

## Effect of chemical modifications caused by heat treatment on mechanical properties of *Grevillea robusta* wood

Francis Mburu <sup>a,b</sup>, Stéphane Dumarçay <sup>a</sup>, Jean François Bocquet <sup>a</sup>,  
Mathieu Petrissans <sup>a</sup>, Philippe Gérardin <sup>a,\*</sup>

<sup>a</sup> *Laboratoire d'Etudes et de Recherches sur le Matériau Bois, UMR INRA 1093 Université Henri Poincaré Nancy 1, Faculté des Sciences et Techniques, BP 239, 54506 Vandoeuvre-les-Nancy, France*

<sup>b</sup> *Department of Wood Science and Technology, Moi University, P.O. Box 1125, Eldoret, Kenya*

Received 19 September 2007; received in revised form 15 November 2007; accepted 19 November 2007

Available online 23 November 2007

### Abstract

*Grevillea robusta*, a Kenyan wood species of low durability was heat treated under inert atmosphere in laboratory conditions at temperatures between 220 and 250 °C. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined for different heat treatment conditions. MOR and MOE reduced with increase in heat treatment weight loss. MOE reduced insignificantly for weight loss less than 16% while reduction of MOR was more significant. For a fixed heat treatment temperature by varying the treatment duration, sugar content was analysed by HPLC after acidic hydrolysis and Klason lignin was determined. The amount of sugars other than glucose decreased with treatment time and was near zero after 7 h, while lignin quantity increased gradually. Wood acidity determined by titration decreased after heat treatment indicating degradation of uronic acids present in hemicelluloses. Chemical modifications of wood components were determined by CP/MAS <sup>13</sup>C NMR analysis. Spectra indicated significant degradation of hemicelluloses. Increase of treatment duration resulted in the appearance of new signals, particularly obvious on spectra of samples treated for 15 h, attributed to carbonaceous materials involved in char formation.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Char; Degradation; *Grevillea robusta*; Heat treatment; Mechanical properties; Sugar content

### 1. Introduction

In Kenya, more than 95% of the population depends on forest resources directly or indirectly [1]. Presently, there is acute wood shortage due to high population growth, logging ban from the government forests and use of low durability agro-forestry trees. *Grevillea robusta*, an agro-forest tree species of low durability is widely used by the local people in Kenya for construction, fencing, and furniture due to its availability. Since the country lies in the tropics biodegradation of wood is quite high. In respect to the environment, improvement of durability to increase the service life for this particular species

would be a great step in forest conservation and general improvement of livelihood for Kenyan people.

Heat treatment has been developed in Europe during the last decade leading to industrialisation and commercialization of heat-treated timbers resulting from the treatment of low natural durability wood species [2,3]. This form of treatment converts wood into a new product called torrefied or retified wood through mild pyrolysis in a temperature range between 200 and 260 °C under inert atmosphere of nitrogen [4].

In previous work [5], thermally treated *G. robusta* was tested against fungi and termites in laboratory and field conditions. Microscopic analysis, FTIR and CP/MAS <sup>13</sup>C NMR were performed to characterize wood chemical and anatomical modifications after treatment. The results showed great improvement in durability towards both fungi and termites, associated with significant degradation of hemicelluloses. According to these results, heat treatment could be a valuable

\* Corresponding author. Tel.: +33 3 83 68 48 40; fax: +33 3 83 68 48 51.

E-mail address: [philippe.gerardin@lermab.uhp-nancy.fr](mailto:philippe.gerardin@lermab.uhp-nancy.fr) (P. Gérardin).

alternative to toxic chemical treatment used in Kenya. However, it was important to carry out further investigations on the effects of chemical modifications occurring during treatment on the mechanical properties to enable us to make recommendations on possible uses.

## 2. Experimental

### 2.1. Heat treatment

Heat treatment was performed under nitrogen on previously dried ( $m_0$ ) *G. robusta* blocks measuring 50 mm × 30 mm × 20 mm in longitudinal, radial and tangential directions in a glass reactor placed in an oven at controlled temperatures and different durations of time. The oven temperature was increased by 20 °C min<sup>-1</sup> from ambient to final temperature. Weight loss (WL) of the wood due to thermal degradations was calculated according to the formula:

$$WL(\%) = 100(m_0 - m_1)/m_0$$

where  $m_0$  is the initial oven-dry mass of the sample before heat treatment and  $m_1$  the oven-dry mass of the same sample after heat treatment.

### 2.2. Mechanical strength test

*G. robusta* boards were cut parallel to grain direction and sawn into samples measuring 120 × 25 × 8 mm (longitudinal, tangential and radial), respectively. These were heat treated at 240 °C as described above varying the treatment time to achieve different weight losses (WL) ranging between 2% and 25%. Control samples for each treatment were cut from the same board. The samples (3 replicates for each treatment condition) were tested for modulus of elasticity (MOE) and modulus of rupture (MOR) at room temperature using an INSTRON 4467 device. Comparisons were done between each control and its thermal treated test samples.

### 2.3. Analysis of sugar composition

The wood was ground into fine powder, passed through 0.315 mm sieve and successively Soxhlet extracted with dichloromethane and toluene/ethanol to remove extractives. Extracted powder (350 mg) was placed in 100 ml flask, mixed with 4 ml of 72% sulphuric acid and stirred at ambient temperature for 1 h for pre-hydrolysis. After this, 84 ml of distilled water was added and the mixture heated for 4 h under reflux. After cooling, lignin was separated by filtration of this mixture through a Buchner funnel, washed with distilled water, dried at 103 °C and weighed. The filtrate containing monosaccharides was transferred into 250 ml graduated flask and diluted with distilled water to the mark. Twenty milliliter of this solution was neutralized using barium hydroxide (Ba(OH)<sub>2</sub>). The pH was adjusted to 5. Centrifugation of this solution was performed for 20 min at 4000 rpm and the clear supernatant

was transferred into 50 ml round bottomed flask and evaporated to dryness under vacuum. Distilled water was used to dissolve sugars to a concentration of 2 mg ml<sup>-1</sup>. The obtained solution was filtered through a Millipore Millex-HA 0.45 µm filter and analysed by HPLC. Each hydrolysis was triplicated. The analysis was performed on a Waters liquid chromatograph (Waters SAS, Saint Quentin-en Yvelines, France) equipped with a system controller 600E, manual injector system with 20 µl loop and a Waters 2420 Evaporative Light Scattering ELS detector (gain = 1, evaporator tube temperature = 60 °C and nebulizer gas pressure 50 psi). The data were recorded with the empowered software. The analytical measurements were obtained on a Supelco (Sigma–Aldrich Chimie, Saint Quentin Fallavier, France) Discovery LC-NH<sub>2</sub> column (250 mm × 4.6 mm i.d.) at 30 °C with an acetonitrile (78%)/water (20%)/methanol (2%) mixture as mobile phase and flow rate of 1.5 ml min<sup>-1</sup>. Each hydrolysate was analysed 3 times and the average calculated. Glucose content in percentage was determined on the basis of glucose and cellobiose contents.

### 2.4. Acidity titration

Wood samples were treated for different durations of time (30 min, 1, 5, 7 and 15 h at 250 °C) and crushed into powder. This was passed through a 115 mesh sieve and dried at 103 °C to constant weight. Acid value (A) was obtained according to a procedure described by Matsuda [6]. Powder (250 mg) was mixed with 1 ml of 0.1 M HCl in 25 ml of distilled water and titrated using 0.01 M NaOH with phenolphthalein as indicator. A was obtained by the following equation:

$$A(\text{meq/g}) = \frac{((v - v_0) \times 10^{-2})}{m}$$

where  $v$  is the volume (ml) of 0.01 M NaOH titration solution used for a given wood sample,  $v_0$  the volume (ml) of 0.01 M NaOH solution used for neutralizing 1 ml of 0.1 M HCl diluted in 25 ml of distilled water and  $m$  the mass of sawdust (g) used for titration.

### 2.5. CP/MAS <sup>13</sup>C NMR analysis

Solid state CP/MAS (cross-polarisation/magic angle spinning) <sup>13</sup>C NMR spectra were recorded on Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Acquisition time was 0.026 s with number of transients of about 1200. All the spectra were run with relaxation delay of 1 ms and special width of 20,000 Hz. Spinning rates were 5 kHz. Chemical shifts are expressed in parts per million (ppm).

## 3. Results and discussion

### 3.1. Heat treatment

Evolution of weight loss against time is represented in Fig. 1. Degradation of *G. robusta* was noted to be important during the first stage of thermal treatment and becomes less

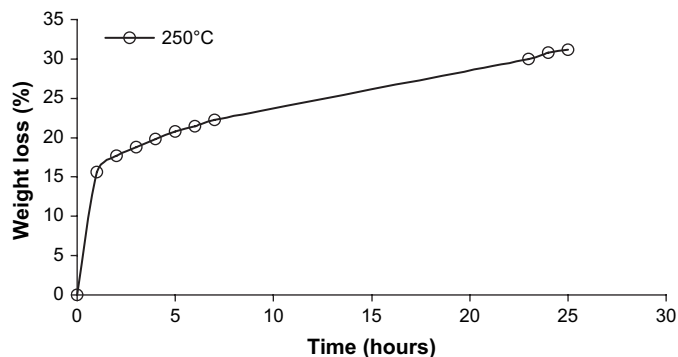


Fig. 1. Weight loss of *Grevillea robusta* after heat treatment at 250 °C.

important in the second stage. The mass loss increases with treatment time as also reported in the literature of other European species [7,8]. According to our previous paper [5], heat-treated *G. robusta* wood becomes durable to the white rot fungus *Coriolus versicolor* due to chemical modifications after heat treatment. It was, however, important to evaluate the effect of these modifications on the mechanical properties.

### 3.2. Mechanical properties

Elasticity implies that deformations produced by low stress are recoverable after the loads are removed. The modulus of elasticity MOE is commonly used for this test. Modulus of rupture (MOR) reflects the maximum capacity of a member in bending and is proportional to maximum moment borne by a specimen. Heating wood to high temperatures changes its physical and chemical properties. As a result, dimensional stability is increased due to reduced moisture intake and decay resistance is enhanced. Strength of wood decreases depending upon the species, anatomical features and treatment methods. However, it is known that an important drawback of heat-treated wood is its mechanical brittleness [9,10,11,12]. Effect of thermal treatment on the mechanical properties is reported in Fig. 2.

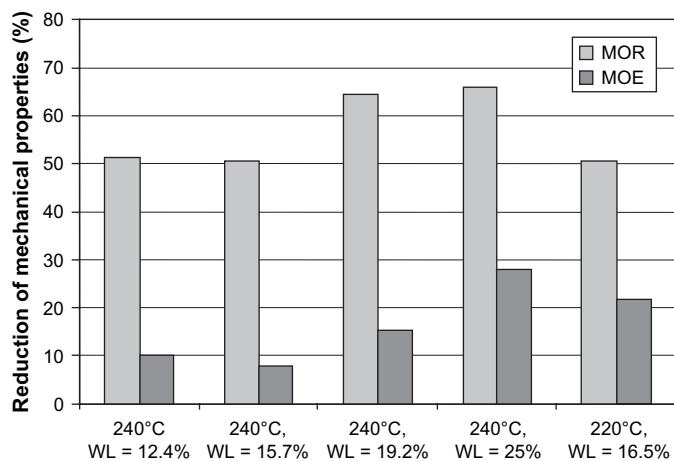


Fig. 2. Reduction (%) in MOE and MOR with weight loss after thermal treatment at 220 and 240 °C.

The results showed that modulus of elasticity (MOE) decreased insignificantly for *G. robusta* samples having weight loss of less than 16% after thermal treatment. There was significant reduction in MOE for heat-treated *G. robusta* with weight loss of 16% and above. Reduction in MOE progressed with increase in weight loss due to thermal treatment. From the results it was found that treatment temperature was not the sole factor contributing to reduction in MOR. Weight loss after thermal treatment seems to be the most important factor influencing the mechanical properties since samples treated at 220 °C with weight loss of 16% showed similar MOR values as those treated at 240 °C with same weight loss. The modulus of rupture decreased with increase in weight loss of *G. robusta* after thermal treatment. The decrease is mainly due to the depolymerization reactions and changes in the amount of hemicelluloses which play an important role in strength properties of wood [12,13]. Neutral softwood galactomannans and birch glucuronoxylans have been shown to increase fibre to fibre bonding [14].

### 3.3. Analysis of sugar composition and lignin content

To evaluate effect of wood polymers degradation on mechanical properties, analysis of sugars composition and Klason lignin were determined after acidic hydrolysis of polysaccharides. Table 1 gives the results after analyzing samples treated at 250 °C for different durations. Analysis shows that xylose, galactose, rhamnose and arabinose which make-up hemicelluloses reduced with treatment time confirming their high susceptibility to thermal degradation. These monosaccharides were totally exhausted from wood after 7 h of thermal treatment. Lignin content increased with treatment time confirming higher susceptibility of hemicelluloses to thermal treatment. Reduction of glucose with treatment time was gradual and even after 15 h of thermal treatment substantial amount was still present in wood.

### 3.4. Acidity titration

Considering that hemicelluloses are constituted of neutral sugars and uronic acids, it seems interesting to investigate the wood acidity in relation with treatment time to evaluate degradation of non cellulosic polysaccharides. Results showed that acidity initially present in wood decreases with time to zero after 7 h of treatment. This could be explained by

Table 1

Sugars and Klason lignin contents in heat-treated and untreated *Grevillea robusta* starting from 350 mg of sawdust

<i>Grevillea robusta</i> treatment at 250 °C	Control	1 h	5 h	7 h	15 h
Weight loss (%)	—	16.0	20.5	22.0	26.0
Lignin (mg)	84.6	126.6	137.0	158.1	167.5
Glucose (mg)	186.2	206.9	180.5	168.7	176.0
Xylose (mg)	45.1	9.6	7.0	9.5	0.0
Galactose (mg)	8.4	3.3	0.0	0.0	0.0
Rhamnose (mg)	2.7	0.6	0.0	0.0	0.0
Arabinose (mg)	0.0	0.0	0.0	0.0	0.0

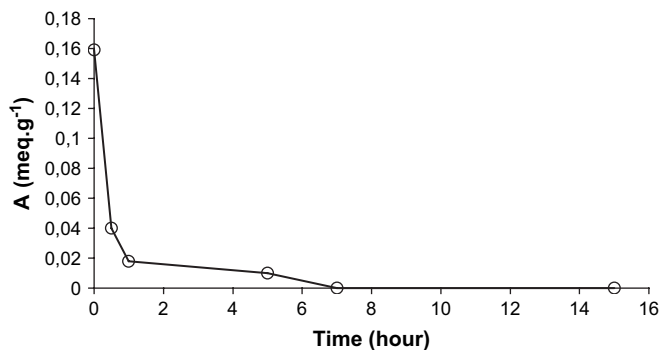


Fig. 3. Evolution of wood acidity with treatment time.

decomposition of uronic acids after degradation of hemicelluloses. Volume of sodium hydroxide used for titration reduced gradually with the increase in treatment time as illustrated in Fig. 3. This may be explained by disappearance of uronic acid present in hemicelluloses as they decomposed during the treatment. Measurements realized on control and water-extracted control confirmed that a great part of the measured acidity was not due to water soluble compounds, but was due to polymeric components of wood.

### 3.5. CP/MAS <sup>13</sup>C NMR analysis

CP/MAS <sup>13</sup>C NMR analysis was also performed to characterize wood chemical modifications after thermal treatment (Fig. 4). The control samples represent untreated wood showing main wood polymer components. Cellulose appears in the region between 60 and 105 ppm. Signals between 72 and 75 ppm correspond to C-2, C-3 and C-5 carbons. C-4 and C-6 are duplicated due to the presence of amorphous and crystalline celluloses. The signals at 84 and 89 ppm are assigned to

the C-4 of crystalline and amorphous celluloses, respectively. The signal at 105 ppm is ascribable to C-1 hemiacetallic carbon. Hemicelluloses signals are less obvious because they overlap with those of cellulose. Shoulder at 102 ppm on the C-1 signal of cellulose is assigned to hemiacetal carbon of hemicelluloses while acetyl groups are detected at 20 and 173 ppm. Methoxyl groups of syringyl and guaiacyl lignin units appear at 56 ppm while aromatic carbons appear between 120 and 160 ppm. Signal at 35 ppm is due to lipophilic extractives such as alkyl and alkenyl resorcinols present in *G. robusta* wood [5].

Signals of methyl at 20 ppm and carbonyl at 173 ppm of acetyl groups are noted to decrease significantly after 7 h of heat treatment. Changes in cellulose and lignin signals are not significant as also reported in the literature. After 15 h of heat treatment, new signals are noted to appear on the spectrum. Thermal degradation leads to the appearance of new signals ascribable to aliphatic carbons (10–50 ppm), aromatic or alkene carbons (110–160 ppm) and carbonyl groups (205 ppm) ascribable to the beginning of char formation. These data confirm the results of our previous study concerning the formation of carbonaceous materials within the wood structure during beech heat treatment by mild pyrolysis [15]. Heat treating wood for long duration of time even at relatively low temperature (250 °C) results in a more or less important cellulose degradation according to the duration of the treatment similar to that observed at higher temperature [16]. These degradations explain the important loss of mechanical properties observed for long-duration treated wood.

## 4. Conclusion

Mechanical properties of wood reduce after thermal treatment. MOE decreased insignificantly for *G. robusta* samples

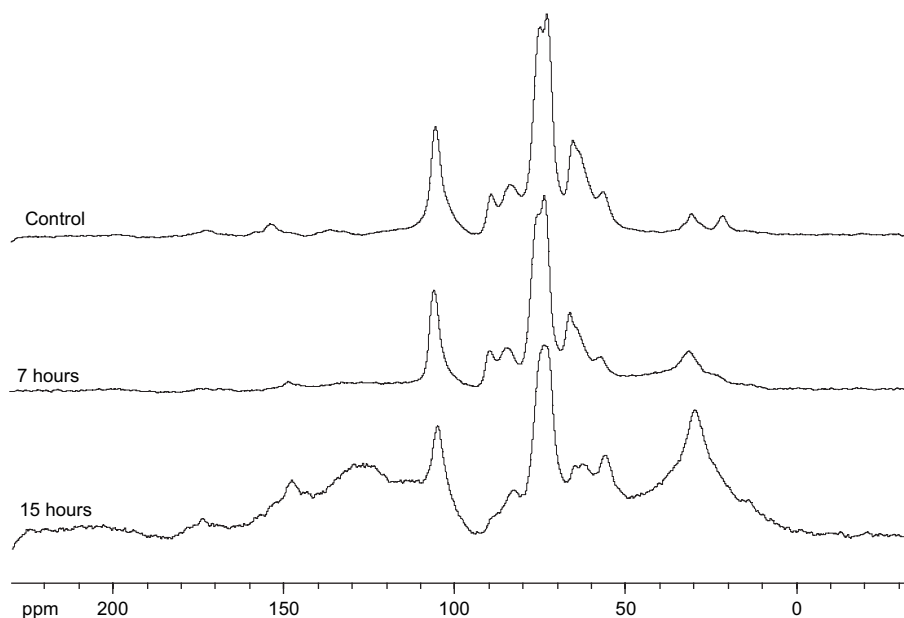


Fig. 4. CP/MAS <sup>13</sup>C NMR spectra of *Grevillea robusta* heat treated at 250 °C.

having weight loss of less than 16% above which the decrease is more significant. Effect of heat treatment on MOR is more important even at low degradation levels and increases with treatment severity. Treatment temperature was not the only factor contributing to reduction in MOR but weight losses directly connected to treatment time seems to be the most important parameter. HPLC analysis of sugar composition shows decrease of hemicellulosic carbohydrate contents and increase of lignin content. Acidity of wood decreases with treatment time and reaches zero after 7 h of treatment at 250 °C indicating that most of the uronic acids have been probably degraded. CP/MAS <sup>13</sup>C NMR analysis indicates important degradation of hemicelluloses after heat treatment. Moreover, analysis of sample treated at 250 °C for a prolonged time indicates the presence of additional products due to the beginning of degradation of cellulose. According to these results and to our previous work, it seems important to adapt the treatment conditions to achieve lower degradation levels allowing to improve resistance to decay without decreasing the mechanical properties. Due to reduced mechanical properties of *G. robusta* after heat treatment, it is recommended for furniture, wall, ceiling, roofing, flooring and selected fencing, where mechanical properties are secondary.

### Acknowledgments

This work was supported by a grant from the French government through the Embassy in Nairobi. The study was carried out in the Laboratoire d'Etudes et de Recherches sur le Matériau Bois, Université Henri Poincaré Nancy 1, France with support of all the staff.

### References

- [1] KFMP. Kenya Forestry Master plan Development Programmes Ministry of Environment and Natural Resources, Government of Kenya; 1994. p. 1–208.
- [2] Patzelt M, Stingl R, Teischinger A. Termische modifikation von holz und deren einfluß auf ausgewählte holzeigenschaften, in modifiziertes holz eigenschaften und märkte. Lignovisionen Band 3 2002 ISSN: 1681-2808:101–49.
- [3] Alén R, Kotilainen R, Zaman A. Thermochemical behaviour of Norway spruce (*Picea abies*) at 180–225 °C. *Wood Science and Technology* 2002;36:163–71.
- [4] Weiland JJ, Guyonnet R. Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. *Holz als Roh und Werkstoff* 2003;61:216–20.
- [5] Mburu F, Dumarcay S, Huber F, Petrissans M, Gerardin P. Evaluation of thermally modified *Grevillea robusta* heart wood as an alternative of wood resource in Kenya: characterisation of physicochemical properties and improvement of bio-resistance. *Bioresource Technology* 2007;98:3478–86.
- [6] Matsuda H. Preparation and utilization of esterified wood having carboxyl group. *Wood Science and Technology*. 1987;21:75–88.
- [7] Hakkou M, Pétrissans M, El Bakali I, Gerardin P, Zoulalian A. Wettability changes and mass loss during heat treatment of wood. *Holzforschung* 2005;59(1):35–7.
- [8] Nuopponen M, Vuorinen T, Jasma S, Viitaniemi P. Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies. *Journal of Wood Chemistry and Technology* 2004;24(1):13–26.
- [9] Santos JA. Mechanical behaviour of eucalyptus wood modified by heat. *Wood Science and Technology* 2000;34:39–43.
- [10] Mouras S, Girard P, Rousset P, Permedi P, Dirol D, Labat G. Propriétés physiques de bois peu durables soumis à un traitement de pyrolyse ménagée. *Annals of Forest Science* 2002;59:317–26.
- [11] Unsal O, Ayrlmis N. Variations in compression strength and surface roughness of heat treated Turkish river gum (*Eucalyptus camaldulensis*) wood. *Journal of Wood Science* 2005;51:405–9.
- [12] Yildiz S, Gezer ED, Yildiz UC. Mechanical and chemical behaviour of spruce wood modified by heat. *Building and Environment* 2006;41:1762–6.
- [13] Hillis WE. High temperature and chemical effects on wood stability. *Wood Science and Technology* 1984;18:281–93.
- [14] Otero D, Sundberg K, Holmbom B, Blanco A, Negro C, Tijero J. Effects of wood polysaccharides on the depositability of wood resin. *Nordic Pulp and Paper Research Journal* 2000;15:607–13.
- [15] Inari GN, Mounquengui S, Dumarcay S, Petrissans M, Gerardin P. Evidence of char formation during wood heat treatment by mild pyrolysis. *Polymer Degradation and Stability* 2007;92(2007):997–1002.
- [16] Zawadzki J, Wisniewski M. <sup>13</sup>C NMR study of cellulose thermal treatment. *Journal of Analytical and Applied Pyrolysis* 2002;62:111–21.