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RHEOLOGICAL ANALYSIS OF BIO-ADHESIVES BASED CASSAVA STARCH AND MILICIA EXCELSA'S TANNIN

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ABSTRACT

This work investigated the rheology of two news adhesives using Vachelia nilotica exudate as a hardener. The first was developed with cassava starch (C1) and the second with Milicia excelsa tannin (C2). The Milicia excelsa species are very rapid growing and have a high percentage of tannin. Their behavior was studied by using Dynamic Mechanical Analysis (DMA) and the evaluation of viscosity and activation energy. Their activation energies calculated at the gel times were respectively 949.25 KJ.mol-1 and 105.565 KJ.mol-1. Their dynamic viscosity decreases with temperature, The C2 adhesive had better damping properties than the first C1. The storage mechanical energy of C2 adhesive was higher than that of the C1 one. Thus, at their transition temperature, their respective stiffness was of 11540 and 11550 MPa respectively. Their glass transition temperatures are 132°C and 150°C respectively. The gel times of C2 at the temperatures studied were shorter than those of C1. The mechanical properties (IB, MOE and MOR) of particleboards PBC2 using bio adhesive C2 are better than of particleboards PBC1 using bio adhesive C1. The average values of IB, MOE and MOR of PBC2 are respectively recorded o are respectively 0.41, 2008.35, 16.74 MPa.

KEYWORDS: Rheology, adhesives, behavior, mechanical properties, reactivity, stiffness.

1. INTRODUCTION

Nowadays, adhesives are among the most present materials in everyday life. Their properties can be adapted and used in a wide variety of field applications. Bio-sourced adhesives are increasingly being developed, and their development has progressed in recent years in terms of global capacity.

Several natural polymers, such as proteins, starches, tannins, etc., are used in the manufacture of composite materials [1, 2, 3, 4]. Some polymers are hard and brittle, others are tough and impact-resistant, while still others are soft and flexible. The manufacture and characterization of polymers are, therefore, at the heart of many industries and specialized research structures. Numerous avenues of research have been developed to improve mechanical properties, such as the development of adhesives using biopolymers (biomass, proteins, lignin, tannin, etc.). Combined with natural fibers, among all such works, we can cite the thermal analysis and aging monitoring approach to bio-sourced resins [5, 6], the development and characterization of soy protein adhesives for wood bonding [7, 8] and the use of tannins, gum arabic or bio hardener in the manufacture of composite materials [5, 9, 10, 11]. In light of this work, the use of adhesives based on tannin, starch, and lignin is an exciting alternative to synthetic resins [12]. Such adhesives are already being used successfully in European, American, and African countries [13]. However, despite the growing interest shown in these materials, much remains to be done, particularly in terms of mastering their mechanical behavior, even though a great deal of work has already been done [5, 14, 15, 16]. With production of over 40 million tonnes per year in Central Africa, cassava feeds half a billion people in the sub-Saharan region. Consumed from leaf to root, cassava has excellent potential to contribute to food sufficiency in the region. In economic terms, it's an opportunity to industrialize the production. What's more, jobs could be created for a commodity that can be grown and processed in any location. Cassava is the second most important source of starch after maize, and recently developed varieties produce starch that is much sought-after by industry [12, 17, 18, 19, 20]. Demand for cassava as a raw material for the production of bioethanol, a biofuel used in gasoline engines, is growing.

The cassava is one of the most widely consumed tubers in Cameroon and Africa in general. It has grown in all the country's agro-ecological zones and has flooded the local market over the years. The *Milicia excelsa* species are very rapidly growing and have a high percentage of tannin, which can contribute to satisfying demand in different parts of the world. Cassava starch and *Milicia excelsa* tannin are under-valorized in the wood and textile industries, particularly by using them as adhesives. The exudate used as hardener were extracted from *Vachelia nilotica* bark. It is widespread in the northern part of Cameroun.

The aims of this study are first to study the physical and rheological behavior of two new adhesives developed with cassava starch (C1) and Milicia excels tannin (C2) using a bio hardener (Vachelia nilotica exudates), which are fundamental to control quality and optimizing the physical-thermomechanical performance of such manufactured materials. Secondly to valorize the tannin of *Milicia excelsa* and promote the use of cassava *Starch ad*hesive in wood industries.

To achieve these objectives, Dynamic Mechanical Analysis, viscosity studies, and physico-mechanical properties were determined.

2. MATERIALS AND METHODS

1.1 Extraction of tannin

Milicia exelsa bark powdered was introduced into a solution containing 2% sodium bisulfite and 0.5% sodium bicarbonate. The ratio of bark to water was 6:1.

The principle consisted of heating the mixture in bath water at 60°C for 4 hours. This step was followed by separation and filtration, and then the tannin was concentrated at 60°C using a rotary evaporator to obtain a pasty, reddish-colored tannin ready for the manufacture of adhesives [2].

1.2 Extraction of the bio-hardener

On a *Vachelia nilotica* tree trunk that has been wounded for at least 2 days, a pasty organic liquid called exudate appears, ready for resin development [9]. For preservation purposes, this liquid can be dried at 30°C.

1.3 Attenuated total reflectance fourier transform infrared (ATR-FT IR) analysis

The *Milicia exelsa* tannin extracts were analyzed with a Perkin Elmer Frontier ATR-FT device equipped with a diamond crystal. The tannin extract was laid on the obtained eye of the equipment above. The spectra obtained was studied in the fingerprint region between 1800 and 600 cm^{-1}.

1.4 Use of cassava starch

The cassava starch was bought from the local market (Mokolo-Yaounde)

1.5 Formulation of adhesives

The principle consisted to mix all the constituents (without hardener and NaOH) in a beaker and stirring it at 60°C for 5 minutes. At the end of this time, add the exudate of Vachelia nilotica as hardener accompanied of NaOH (33%) solution to adjust the pH. Then, heat the mixture again for 5 min [2]. The different percentages of adhesives constituents are summarized in Table 1.

Table 1. Adhesives constituents

	adhesives 1 (C1)				**adhesives 2 (C2)**			
Constituents	NaOH (g)	Cassava starch(g)	Water (g)	hardener (g)	Tannin (g)	Eau (mg)	NaOH (g)	hardener (g)
Quantities	0.33	30	65	5	30	65	0.33	5

1.6 Gel time

The principle of gel time determination consisted to introduce about 10 g of adhesive into a test tube, then immerse this tube in a beaker containing hot water at variable temperature and stirring the solution using a twisted wire until gelation was reached. Gel time was measured from the moment the tube was introduced into hot water at a T_i temperature (i =60°C, 65°C, 70°C, 75°C, 80°C, 85°C).

1.7 Dynamic Mechanical Analysis (DMA): Storage- modulus, loss – modulus, complex-modulus and glass transition temperature analysis

The principle consisted of applying 25 mg of adhesive onto two beechwood plates, each measuring 17 x 5 x 1.1 mm. Then, they were placed directly against each other in the thermodynamical analyzer oven. They were tested in three-point flexion over a range of 18 mm by applying a force cycle of 0.1/0.5 N on the specimens, each force cycle of 12 s (6 s/6 s). The METTLER TOLEDO TMA 40 (Switzerland) thermodynamic analyzer used was connected to a TC11 processor and a computer. The moisture content of the two beechwood plates was between 8 and 12% [2]. Modulus as a function of time or temperature is measured and provides information on phase transitions

The temperature at which the loss factor is the highest is called the glass transition temperature Tv.

1.8 Activation energy

The activation energy was deduced from Arrhenius' law using gel time method determination. It was taken as the slope of equation (1). This energy was calculated at five different temperatures. It is at these temperatures that, different gel time are obtained.

The slope obtained from the curve $ln(t_{gel}) = f(1/RT)$ is equal to the Activation Energy.

$K = a\, e^{(-E/RT)}$

$lnK = A + (E/RT)$

$$ln\,(t_{gel}) = A + \frac{E}{RT} \quad (1)$$

A= Constant
E = Activation Energy
t_{gel}=Gel time of adhesive at natural pH (s)
R= Perfect gas constant =8.3145 J. mol^{-1}. K^{-1}
T=Temperature in °K

1.9 Viscosity of adhesives

The Brookfield RV viscometer (Brookfield, ES distributors, Garches, France) at 27, 20 ,100 rpm was used to determine viscosity for temperatures between 30 to 75°C.

1.10 Internal Bond (IB) strength

The Internal Bond of particleboards was determined according the International standard NF EN 312-2 (1996), using INSTRON 4467 universal testing machine [21].

1.11 Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

The Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) were determined according to International standard NF EN 310 (1993) using INSTRON 4467 universal testing machine. The values of MOE and MOR retained correspond to the average of 10 samples in each case. These values were calculated using the formulas below [22]:

$$\mathrm{MOE} = \frac{L^3}{4be^3}\frac{F_2 - F_1}{a_2 - a_1}$$

$$MOR = \frac{L^2}{2be^2}F_r$$

$F_1 = 10\%F_r$ $\qquad$ $F_2 = 40\%F_r$

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;
F1: strength causing a displacement ai, i = <1, 2 >
Fr: breaking strength,

1.12 Thickness Swelling and Water Absorption

The Thickness Swelling ratio (TS) and the water absorption rate (TA) were determined according to standard NF-EN 317 on 10 test specimens of dimensions 50 mm × 50 mm × 12 mm. The thicknesses and masses are initially measured using a Vernier caliper and a scale, then each sample is immersed in water for 2 and 24 hours. After removing each sample in water, they were dehydrated and placed in a refrigerant for 1 hour.

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

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

Where ei : thickness of the specimen before immersion (mm);
ef : thickness of the specimen after immersion (mm).
mi initial mass of the specimen before quenching (g);
mf final mass of the test piece after quenching (g)

3. RESULTS AND DISCUSSION

The Examination of the ATR-FTIR spectrum (Fig 1) of *Milicia excelsa* tannin extract in the 1800-600 cm^{-1} range revealed various functional groups, which are recapitulated in Table 2 with three commercial tannins (Chestnut, Pine and Quebracho). The peak located at 1735 cm^{-1} is associated with the C=O of flavonols or to the oxidation of some OH groups of the flavanol molecules [23]. The 1702 cm^{-1} peak is specially attributed to the C=O of flavanols. The peaks 1610, 1514 cm^{-1} are specially represented the tannins [24] and they represented also the vibrations of the C=C bonds of the aromatic rings [25], or the aromatic structure of the OH group which keeps it in its orthogonal position. The vibrations of the C=C bonds of the aromatic rings, the presence of the catechin, the asymmetric and symmetric stretching of the aromatic C-O, as well as the OH groups of the hydrolysable tannin were associated with the peak 1522 cm^{-1}. The 1485 cm^{-1} peak is assigned to the vibrations of the C=C bonds of the aromatic rings. The peak 1363 cm^{-1} is assigned to the C–H deformations region and ring substituent [25]. The 1286 cm^{-1} peak is represented the symmetric elongation of the C-OH group of the pyran ring of condensed tannins. The peak at located at 1237 cm^{-1} is attributed to the stretching of C–O carboxyl group which stands for gallic acid or some carbohydrates residues. The 1195 cm^{-1} peak is occupied by aromatic C-H bending and aliphatic C-OH stretching specific to proanthocyanidins and prodelphinins [25]. The peak at 817 cm^{-1} is attributed to aromatic C–H out of plane bending. 777 cm^{-1} peak is attributed to the C–H out of plane bending of the B ring of flavonoids [26]. This peak located at 777 cm^{-1} can be attrivuated to the presence of a condensed tannin group. Because of the presence of numerous polyphenolic groups in its chain, the extracted tannin demanded the presence of condensed type tanning material-rich compounds [26]. All these findings show the existence of condensed tannin in *Milicia excelsa* tannin extract. In addition, the FTIR peaks assignment in **Table 2** revealed several similarities with other commercial tannins. The *Quebracho*, *Pine* tannin and *Milicia* excelsa have several common peaks. This experimental tannin showed a similar pattern to *Quebracho*, *Pine* tannin [27, 28].

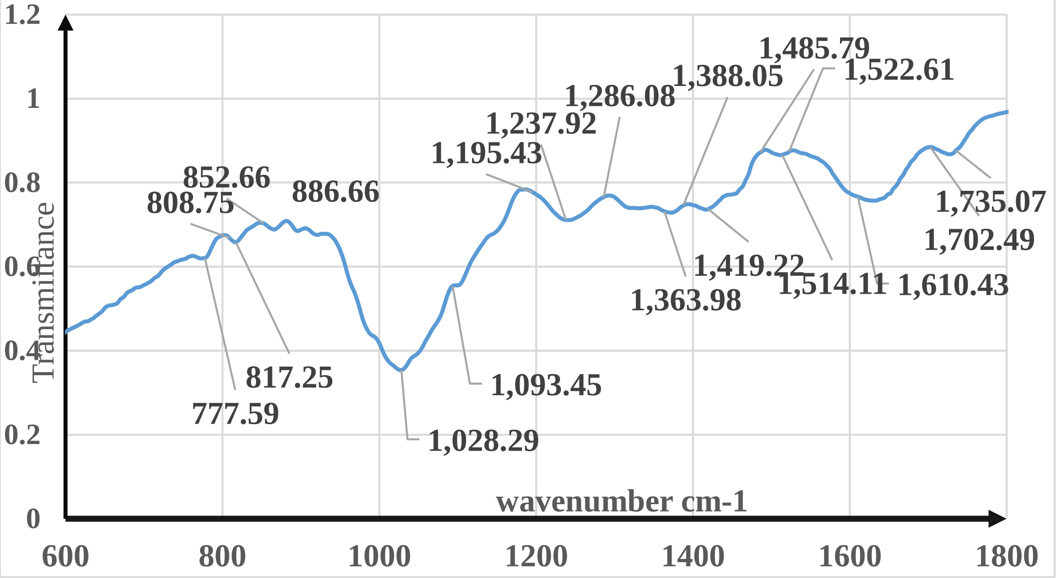

Figure 1: ATR-FT IR spectrum of Milicia excelsa tannin in the range 1800 and 600 cm^{-1}

2.1 Gel time and adhesives activation energy

The curves of gel time of adhesives C1 and C2 as a function of temperature, at natural pH (pH=5.6 and pH=7.9 respectively) are shown in figure 2.The gel time of adhesive C2 at all the temperatures studied was shorter than that of C1, this being due to the higher reactivity of tannin and other adhesives components. The gel time of both formulations decreases with temperature. The shortest gel times occur at 85°C, meaning that the C2 adhesive loses its flow properties before the C1 one. The know these gel times is very useful for determining the pressure cycle during materials manufacturing, because the pressure applied before the gel point causes adhesives creep [29].

Table 2. Summary of ATR FT-IR signals and related assignment of Milicia ex.tannin and three commercial tannins

Chestnutt[27]	*Pine* [28]	*Quebracho*[27]	*Milicia ex.*	**Assignment**
1713	1734		1735 1702	C=O of esters or flavonols or to the oxidation of some OH groups on the flavanol.
1612	1612	1609	1610	Vibrational motions of C=C groups in the aromatic rings or the aromatic structure of the OH group which keeps it in its orthogonal position.
1516	1518	1512	1514	Aromatic C=C asymmetric stretching H of phenol, ellagic acid, pyrogallol, pyrocatechol and epi-catechin.
1531		1524	1522	Aromatic C=C symmetric H stretching gallic acid, resorcinol, phenol, pyrocatechol, and catechol.
1450	1448	1450	1485	Aromatic asymmetric C-H bending, ring B C-C stretching, aromatic C-O stretching of gallic acid, ellagic acid, flavanone, and n- and epi-catechin.
1416			1419	Deformation of aliphatic C-H of flavanol, and glucose.
1377	1359	1373	1388 1363	C-H symmetric bending and O-H bending of phenol, resorcinol, pyrocatechol, hydroquinone, flavone,pyrogallol, catecol, and n- and epi-catechin.
1315				Gallic/ pyrogallic ring C-O stretching of phenol, resorcinol, pyrocatechol, flavanone, and Pyrogallol.
	1284		1286	Symmetric elongation of the C-OH group of the pyran ring

				of condensed tannins.
1254	1237		1237	C-O single stretching of gallic Acid.
1215			1195	Aromatic C-O stretching, ester carbonyl C-O-C stretching, ring gallic /pyrogallic C-O. stretching, aromatic symmetric C-H bending of pyrocatechol, hydroquinone, ellagic acid. and pyrogallol, and OH in plane deformation of gallic acid
1150	1163			C-O aromatic ring stretching of phenol, resorcinol, pyrocatechol, and hydroquinone.
1142				C-O-C glycosidic C-O ring stretching of flavone, and n-catechin
1107	1073	1099	1093	C-H bend. phenolics in-plane of pyrocatechol and hydroquinone.
1072				H-C=C bend. (Ring) CH deformation of phenol, resorcinol, and flavanone.
1022		1026	1028	Aromatic (esters)C-O stretching and aromatic symmetric C-H bending in-plane of pyrocatechol, glucose, and ellagic acid
995		999		C=C aromatic stretching deformation of hydroquinone, glucose, and pyrogallol.
1215			1195	Aromatic C-O stretching, ester carbonyl C-O-C stretching, ring gallic /pyrogallic C-O. stretching, aromatic symmetric C-H bending of pyrocatechol, hydroquinone, ellagic acid and pyrogallol, and OH in plane deformation of gallic acid.
1150	1163			C-O aromatic ring stretching of phenol, resorcinol, pyrocatechol, and hydroquinone.
1142				C-O-C glycosidic C-O ring stretching of flavone, and n-catechin.
1107	1073	1099	1093	C-H bend. phenolics in-plane of pyrocatechol and hydroquinone.
1072				H-C=C bend. (Ring) CH deformation of phenol, resorcinol, and flavanone.
1022		1026	1028	Aromatic (esters)C-O stretching and aromatic symmetric C-H bending in-plane of pyrocatechol, glucose, and ellagic acid
995		999		C=C aromatic stretching deformation of hydroquinone, glucose, and pyrogallol

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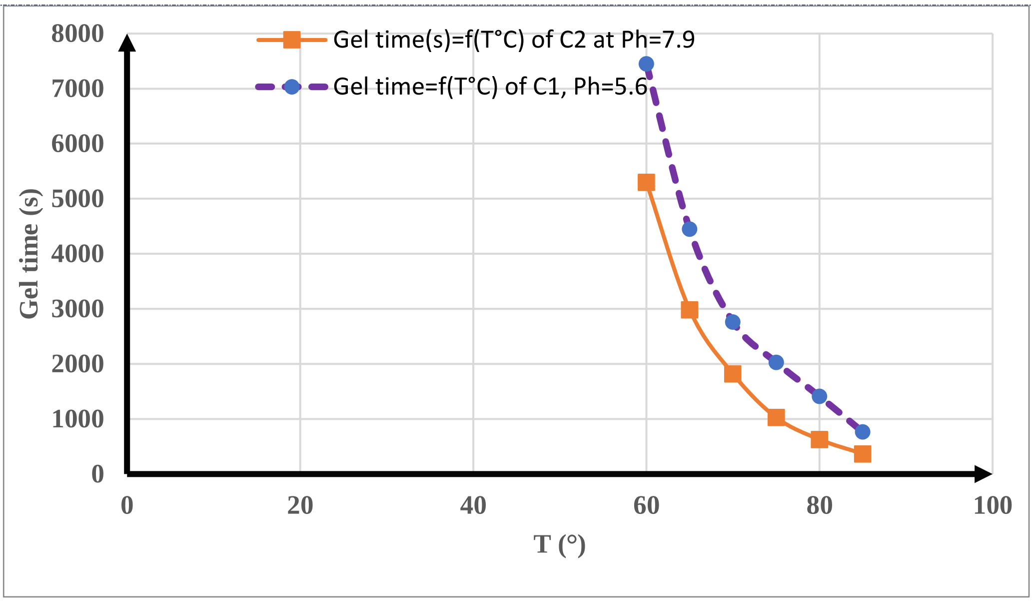

Figure 2. Gel time depending temperature of C1 and C2 at natural pH

According to figures 3 and 4, the activation energies of the C1 and C2 adhesives calculated at the gelation temperatures are 949.25 kJ.mol^{-1} and 105.565 kJ.mol^{-1} respectively. This means that the activation energy of the C2 adhesive polycondensation reaction of tannin with its hardener is lower than that of the C1 one. C2 molecules must collide at high speed and temperature compared to those of C1. Such a low level of the activation energy of C2 explains its better reactivity and thus its shorter gel times than C1[29].

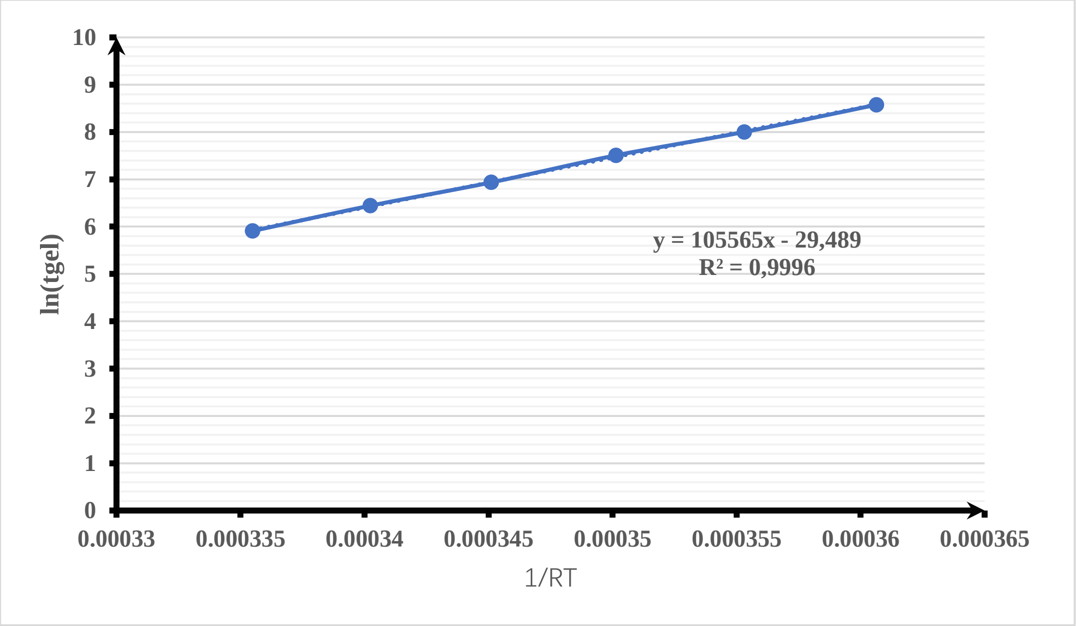

Figure 3. Activation Energy of adhesive C2

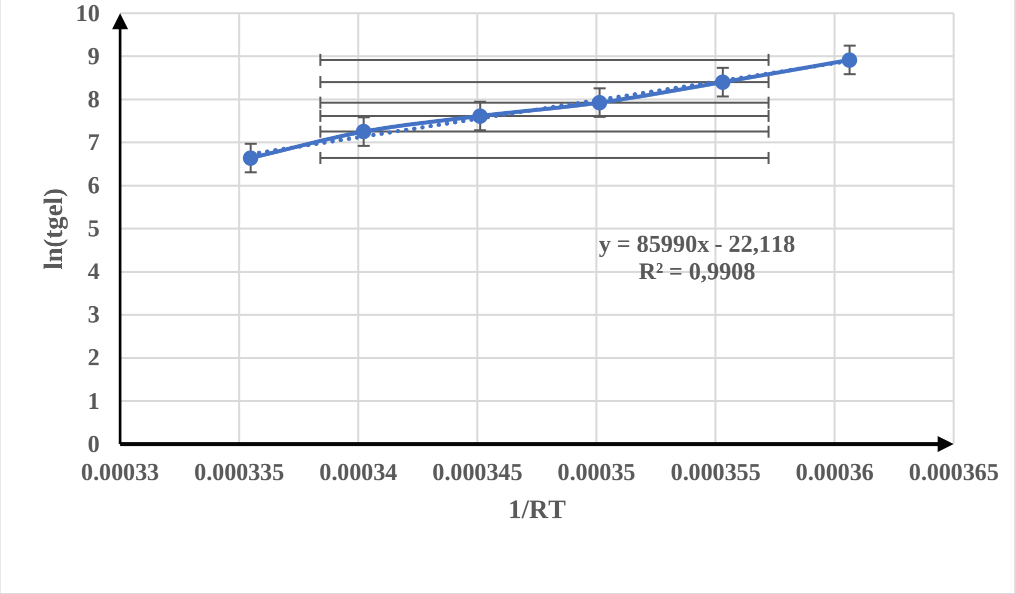

Figure 4. Activation energy of adhesive C1

2.2 Viscosity of adhesives

Figure 5 shows the dynamic viscosity variation of adhesives C1 and C2 as a function of the temperature. For temperatures between 30 and 70°C, the dynamic viscosity of C2 and C1 decreases. This means that high temperatures allow polymer chains to move freely reducing resistance to flow, while at low temperatures, the relative motions of the polymer chains are restricted, resulting in a higher viscosity. The C2 adhesive is more viscous than C1, which could be due the higher molecular weight oligomers in C2. Thus, temperature control is primordial to achieve the desired flow behavior during material manufacture.

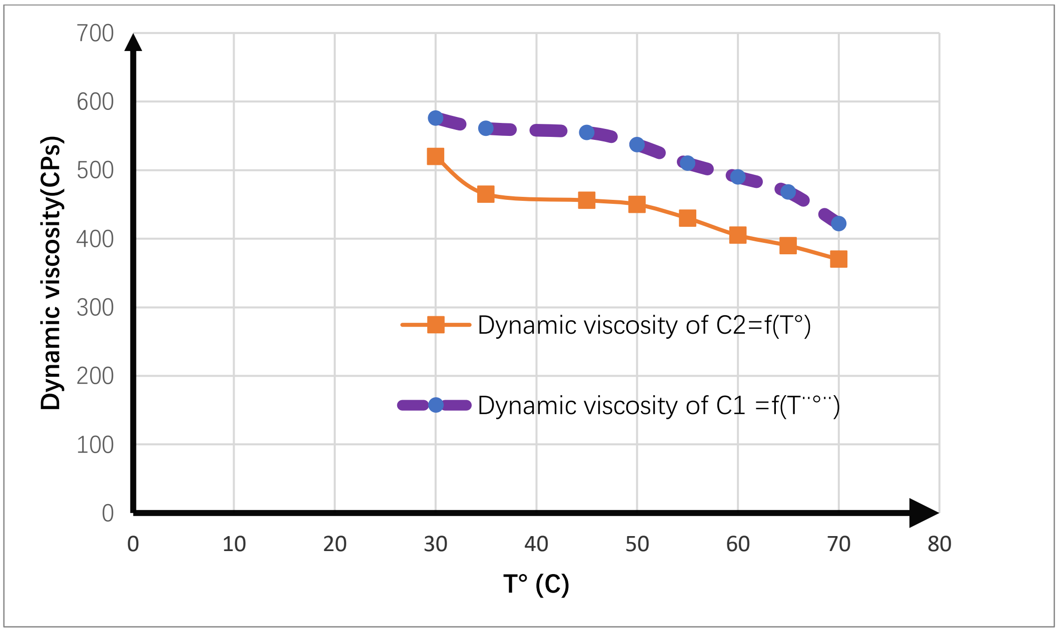

Figure 5. Dynamic viscosity depending the temperature

2.3 Dynamic Mechanical Analysis (DMA)

2.3.1 Storage- modulus, loss - modulus and complex-modulus

The curves in Figures 6 and 7 shows respectively the variation of the storage-modulus (E') and of the loss-modulus (E") as a function of the temperature. The loss modulus represents the damping behavior, indicating the adhesive's ability to disperse mechanical energy through internal molecular movements. Thus, as the curves of the C2 loss modulus are higher than those of the C1 one, the C2 adhesive has a better damping behavior than the C1 one. The C2 storage modulus, corresponding to the mechanical energy stored by C2 during loading, is also higher than that of C1 from their cross-over point at 135°C, this being considered to be the glass transition point [30, 31].

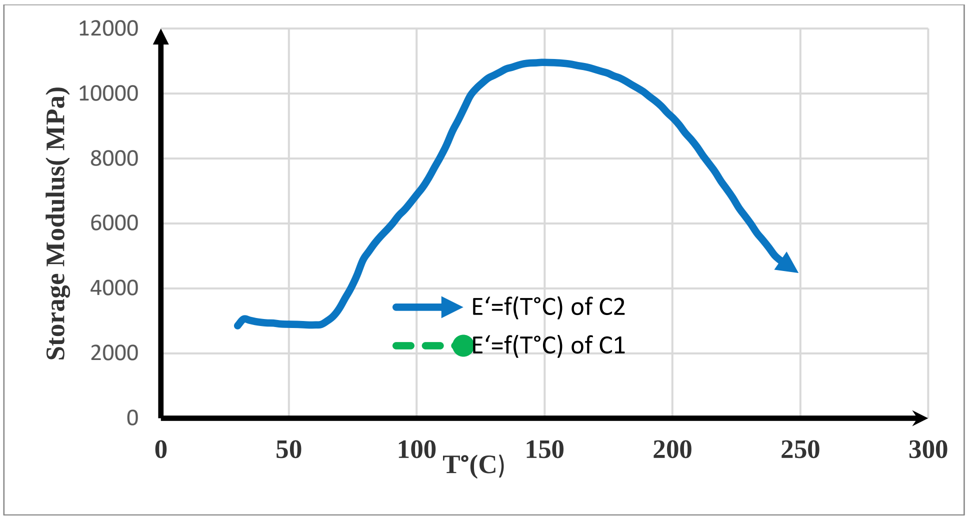

Figure 6 . Variation of storage-modulus depending the temperature

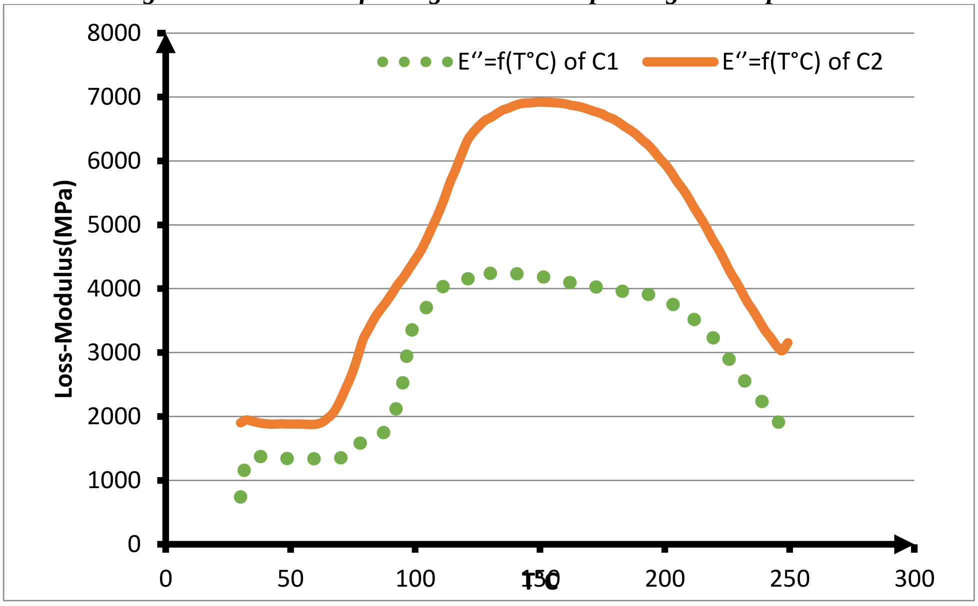

Figure 7. Variation of loss-modulus depending the temperature

The curves in figure 8 shows that C1 loss modulus is higher than its storage modulus at temperatures above 34°C. After 34°C, no intersection point E' = E" could be observed and none of the curves obtained correspond to the case E' > E. It seems that this rheological behavior is characteristic of much more alkaline solutions [30].

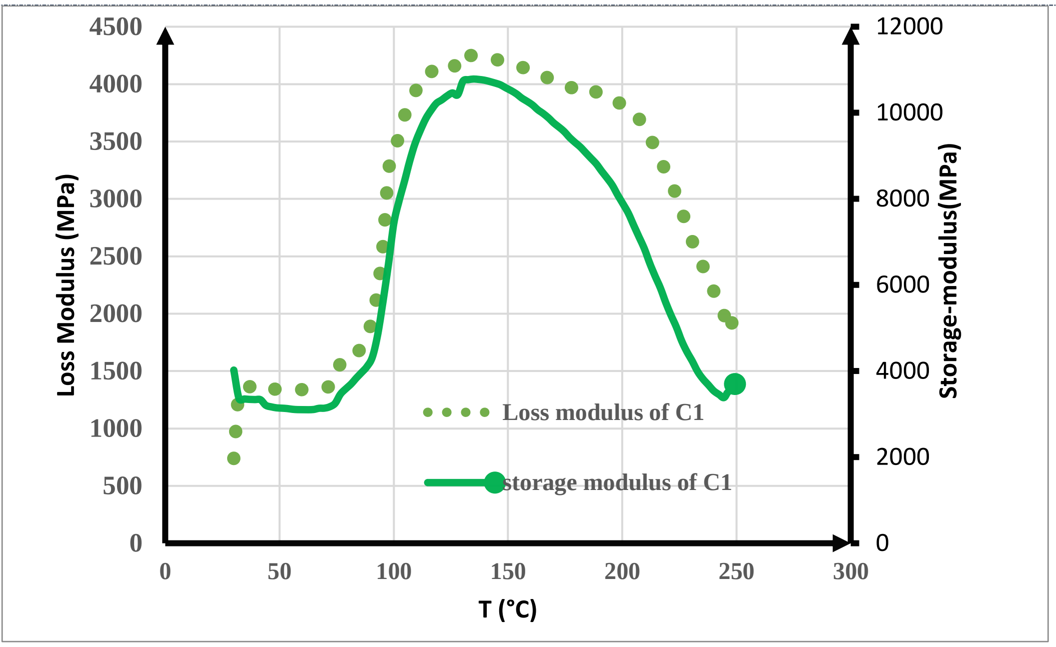

Figure 8. Loss modulus and storage modulus of C1 depending the temperature

In figure 9, it can be seen that between 118°C and 200°C, E' > E", this phase corresponds to the hardening of the resins. Beyond this phase, the two moduli are almost identical.

The figure 10 and 11 shows the variation of C1 and C2 complex modulus depending temperature. The norm of the complex modulus |E*| is an indicator of the material's stiffness. The maximum value of each curve corresponding to C1 and C2 stiffness are 11540 and 11550 MPa respectively. This means that the stiffness of C2 is slightly higher than that of C1. These values are 132°C and 150°C respectively. The ratio between loss modulus and the complex modulus, on the one hand, and that of storage modulus and complex modulus, on the other gives:
$E^*=E''/\sin\delta$
$E^*=E'/\cos\delta$

The complex modulus breaks down into two parts [31]: a real part and an imaginary part. we can write:
$e^{i\phi} = \cos\phi + i\sin\phi$. Consequently: $|E^*|\,e^{i\phi} = |E^*|\cos\delta + i\,|E^*|\sin\delta$
The complex modulus is then: $E^* = E' + i\,E''$
The E' component represents the real part of the complex modulus and quantifies the stored elastic energy [29, 32].
E’’ is the reversible modulus associated with the elastic part of adhesives.

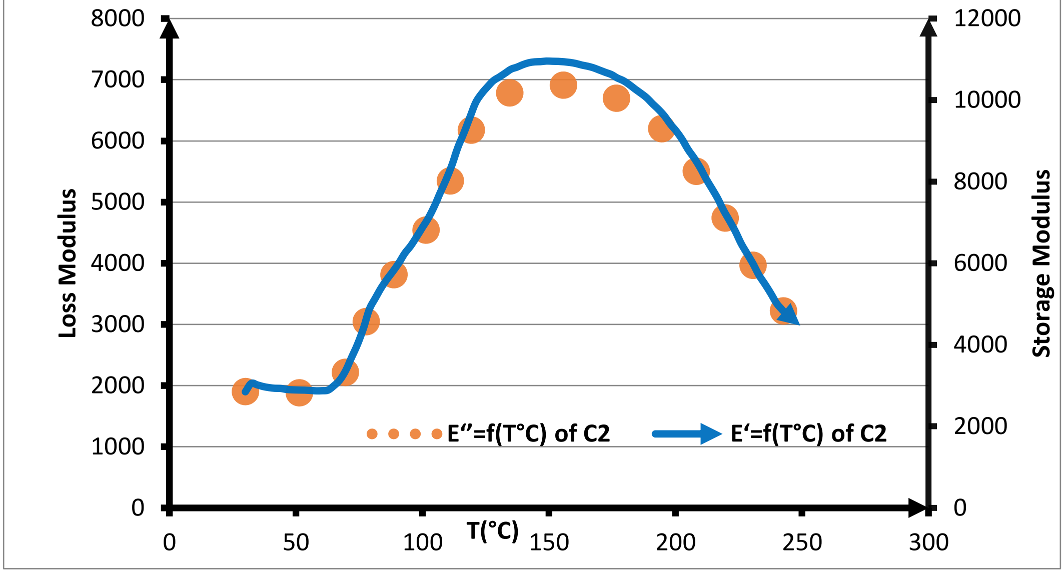

Figure 9. Loss modulus and storage modulus of C2 depending the temperature

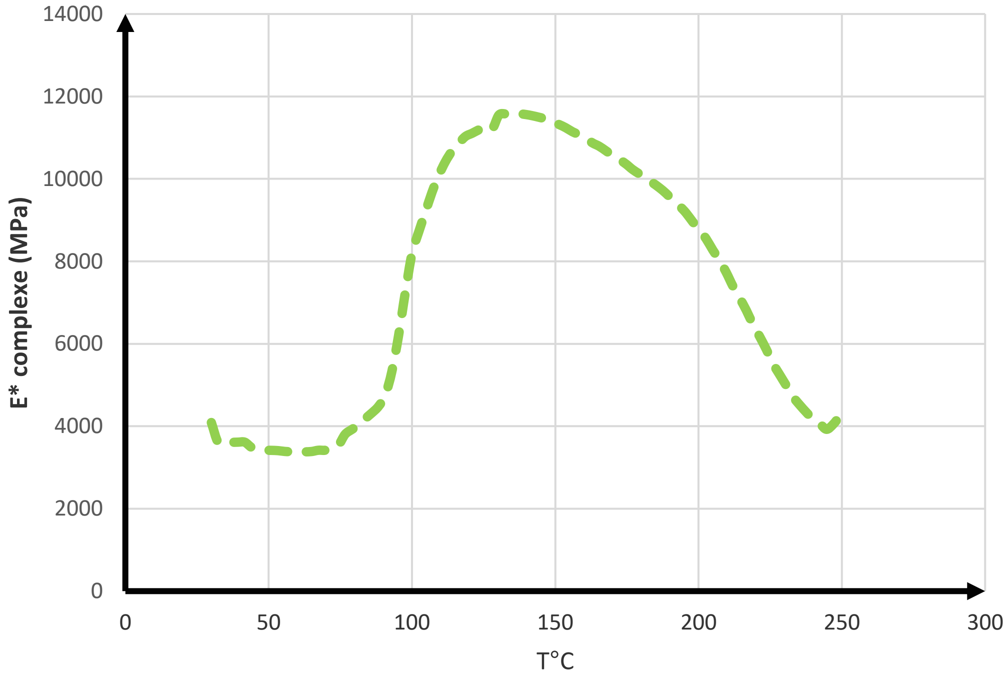

Figure 10. Complexe modulus of C1 depending the temperature

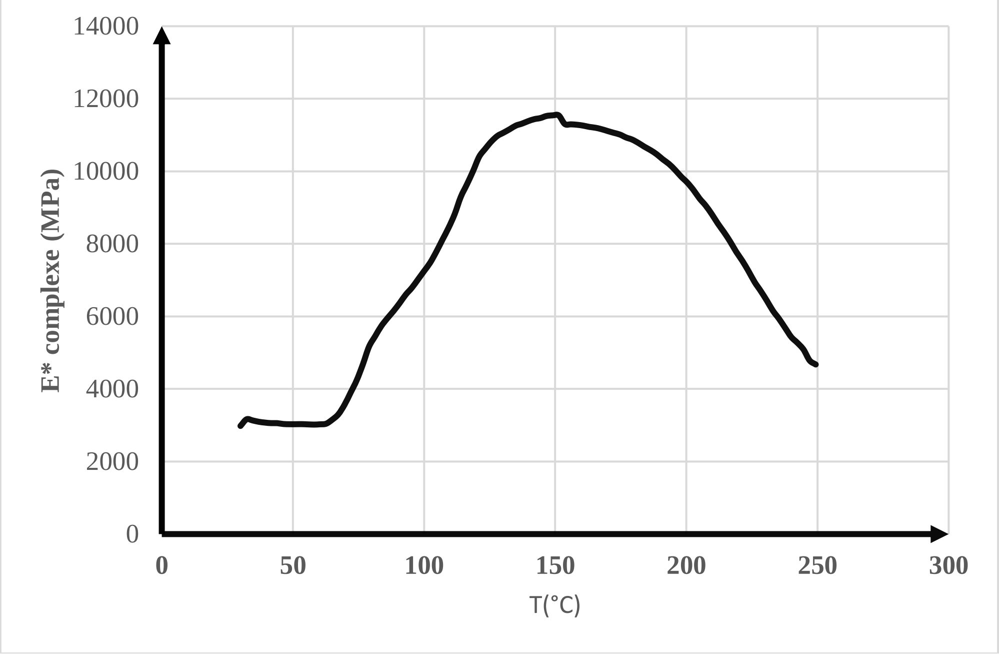

Figure 11. Complexe modulus of C2 depending the temperature

2.3.2 Glass transition temperature

The curves of Figure 7 show that the C1 and C2 loss modulus reach their maximum values at 132°C and 150°C, respectively. These values are 4248 MPa and 6919 MPa. These temperatures (Tv=132°C and Tv=150°C) are considered glass transition temperatures. It is at these temperatures that each adhesive changes from a hard, rigid state to a more flexible, supple one. Each of these Tv occurs in a temperature range in which the mobility of the polymer chains increases significantly.

2.4 Internal Bond (IB), Modulus of Elasticity (MOE) and Modulus of Rupture (MOR)

The mechanical properties (IB, MOE and MOR) of particleboards PBC2 using bio adhesive C2 are better VIVthan of particleboards PBC1 using bio adhesive C1. The average values of IB, MOE and MOR of PBC2 are respectively recorded o are respectively 0.41, 2008.35, 16.74 Mpa and those of particleboard PBC1 using bio adhesive C1 are respectively 0.37, 1890.48, 14.66 Mpa. All the value are higher than standard value NF EN319 (table 1). The tannin use had a good reactivity with the bio hardener used. Thus, the C2 has good stiffness than C1. These two particleboards can be use in external environments (EN 319 1993).

2.5 Thickness Swelling and Water absorption

The particleboards PBC2 using C2 bio adhesive are resistant to boiling water for 2 h and in a cold water for 24 h contrary to particleboards PBC1(Table 3). These poors values of PBC1 is probably due to the excess of moisture-sensitive carbohydrate oligomers added with the bio hardeners.

Table 3. Results of particleboard bonded with C2 and C1 bio adhesives

Particleboard sample	**IB (MPa)**	**MOE (MPa)**	**MOR (MPa)**	**TS (%)**	**TA(%) 2H-24H**
PBC2	0.41	2008.35	16.74	16-19	35-50
PBC1	0.37	1890.48	14.66	13-17	48-66
NF EN 319	0.35	1800	14	15	

1. CONCLUSION

The Tannin extract of *Milicia excelsa* and cassava starch have been studied in view to valorize them in the wood industry in Africa. The Thermo-Mechanical and Rheological of two news adhesives C1 and C2 were studied by using Dynamic Mechanical Analysis (DMA) and the evaluation of viscosity and activation energy. The mechanical properties (IB, MOE, and MOR) of particleboards made with these bioadhesives and their physical properties were evaluated. Both adhesives show interesting thermomechanical behavior for the development of composite materials. They can be use as adhesives in wood industry and particularly in external environments. The material manufactured with the adhesives of this tannin has better thermomechanical properties than that elaborated with cassava starch adhesives.

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