are respectively 442Da; 318 Da; 306Da; 302 Da; 287 Da; 274 Da; 270 Da, 208 Da and 68 Da (for furan). Some of these oligomers are protonated and others are linked or not with the Na⁺ used to enhance MALDI spectra. The presence of Na⁺ (23 Da) is due to the NaCl added to the matrix. The normal values of different molecular weight are obtained by deducting 23 Da from the Da value of each different peak. From the different monomeric units constituting this tannin extract (Table 3), it is clear that this extract is of the condensed type with a predominance of quercetin, chalcone and some residues of furan. Thus, it can be used as an adhesive for wood [1, 2]. The preponderant presence of the two monomers above confers to this tannin a theurapeutic power usable in the pharmaceutical industry because quercetin is an important flavonoid that protects the human body from the damaging effects of free radicals and oxidative damage, reduces inflammation and associated pain, protects the brain and nervous system, and facilitates blood flowing [21]. Quercetin is also important in the production of

collagen, essential in the formation of body tissues and reduces hypertension [22]. As for chalcone, it is considered to have antibacterial, antihelmintic, antiulcer, antiviral and insecticidal properties [23].



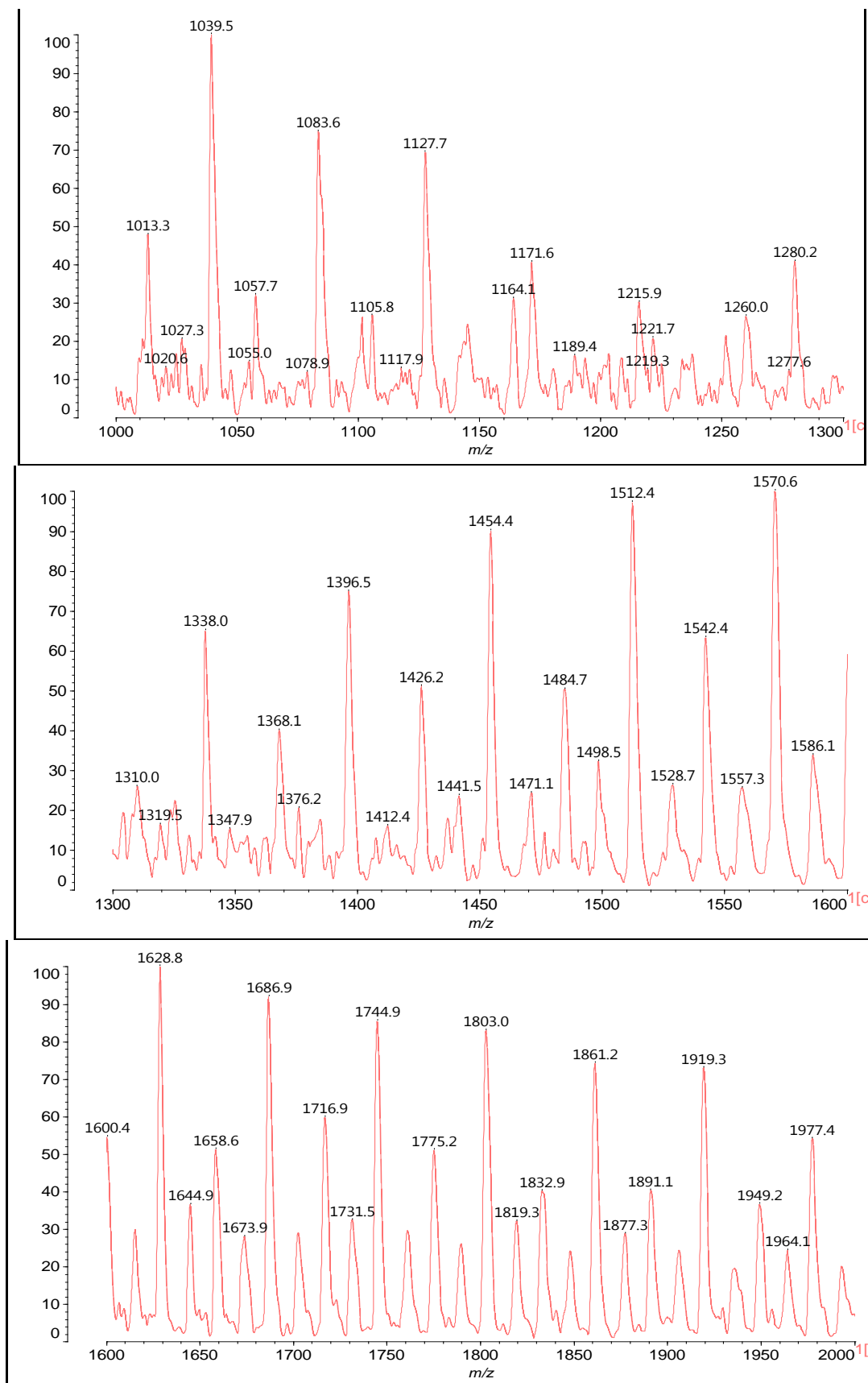


Figure 2. MALDI TOF curve of *Vitellaria paradoxa* bark tannin extract in the range 400 to 2000

Table 3: Monomers and oligomers present in tannin extract

A : Monomers ;

B : Peaks

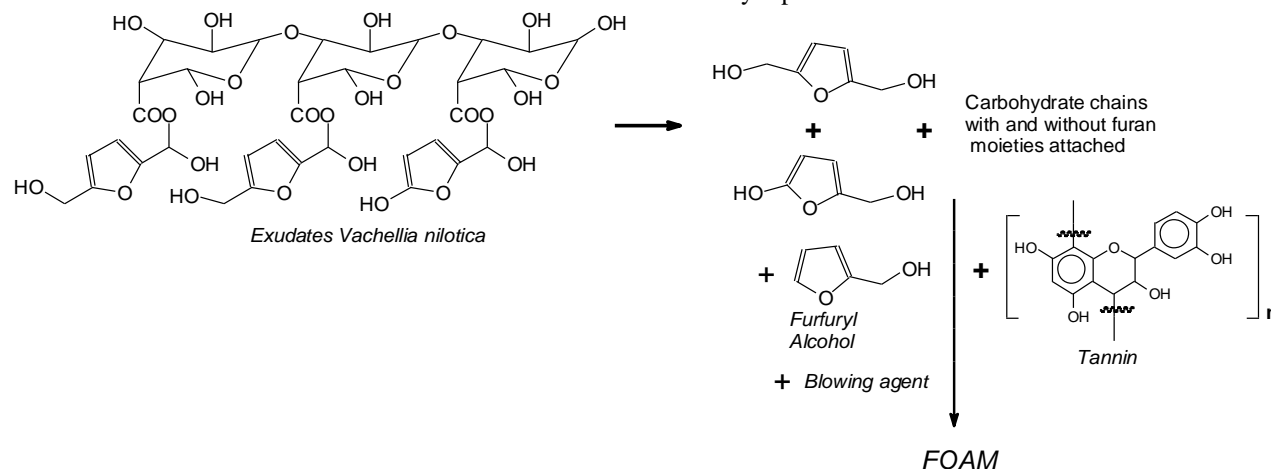
A \ B	442	318	306	302	290	287	274	270	208	68	23	+1	-1
408		1								1	1		1
412							1			2		2	
440									2		1	1	
466	1										1	1	
482							1		1				
510				1					1		1	1	
534				1					1		1	1	
566							1	1			1		
575				1			1						
577				1			1					1	
588					1		1				1	1	
616			1	1							1	1	
630					1		1				1	2	
642		1		1							1		1
654					1		1			1	1		1
656					1		1			1	1	1	
658		2									1		1
685								1	2				
700			1	1						1	1	1	
705						1			2			2	
713							1		2		1	1	
720				1					2			2	
722			1						2				
731					1				2		1	2	
744	1			1									
749	1		1									1	
757	1		1								1	2	
766	1			1							1		1
775							1	1	1		1		
793			1					1	1		1	2	
802				1				1	1		1		1
811				2					1				
819			2						1				
834				2					1		1		1
837				2					1			2	
840			1	1					1		1	1	
863				2	1			1				1	
869				1			1	1			1		

881				1				1	1			1	
890				1	1		1				1	1	
897		1				1		1			1		1
907	2										1		
923			1	1	1								
925			2		1						1		
943			3								1	2	
951				1					3		1		
965		1							3		1		
969				2			1			1	1		
985			3							1			1
995		1	1	1						1			
1013	1						2				1		
1020			1				1		2		1		
1027	1				1			1			1	2	
1039	1				1								
1055	1				2							1	
1057	1			1	1						1		
1078	1				2						1	1	
1083				2				1	2				
1105				2				1	1		1		
1117				2	1				1				
1127	2	1									1	2	
1164				2	1			1					
1171	2					1							
1189				2	1			1			1	2	
1215	2		1								1	2	
1219				2	1						1		
1221			1	3							1	2	
1260		3	1										
1280		3	1								1		2
1277	2			1						1	1		
1310	1	1			1			1			1		
1319	1		1	1				1					1
1338		1		2				2					
1347	1			3									
1368	1	1	1	1									
1376	1		1	2							1	1	
1396				2	1			1	1			1	
1412			1	2				1	1		1	1	
1426				3	1				1		1		

1441				4					1		1	2	
1454									7				
1471	2	1						1					
1484	1			2					2		1		
1498			1	2	1		1				1	1	
1512	2			2							1	1	
1528			2	2	1						1		1
1542			2	3							1	1	
1557			1	2					3		1		
1570			1	3	1					1			
1586		3	1	1							1	1	
1600	3						1						
1628	1			2	1			1			1		1
1644	1		1	2				1			1		1
1658	1		2	2									
1673	1			4							1		
1686				4				1	1				
1716				5					1				
1731			1	3					2			2	
1744			1	4					1		1		1
1775				4			1	1			1		
1803				5					1		1		
1819			2	4									1
1832				4					3				
1861			1	3					3		1	2	
1877													
1891				3			1	1	2		1	2	
1919				4				1	2		1	2	
1949	1			4			1				1	2	
1964	1			4	1						1	1	
1977	1			5							1	2	

3.3. Rigid bio-foams elaboration

The mechanism of formation of these bio-foams can be schematically represented as follows:



The chemical characteristics of the various components and their chemical interactions have been described in detail in a number of articles [1, 2, 3, 4, 8, 11].

3.4. Thermomechanical characterization of rigid bio-foams

- Compressive strength

From the compressive strength results (Table 4), it is necessary to provide sufficient energy to achieve complete crushing of these materials, i.e. 0.4 MPa for M₂, 0.22 MPa for M₁ and 0.17 MPa for M₃. The M₃ sample without *Andropogon* fiber particles does not resist to compression. The compressive strength of the M₁ and M₃ foams are slightly inferior to that of Phenol-Formaldehyde-chestnut tannin (PFT) foams [24]. The M₂ sample which contains more *Andropogon* fiber particles than M₁ presents good mechanical characteristics. This means that these particles improve the mechanical performance of rigid bio-foams. The shape of the obtained stress-strain curves (figure 3) is typical of other phenol-formaldehyde foams [25, 26] and of other structural foams in general [27], with a long serrated plateau originating from the coexistence of collapsed and uncollapsed zones, representative of brittle foams undergoing successive cell wall fractures [5].

Table 4: Thermomechanical properties of rigid bio-foams

Characteristics	M ₁	M ₂	M ₃
Density (g/cm ³)	0.05	0.05	0.05
Compressive strength (MPa)	0.22	0.4	0.17
Thermal conductivity (W/m K)	0.03	0.021	0.07
Thermal resistance (m ² . K /W)	0.5	0.714	0.214

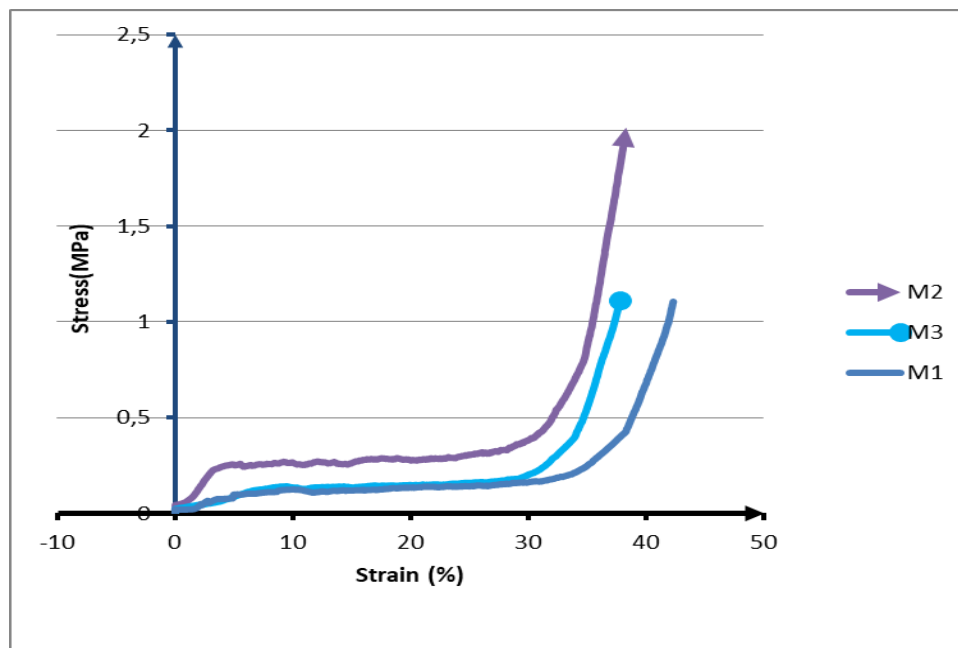


Figure 3. Stress–strain curves of bio- foams elaborated

- Conductivity and thermal resistance

The thermal conductivity calculated represents the heat ($W / (m.K)$) which can be transferred in rigid bio-foams in a given time. Thermal resistance (R) expresses the foam ability to resist heat exchange. The lower is the thermal conductivity, the better as insulating materials are the bio-foams prepared. The thermal conductivities of M_1 foams ($0.03 (P / M k)$) and M_2 ($0.021 (P / m k)$) are lower than those of PF foam ($0.0435 W / M k$) but being slightly denser, it means that they are slightly better insulating materials than Phenol-Formaldehyde (PF) foams [24]. The rigid bio-foams M_1 and M_2 can be considered as thermally insulating, their thermal conductivity (λ) values being lower than those of some various insulating materials used in the building industry [28, 29].

- Rigid bio-foams thermogravimetric analysis

The examination of the TG and DTG curves (Figures 4, 5, 6 and 7) showed three mass degradation phases of the rigid bio-foams as a function of temperature. Figure 4 shows the mass loss of the M_2 sample. Three important phases are identifiable on the TG curve in Figure 3: the first is located between the starting temperature and $147^\circ C$. It reflects the beginning of the component degradation such as unreacted furfuryl alcohol whose flash point is between $65^\circ C$ and $75^\circ C$; the paratoluen sulfonic acid mass loss whose melting temperature is at 106° ; the decomposition of the chalcone, whose melting temperature is between $57^\circ C$ and $59^\circ C$, and of certain volatile organic compounds. The second phase of the M_2 mass loss curve is between $147^\circ C$ and $450^\circ C$ with its decomposition peaks located at $290^\circ C$ and $400^\circ C$. It reflects the start of the degradation of some of the rigid components such as furanic oligomers the degradation of which begins at $170^\circ C$. At $390^\circ C$, furan residues contained in the foams and the furfuryl alcohol ignite. The quercetin which predominates in the tannin used begins to decompose at $316^\circ C$ [31].

The third phase of the M_2 rigid bio-foam degradation occurs between $450^\circ C$ and the end of thermal analysis. It is during this phase that materials which had already started to degrade in phase 1 and certain rigid elements such as paratoluen sulfonic acid complete their decomposition [31].

The three degradation phases of M_1 rigid bio- foams are in the ranges: [$40^\circ C - 140^\circ C$] with a peak located at $48^\circ C$; [$140^\circ C - 575^\circ C$] with a peak located at $250^\circ C$, $470^\circ C$ and [$470^\circ C - 900^\circ C$] a peak located at $765^\circ C$.

The three mass loss ranges of the M_3 sample are: [$40^\circ C - 165^\circ C$], [$165^\circ C - 439^\circ C$] and [$439^\circ C - 900^\circ C$].

The TG curves in Figures 4, 5 and 6 show that M_1 , M_3 and M_2 rigid bio-foams have the same degradation behavior, but the phases limits (inferior and superior) of these three rigid bio-foams differs [31].

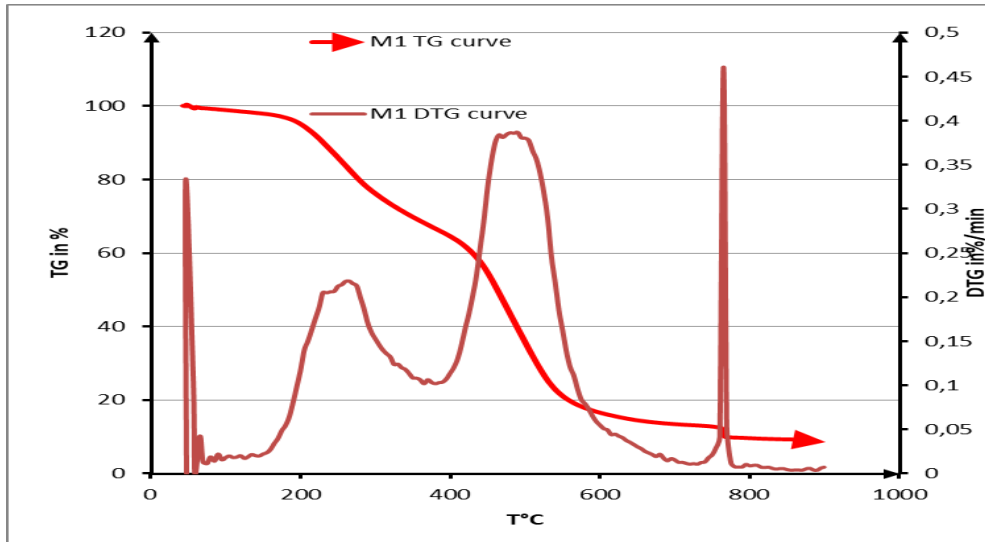


Figure 4. TG and DTG curves of thermogravimetric analysis of rigid bio-foam M₁.

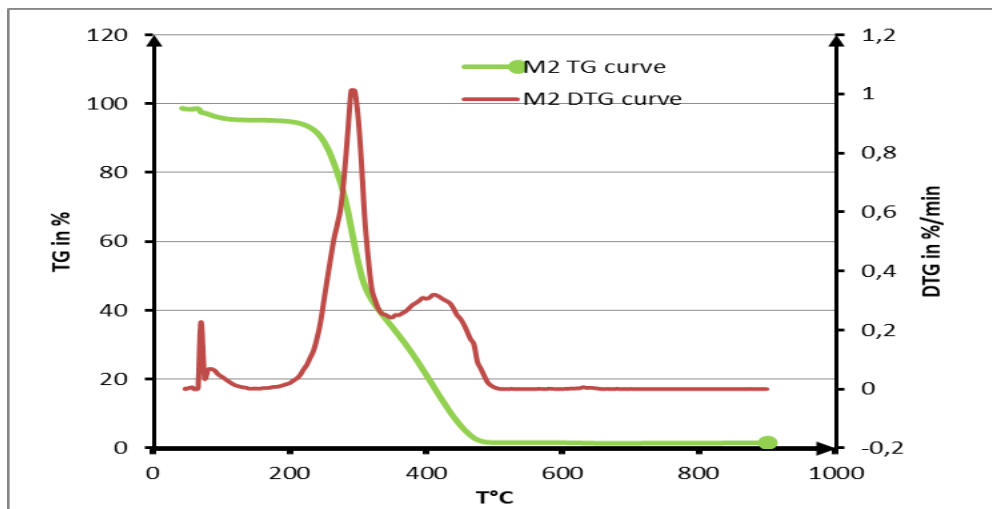


Figure 5. TG and DTG curves of thermogravimetric analysis of rigid foam M₂.

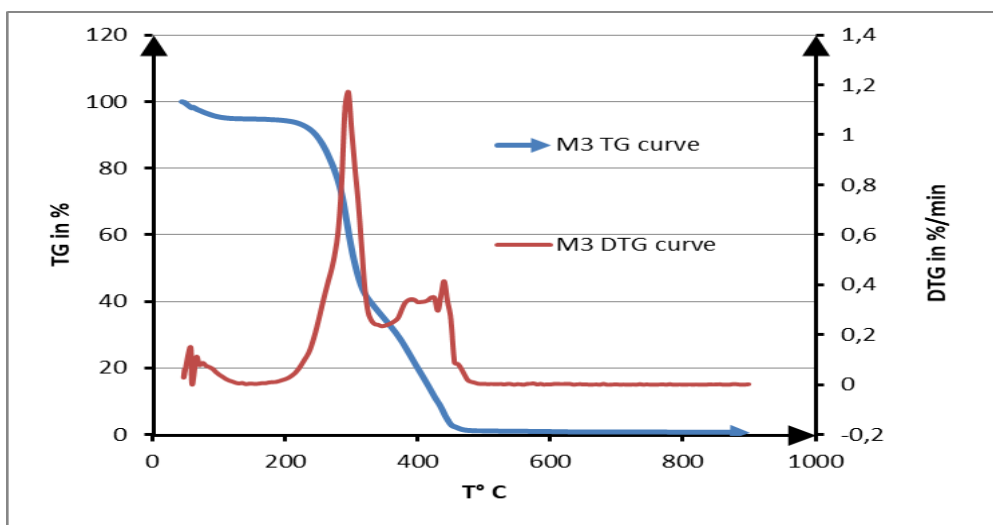
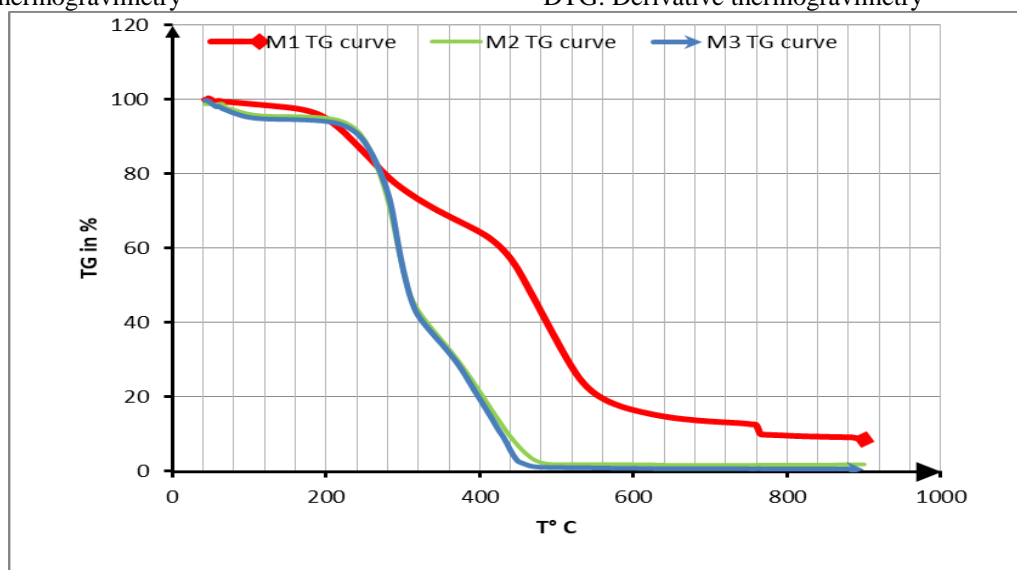


Figure 6. TG and DTG curves of thermogravimetric analysis of rigid foam M₃.

TG: Thermogravimetry

DTG: Derivative thermogravimetry

Figure 7. TG curves of M₁, M₂ and M₃ rigid bio-foams

IV. Conclusion

African resources have been evaluated for the production of rigid bio-foams. Tannin, furfuryl alcohol and bio-hardeners extracted exudates are of considerable interest for the African economy. The use of these local resources in the manufacturing of rigid foams is of primary interest. The *Vitellaria paradoxa* tannin extracts, *Vachelia nilotica* bio-hardener and sugar cane bagasse will help to limit the importation of materials usable in the production of composite materials and will effectively contribute to the fight against environmental pollution. The use of *Andropogon* fibers improves the mechanical characteristics of the rigid foams produced.

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