

# Thermal and Rheological Studies of *Ricinodendron Heudelotii* Wood for Its Pulp Production Potential

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## Abstract

Thermal stability and rheological behaviors of *Ricinodendron heudelotii* wood were investigated. Thermogravimetric analysis conducted at a heating rate of 10°C/min from 20 to 600°C in a nitrogen atmosphere indicated that there was no variation in the decomposition of the onset and final temperature for all the polymers. The thermal behaviours were investigated at a temperature range from 130 to 0°C at 3°C/min, multi-frequencies of 0.1-10 Hz using dynamic mechanical analysis. N-methyl-2-pyrrolidone saturated specimens were tested while submerged under the same solvent. Polymers decomposition pattern during thermogravimetric analysis are similar in the radial position of the wood. The glass transition temperature (T<sub>g</sub>) of *R. heudelotii* is 45±1°C at 0.1 Hz. The T<sub>g</sub> differs from the innerwood to outerwood. The T<sub>g</sub> showed that N-methyl-2-pyrrolidone saturated *R. heudelotii* would require low energy consumption during chemi-thermomechanical pulping.

**Key Words:** thermogravimetric, thermal behaviour, polymers, glass transition temperature, *Ricinodendron heudelotii*

## Introduction

Paper and paperboard consumption continues to increase, an estimate suggested that global paper consumption in 2025 will amount to 500 million tonnes, which means an annual growth of about 1.6% (Bajpai 2013). Unfortunately, wood has many other utilization that competes with its use for paper production. Other uses of wood include construction and building applications. In Nigeria, an increase in population has resulted in an increased pressure on timber resources because of high demand for wood and its products as raw materials for construction and building purposes (Izekor 2010). This has led to over-exploitation and rapid shrinkage in natural forests. The over exploitation

of the existing forest resources and the disappearance of commonly utilized hardwood species are of great concern to the wood scientists, technologists and users. Shortage of conventional raw material for the pulp and paper productions together with the increasing world demand for paper has renewed interest in expanding the fibers sources. Increasing the range of fibrous raw material source is a central component of current efforts to increase fibre supply for pulp and paper production (Markets Initiative 2007). Hence the consideration of some indigenous fast growing hardwood species like *Ricinodendron heudelotii* in the Nigeria natural forest as a potential fibre source for pulp production is a right step towards meeting the demand for pulp. However, one of the main challenges facing pulp pro-

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duction is the high energy consumption especially with the mechanical pulping. Therefore, prior to recommending any wood species for pulp production, one of the properties information needed for pulp production and paper performance is the thermal behaviour of such wood. The thermal behaviour can be investigated by considering the stability and flow of polymers in the wood.

Thermal stability of any polymer material, usually studied by Thermogravimetry (TG) (Shebani et al. 2008), is essential to its determination of the thermo-mechanical properties. Thermogravimetric analysis (TGA) which is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere (Fabiya et al. 2011). TGA has been widely applied to the study of wood and cellulose materials. Thermal stability of wood materials is known to present different degradation profiles depending on the wood composition. Cellulose presents higher thermal stability than hemicelluloses and lignin. Holocellulose is a combination of cellulose (a glucan polymer) and hemicelluloses (mixtures of polysaccharides) (Pettersen 1984). This behavior was related to the fact that cellulose is highly crystalline and hemicelluloses and lignin are amorphous (Hill 2006). Hemicelluloses are the least thermally stable of the wood components, due to the presence of acetyl groups (Bourgeois et al. 1989). It was also reported that lignin degradation starts at relatively low temperatures, proceeding over a wide range of temperature (Nassar and MacKay 1984). TGA is best known for its ability to provide information on the bulk composition of compounds. The usefulness of TGA for analyzing complex systems is greatly enhanced by the ability to record simultaneously the first derivative of the weight loss, that is, the derivative of the thermogravimetric curve (Zhang 2004). Thermal behavior (viscoelastic and glass transition temperature) is one of the basic information required in order to enhance proper temperature setting that wood can tolerate during thermomechanical pulping (Uhmeier et al. 1998). The measurement of rheology (viscoelastic) has been made possible with the use of dynamic mechanical analysis (DMA), which is a technique where a small deformation is applied to a sample in a cyclic manner. DMA combines both mechanical and rheological characterization of polymer samples as a function of temperature,

time, and frequency of the applied oscillating deformation force (Menard 2008).

Blechsmidt et al. (1986) states that the familiarity with the mechanical and thermal processes in the mechanical defibering of wood is a prerequisite to an understanding of mechanical pulping methods. One of the significant properties in this respect is the thermal softening behavior of wood components known as glass transition. The softening and dissolution of lignin are the important phenomena during pulping as it contribute to the energy requirement of the process (Salmén 1984; Eriksson et al. 1991).

*R. heudelotii* species was used in this study because it is a fast-growing tree and a lesser utilised timber species (Orwa et al. 2009). It normally reaches up to 50 m in height and 2.7 m in girth. It has a straight bole with short buttress. It is a white, fibrous, soft, light and perishable wood. It has various uses such as rough planks, curved into spoons, ladles, plates, platters, bowls, dippers and stools. In southern Nigeria, it is carved to make the whole or the resonant parts of musical instruments. More importantly, many research articles have been published on the kernels of this tree as a non-forest timber product (Mollet et al. 1995; Plenderleith 2004; Cosyns et al. 2011) without much attention to the utilization of its wood as a source of fibrous raw material for pulp and paper production.

Based on these facts, it is very important to have a well documented information on the thermal and rheological behaviour of *Ricinodendron heudelotii* wood species. The objective of this study is to investigate the thermal and rheological behavior of *Ricinodendron heudelotii* wood for its pulp production potential.

## Materials and Methods

Trees of *Ricinodendron heudelotii* were obtained from a free forest at a natural forest in Ilaromokin, Ondo State, Nigeria, located between 7.321°N 5.145°E and 7.389°N 5.097°E. Three trees were randomly selected and used for destructive sampling procedures. The ages of these trees could not be ascertained because they were felled from a natural forest and also their growth ring boundaries are either absent or indistinctive. The specific gravity of *R. heudelotii* wood as measured in this study is 0.6 (detail analysis not reported here). Both the sapwood and heartwood are

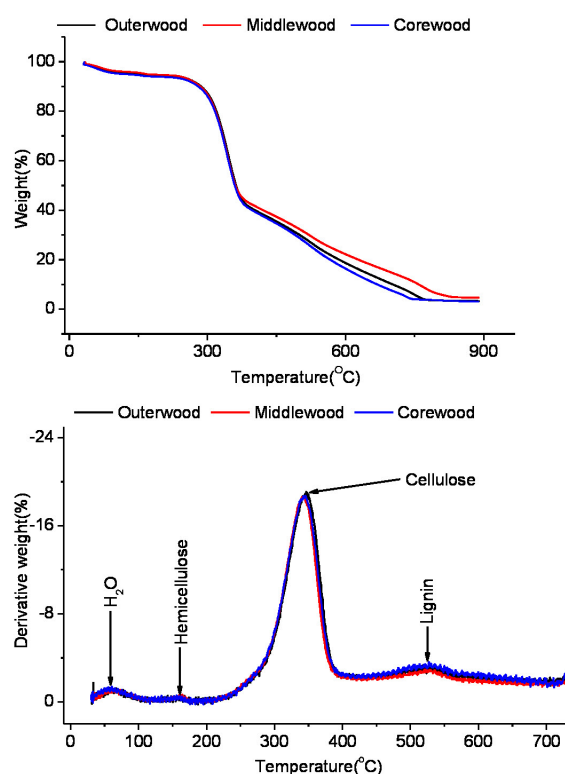
basically grey in colour. Bolts of about 70 cm were cut from the felled trees at three different merchantable height levels of 10% (base), 50% (middle), and 90% (top). The bolts were sawn through the pith into four parts while three radial positions from each part: core-wood, middle-wood and outer-wood were obtained.

Thermogravimetric analysis (TGA) was conducted using a TA Q500 Thermogravimetric Analyzer. Samples from the surface of *R. heudelotii* wood (at ten different sampling locations) were collected from 5 mm deep into the wood block of 20 mm × 50 mm × 100 mm and ground into fine particles (0.25 mm size). Test specimens (from the ground fine particles) of about 6–8 mg were measured in replicate. Specimens were conditioned at 12% m.c. prior analysis. The two specimens per wood sample (depending on location of the selection from the longitudinal and radial positions) were analyzed at a heating rate of 25°C/min from room temperature to 1000°C in a nitrogen atmosphere (flow rate 60 mL/min) to prevent wood degradation and ignition. The weight change was recorded as a function of temperature. Derivative peak temperature was taken as the maximum temperature acquired from the differentiation of the weight change as a function of temperature.

The thermal behaviour determination was achieved using *R. heudelotii* wood specimens cut into cylindrical discs (8 mm diameter and 5 mm thick) with a commercially available “plug-cutter.” The experiment was conducted with a TA Instruments known as ARG2 rheometer. Compressive-torsion disc specimens were tested in parallel-plate torsion, such that the cylinder axis (thickness direction) was parallel to the torsional axis and the cylinder ends were in contact with the parallel plates in accordance with Chowdhury et al., (2010). In this study, the only grain orientation tested was defined as TR. The first letter indicates the wood surface contacting the parallel plates, perpendicular to the torsional axis (T, tangential); the second letter indicates the grain direction parallel to the torsional axis (R, radial). The positioning of the growth rings within the specimen geometry was random.

Sample preparation and testing procedure were adopted from the previously conducted study by Fabiyi et al. (2011). However, specimens were saturated with N-methyl-2-pyrrolidone (NMP, C<sub>5</sub>H<sub>9</sub>NO, flash point: 93°C) at room temperature. This solvent was chosen with the aim of using

it as a potential solvent for chemi-thermomechanical pulping and because it is a better plasticizer than water; so the relaxation transition of *R. heudelotii* wood can be clearly and distinctively observed. Solvent-submersion analysis was conducted with modified 8 mm diameter parallel-plates such that the bottom plate was surrounded by a stainless steel cup that maintained specimen immersion. The purpose of the solvent submersion was to make sure that the specimens for analysis maintain solvent saturation throughout the experimentation. An aluminum solvent-cup cover was placed on top of the cup in order to reduce solvent evaporation. During analysis, specimens were maintained under a 15 N compressive force; required to prevent plate slippage, but less than the required force to cause crushing (computed from compressive strength). Anhydrous N<sub>2</sub> gas was directed through the heating chamber to prevent ignition since organic solvent is used as specimen plasticizer. All analyses were conducted within the linear viscoelastic response (LVR) region (Fabiyi et al. 2011).



**Fig. 1.** Thermogravimetric analysis thermograms showing the thermal stability of *Ricinodendron heudelotii* wood with weight loss (top) and first derivative,  $\delta\text{mass}/\delta\text{temp}$  plots (bottom).

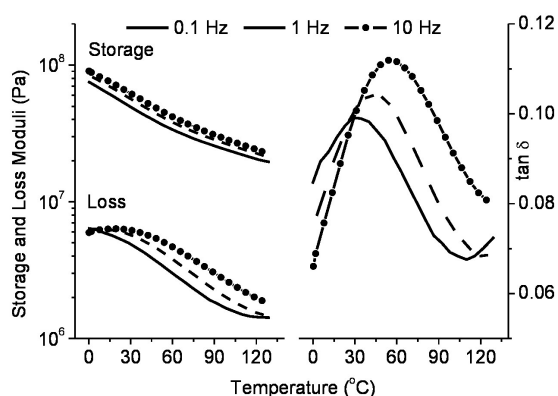
The thermal behaviour of all the wood samples was conducted under cooling scans. They were equilibrated at 130°C for 10 min; cooled to 0°C at 3°C/min under the multi-frequencies of 0.1-10 Hz. Two specimens were analyzed within each sub-sample. Average storage modulus, loss modulus, and tan δ traces were created using OriginPro software version 8.0.63 (OriginLab, Northampton, MA, USA).

### Results and Discussion

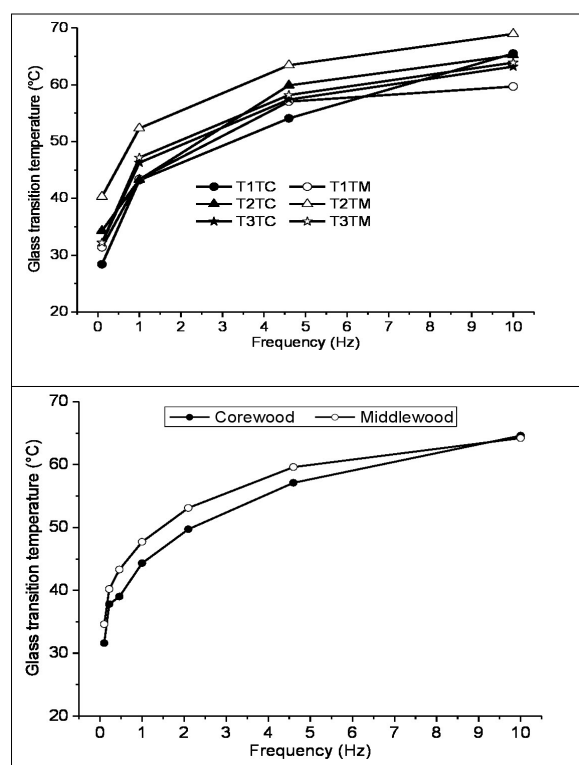
The thermogravimetric analysis thermograms of *R. heudelotii* across the radial position and the rate of weight loss are shown in Fig. 1. Three stages of weight loss due to thermal degradation were observed. Kim et al. (2006) stated that the degradation of hemicelluloses, lignin, and cellulose occurred between 180 and 350°C, 250 and 500°C, and between 275 and 350°C, respectively. Therefore, the decomposition temperature peaks at 161, 345 and 526°C are presumed to be hemicelluloses, cellulose and lignin, respectively. The decomposition temperature of hemicelluloses of *R. heudelotii* is similar to that of poplar (hemicellulose begins to decompose at 160°C) reported by Golnaz (2007). The decomposition of the hemicelluloses from the corewood to outerwood of *R. heudelotii* occurred at almost the same onset and final decomposition temperatures of 132 and 184°C, respectively. This could be attributed to the fact that the dominant of acetyl-4-O-methylglucuronoxylan in hardwood hemicelluloses is not structurally different for core-

wood and outerwood of the *R. heudelotii* considered in this study. Generally, hardwood contains both xylan and mannan, which must have contributed to the decomposition ascribed to hemicelluloses of *R. heudelotii*. Ramiah and Goring (1967) and Forest Products Laboratory (1970) investigated the thermal degradation of isolated wood components; decomposition of birch xylan began at 117°C while pine glucomannan began degradation at 127°C because of glucomannan's partial crystallinity. Their findings fall within the range of decomposition temperature of hemicelluloses observed in this study. Therefore, *Ricinodendron heudelotii* wood compare favorably with birch and pine commonly used for pulp production.

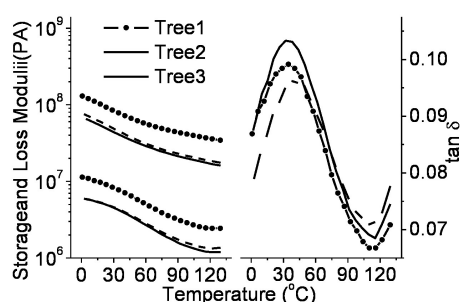
The rheological property of *Ricinodendron heudelotii* wood samples at 0.1, 1.0 and 10 Hz (multi-frequencies) with cooling rate of 3°C/min from 130 to 0°C illustrated in Fig. 2 showed that the storage modulus decreased with increasing temperature due to the softening of the material.



**Fig. 2.** Dynamic mechanical analysis cooling scans (3°C/min) for *Ricinodendron heudelotii* wood saturated with N-methyl-2-pyrrolidone as a function of frequency.



**Fig. 3.** Variations among trees and radial position in the glass transition temperature of *Ricinodendron heudelotii* wood (average of overall corewood and middlewood obtained at 90% merchantable height) saturated with N-methyl-2-pyrrolidone as a function of frequency.



**Fig. 4.** Variations among trees in the dynamic mechanical analysis cooling scans ( $3^{\circ}\text{C}/\text{min}$ , 0.1 Hz) for *Ricinodendron heudelotii* wood (average of overall middlewood obtained at 90% merchantable height) saturated with N-methyl-2-pyrrolidone.

There was no difference between the storage modulus ( $G'$ ) of 0.1 and 1 Hz, while the storage modulus of 10 Hz is slightly higher than that of 0.1 or 1 Hz. However, the higher the frequency, the lower the  $\tan \delta$  intensity below  $30^{\circ}\text{C}$  but the higher the  $\tan \delta$  intensity above  $30^{\circ}\text{C}$ .

Storage and loss moduli,  $\tan \delta$  intensities and maxima differed among trees of *R. heudelotii* (Fig. 2).  $\tan \delta$  intensity at glassy state ( $0^{\circ}\text{C}$ ) for these trees was very similar except for tree 1 (Fig. 2). The glass transition temperatures of N-methyl-2-pyrrolidone saturated *R. heudelotii* at 0.1 and 10 Hz are  $45^{\circ}\text{C}$  and  $62^{\circ}\text{C}$ , respectively (Fig. 3, top). For the variation of the glass transition temperature across the radial position, middlewood had higher glass transition temperature than the corewood irrespective of the frequency at which the experiment was conducted (Fig. 3, bottom). The glass transition is predicted to occur over a temperature interval spanning the approximate temperature range of  $100\text{--}170^{\circ}\text{C}$  within which most thermomechanical pulping is carried out (Irvine 1985). Hence, the  $T_g$  showed that N-methyl-2-pyrrolidone saturated *R. heudelotii* would require low energy consumption during pulping.

At the glassy state ( $0^{\circ}\text{C}$ ) through rubbery ( $130^{\circ}\text{C}$ ), trees 2 and 3 had similar storage and loss modulus; however, tree 1 was higher than the trees 2 and 3 (Fig. 4). Age differences (30, 25 and 20) of the trees could be responsible for the variation. The  $\tan \delta$  maximum (glass transition temperature) for the trees differs; therefore, there is the need to first of all have the knowledge of the  $T_g$  of a wood obtained from a tree so as to set the processing temperature a little higher than its  $T_g$ . This approach would enhance pulping process optimisation.

## Conclusion

In this study, the thermal stability and rheological behaviour of *Ricinodendron heudelotii* wood were investigated. Three stages of weight loss due to thermal degradation were observed at the temperature peaks of 161, 345 and  $526^{\circ}\text{C}$ . Storage and loss moduli,  $\tan \delta$  intensities and maxima differed among trees of *R. heudelotii* were also studied. The storage modulus decreased with increasing temperature due to the softening of the material. The softening transition of *R. heudelotii* wood saturated with N-methyl-2-pyrrolidone appeared between  $30\text{--}70^{\circ}\text{C}$  which has been assigned to lignin relaxation. Based on the observed low glass transition temperature range of the N-methyl-2-pyrrolidone saturated *R. heudelotii*, this pre-treatment favors the lowering of the energy consumption during the chemi-thermomechanical pulping of this wood species.

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