Available online at www.sciencedirect.com
ScienceDirect
Bioresource Technology 98 (2007) 3478–3486
BIORESOURCE TECHNOLOGY

Evaluation of thermally modified *Grevillea robusta* heartwood as an alternative to shortage of wood resource in Kenya: Characterisation of physicochemical properties and improvement of bio-resistance

Francis Mburu [a,b], Stéphane Dumarçay [a], Françoise Huber [a], Mathieu Petrissans [a], Philippe Gérardin [a,*]

[a] *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*
[b] *Department of Wood Science and Technology, Moi University, P.O. Box 1125, Eldoret, Kenya*

Received 12 September 2006; received in revised form 27 October 2006; accepted 4 November 2006
Available online 29 December 2006

Abstract

Heat treatment of *Grevillea robusta*, a tropical wood species of low natural durability, was carried-out under inert conditions to improve its decay resistance. Resistance of heat treated samples was evaluated by malt agar block tests after three months of exposure to several wood rotting fungi. Also resistance of heat treated wood against termites was tested in the laboratory and in the field. Results showed that durability against fungi and termites was greatly improved after treatment. There was a good correlation between decay resistance and mass loss due to thermal treatment. Microscopic, FTIR and ^{13}C MAS NMR analysis were performed to characterize wood chemical and anatomical modifications that occur after treatment to understand the reasons of the durability improvement.

Keywords: Durability; *Grevillea robusta*; Heat treatment; Rotting fungi; Termite

1. Introduction

In Kenya, forests resources rank high among other important natural resources. Forest ecosystems are complex natural resource base which provides environmental goods and services for social, cultural and economic development. It is therefore important that the resource is conserved, protected and sustainably utilized for national development. Kenya like other developing countries is confronted with challenges of over reliance on natural resources.

Timber demand in Kenya is rising each year unlike its supply. If this trend continues it is projected that by the year 2020 Kenya will have a deficit of 6,841,000 m^3 of wood (KFMP, 1994). The deficit is increased by premature failures of wood in service as a result of biological deterioration, failures in establishing new and expanding forest plantations, repeated excisions with no compensatory additions and changes of forest land use. One way of counteracting this problem of timber deficit and deforestation is to make the timber last longer in service, through effective treatment methods.

The Kenyan forest plantations are constituted of 31% Pines, 45% Cypress, 10% Eucalypts and others 14%, which are the main base for industrial raw materials before the logging ban effected by the government in the year 1999. Private forests cover about 70,000 ha consisting mainly

* 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 (P. Gérardin).

0960-8524/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2006.11.006

acacia species and *Grevillea robusta* out of which *G. robusta* is about 75% of the area. It is a fast growing multipurpose agro-forest tree, widely distributed in Kenya especially in the agricultural prime areas. Due to the logging ban in the government forests, there has been acute shortage of wood for construction, fencing and other purposes. Increase of population in Kenya has also caused depletion of the natural forests leading to shortage in industrial raw material. This has forced the farmers to look for alternative sources of wood. Most of them have resorted to use *G. robusta* due to its availability, but its low durability against bio-degraders is a great challenge to all wood users and the Kenyan government. Presently, copper chrome arsenate (CCA), pentachlorophenol (PCP) and creosote oil are the most used biocides for wood preservation in Kenya using dipping or pressure processes.

The increasing environmental pressure and awareness over the last few years has led to an important change in the field of wood preservation in industrialised countries in regard to biocide toxicity. This has lead to development of "non biocidal" alternatives like chemical or thermal treatments (Hill, 2005). Heat treatment has been particularly developed in Europe during this last decade leading to industrialisation and commercialization of heat treated timbers resulting from the treatment of low natural durability wood species like pine, spruce, poplar or beech (Patzelt et al., 2002; Alen et al., 2002). The aim of our study was to investigate effect of such treatments on durability of *G. robusta*, a tropical wood species of low natural durability, to allow its development and uses in Kenya for applications where mechanical properties are not required. Indeed, it is known that an important drawback of heat treated wood is mechanical brittleness (Santos, 2000; Mouras et al., 2002; Unsal and Ayrilmis, 2005; Yildiz et al., 2006). For these reasons, heat treated wood is not recommended for use in load-bearing constructions, but can find valuable applications for furnitures, wall, ceiling, roofing, flooring and fencing.

2. Experimental

2.1. Material

G. robusta heartwood was used in this study. Wood blocks measuring 50 mm × 30 mm × 20 mm in longitudinal, radial and tangential directions were cut and oven dried at 103 °C (approximately 48 h) before determination of their anhydrous weights (m_0).

2.2. Heat treatment

Heat treatment was performed on previously dried blocks in a reactor placed in an oven at different temperatures (240, 250 and 260 °C) during different time (0.5, 1, 5, 7 and 15 h) under a nitrogen atmosphere. The oven temperature was increased by 20 °C mn^{-1} from ambient to the operating temperature. After the treatment, the temperature decreases slowly to the room temperature. Mass loss after heat treatment was calculated according to the formula:

$$\text{ML } (\%) = 100 \times (m_0 - m_1)/m_0,$$

where m_0 is the initial oven dried mass of wood sample and m_1 the oven dried mass of the same sample after heat treatment.

2.3. Exposure to fungi

Two kinds of experiments were performed to evaluate fungal durability after heat treatment. The first was resistance evaluation of samples treated at 250 °C for different duration of time against *Coriolus versicolor*. The second was evaluation of heat treated blocks at 250 °C for 7 h against different wood rotting fungal species, two white rots (*C. versicolor* and *Pycnoporus sanguineus*) and two brown rots (*Poria placenta* and *Antrodia* sp.). The choice of the heat treatment conditions (250 °C for 7 h) was based on previously reported experiments performed on beech indicating that improvement of durability can be achieved for mass losses of approximately 20% (Hakkou et al., 2006). Heat treated *G. robusta* blocks were cut into smaller blocks of 25 mm × 25 mm × 5 mm in longitudinal, radial and tangential directions. These were used for fungal durability evaluation after conditioning in an oven at 103 °C for one night (m_2). Petri dishes (9 cm diameter) were filled with sterile culture medium prepared by mixing 30 g malt and 40 g agar in distilled water (1 l), inoculated with the different fungi and incubated at 22 °C and 70% relative humidity to allow full colonization by the mycelium. Two blocks (treated or untreated as control) were placed in each Petri dishes and incubated during three months to evaluate the effect of heat treatment. Each experiment was duplicated or triplicated (see after). After this period, mycelia were removed and the blocks were dried at 103 °C and weighed (m_3) to determine the weight loss caused by the fungal attack

$$\text{WL } (\%) = 100 \times (m_2 - m_3)/m_2,$$

where m_2 is the initial oven dried mass of wood block before attack and m_3 is the oven dried mass after attack.

Moisture content of the wood after fungal attack was determined as followed:

$$\text{MC } (\%) = 100 \times (m_{3'} - m_3)/m_3,$$

where $m_{3'}$ is the wet weight of the sample after attack measured after removal of the mycelium and m_3 is the oven dried mass after attack.

2.4. Exposure to termites

Heat treated *G. robusta* samples (7 h at 250 °C) were also exposed to *Macrotermes natalensis* widely distributed in Kenya in laboratory conditions according to a procedure adapted from AWPA E1-97 standard (Standard

method laboratory for evaluation to determine resistance to subterranean termites, 1997). *Pinus sylvestris* and untreated *G. robusta* were used as control. The tests were done in chambers free of organic material in glass jars 80 mm diameter by 100 mm in height. Prior to use, all containers were sterilized in autoclave. One hundred and fifty grams of sand were added to each container, followed by 30 ml of distilled water then allowed to stand for 2 h. Two dried weighed (m_2) test blocks, 30 mm × 10 mm × 20 mm in longitudinal, radial and tangential directions, were placed on the surface of each jar with two corners against the side of the container. Four-hundred termites were added to each container at a ratio of 360:40 workers to soldiers respectively. All containers were maintained at 25 °C for 28 days. Percentage change in dry mass of the test block was determined.

Blocks were then dried at 103 °C and weighed (m_4) to determine the weight loss caused by the termite attack

$$\mathrm{WL}\ (\%) = 100 \times (m_2 - m_4)/m_2,$$

where m_2 is the initial oven dried mass of wood block before attack and m_4 is the oven dried mass after attack.

Resistance to termite was also investigated using field test conditions. Tests were carried out according to a method adapted from AWPA E7-93 standard (Standard method of evaluating wood preservatives by field tests with stakes, 1993) especially as concerns the sample size which was reduced to fit with our heat treatment equipment. An active termite nest constituted of *M. natalensis* was identified and cleaned from all the cellulolytic materials. The site was then watered and covered with an opaque plastic sheet to activate the termites. Samples measuring 50 mm × 25 mm × 25 mm in longitudinal, radial and tangential directions respectively were buried down at a radius of 1 m from the termite nest. Three kinds of samples were used: 24 samples of heat treated *G. robusta* (7 h at 250 °C), 24 samples of untreated *G. robusta* and 24 samples of *P. sylvestris*. The moisture at the test site was improved by watering to maintain and attract more termites. Evaluation was done every month by removing six stakes for each treatment and the values averaged.

2.5. Determination of the amount of extractive

Untreated and heat treated *G. robusta* blocks were ground to sawdust and dried at 103 °C before extraction with dichloromethane in a Soxhlet extractor for 16 h at the rate of 8–12 cycles per hour. After extraction the solvent was evaporated under reduced pressure and the residue dried over P_2O_5 in a desiccator before weighing.

2.6. Spectroscopic analysis

2.6.1. FTIR analysis

FTIR spectra were recorded as KBr disks on a Perkin Elmer FTIR spectrometer SPECTRUM 2000 between wave number range of 4000 and 400 cm^{-1}. Finely divided 9 mg wood samples, obtained after grinding of blocks and drying at 103 °C, were dispersed in a matrix of KBr (300 mg) and pressed to form pellets. Due to the difficulty to define a reference spectral band, which remains completely invariable, to perform quantitative measurements, all comparisons were made qualitatively.

2.6.2. CP/MAS ^{13}C NMR analysis

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

2.6.3. ^{1}H NMR analysis

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM 400 spectrometer. Chemical shifts were expressed in ppm and calculated relative to TMS.

2.7. Contact angles measurements

Contact angles of untreated and heat treated blocks were recorded with a goniometer using water as probe liquid. Five microliters of distilled water were deposited on the wood surface (tangential face) with a microsyringue and contact angle measured after the total relaxation of the drop (equilibrium state). Six measurements were performed on each block and the values were averaged.

2.8. Microscopic analysis

Microscopic observation were performed with an environmental scanning electron microscope (ESEM Quanta 200) on a small block of 20 × 15 × 15 mm (L, T, R). The transversal section of the block was prepared with a microtome, repaired with marks and observed under the scanning microscope. After observation, the sample was heat treated for 4 h at 250 °C under nitrogen and then, observed again using scanning microscope at the marked points to compare wood anatomy before and after treatment. This methodology allows to avoid problems of surface preparation on heat treated samples which were generally very brittle.

3. Results and discussion

Fig. 1 represents the evolution of mass loss according to time at different temperatures.

Degradation of *G. robusta* wood is important during the first stage of the thermal treatment process and becomes less important in a second stage. The mass loss increases with time and temperature. As reported in the literature on European wood species (Nuopponen et al., 2004; Wikberg and Maunu, 2004; Hakkou et al., 2005), these mass

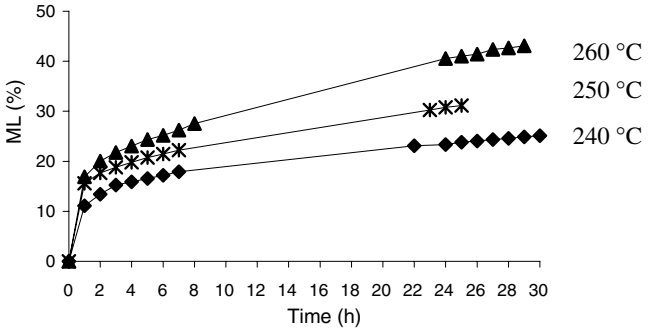


Fig. 1. Mass loss of *Grevillea robusta* wood after heat treatment.

losses are probably due to important degradations of hemicelluloses during the treatment. To confirm these assumptions, FTIR and CP/MAS ^{13}C NMR analysis were performed to characterize wood chemical components (Figs. 2 and 3).

CP/MAS ^{13}C NMR spectra of untreated and thermally modified *G. robusta* wood are presented in Fig. 2. Untreated sample indicates classical signals ascribable to main wood polymer components. Cellulose appears in the region between 60 and 105 ppm. The signals at 72–75 ppm are assigned to C-2, 3, 5 carbon, the signal at 65 ppm assigned to C-4 carbon and this at 105 ppm to C-1 hemiacetallic carbon. C-6 signal of cellulose is duplicated due to the presence of amorphous and crystalline cellulose appearing at 84 and 89 ppm respectively. Signals of hemicelluloses are less obvious due to their overlapping with those of cellulose. The shoulder at 102 ppm on the C-1 signal of cellulose is assigned to hemiacetallic carbon of hemicelluloses. Acetyl groups of hemicelluloses are detected at 20 and 173 ppm. Methoxyl groups of syringyl and guaiacyl units of lignin appears at 56 ppm, while aromatic carbons appear between 120 and 160 ppm. Aliphatic carbons of phenylpropane units of lignin are partially masked by polysaccharidic signals.

Evolution of NMR spectra recorded after heat treatment indicates that the main modifications appear rapidly after the first hour of treatment. Degradation of hemicelluloses is particularly obvious. The signal of the methyl of the acetyl groups at 20 ppm, mainly present on hemicelluloses, disappears totally after heat treatment. The shoulder at 102 ppm on the C-1 signal of cellulose at 105 ppm decreases as well after heat treatment confirming hemicelluloses degradation. Similar observations have been reported in the literature on different non durable European species (Tjeerdsma et al., 1998; Sivonen et al., 2002; Weiland and Guyonnet, 2003). As reported in the literature, cellulose crystallinity was more important after heat treatment. The signal at 89 ppm due to C-4 of crystalline cellulose increases slightly compared to the signal at 82 ppm due to amorphous cellulose C-4 (Wikberg and Maunu, 2004). General behaviour of NMR spectra is similar to spectra of other wood species reported in the literature excepted for the signal at 30 ppm which is very unusual. Explanation of this signal

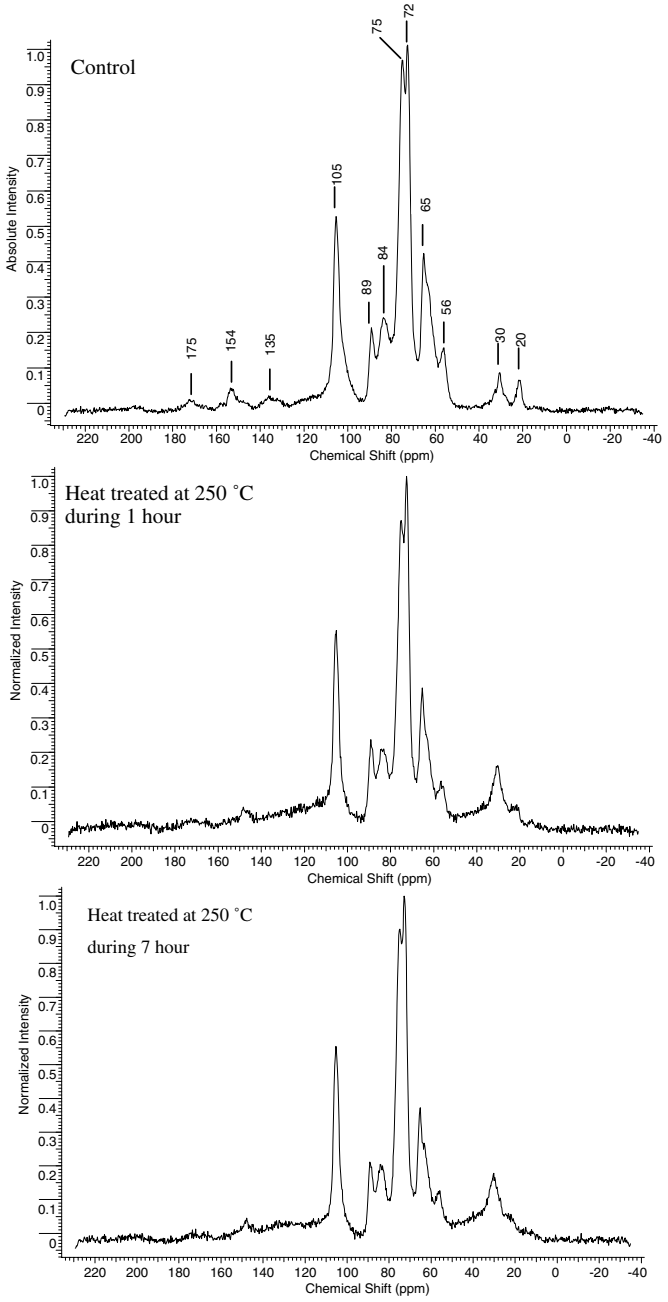


Fig. 2. CP/MAS ^{13}C NMR spectra of *Grevillea robusta* wood after thermal treatment.

is due to the presence of important quantity of lipophilic extractives, approximately 5%, identified after Soxhlet extraction with dichloromethane and ^{1}H NMR analysis to be mainly constituted of *n*-alkyl and *n*-alkenylresorcinols (Ritchie et al., 1965; Ridley et al., 1968; Cannon et al., 1973). Changes in the lignin signals are less significant indicating its higher stability. The appearance of new broad aromatic or alkenic resonances (110–135 ppm) and aliphatic resonances (10–50 ppm) after heat treatment indicate structural modifications of wood polymers due probably to a beginning of destruction of the amorphous cellulose

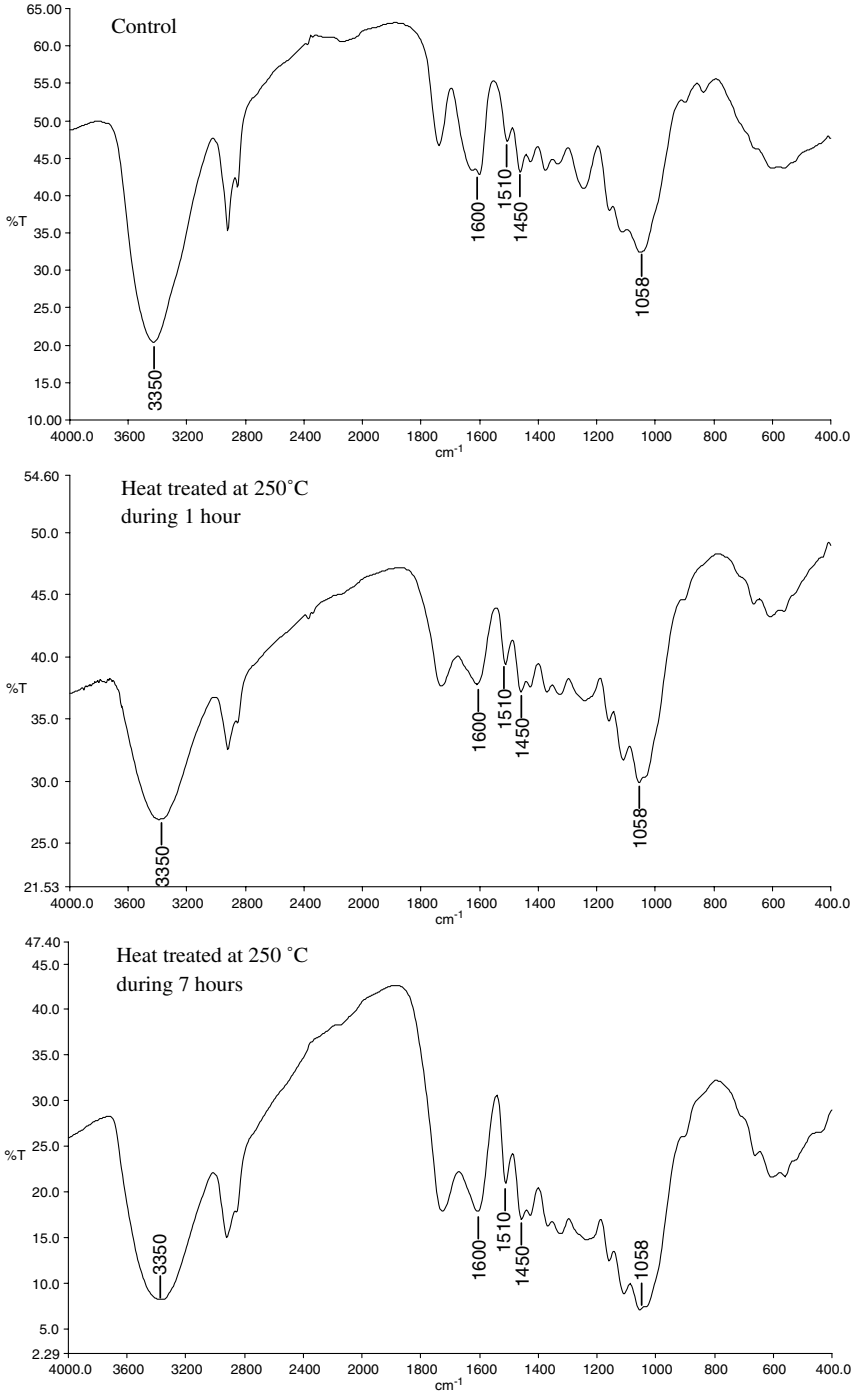


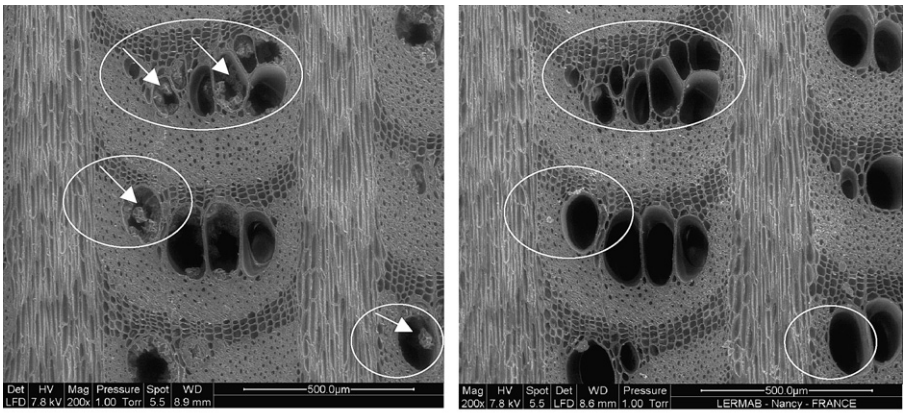
Fig. 3. FTIR spectra of *Grevillea robusta* wood after thermal treatment.

structure. Such modifications, previously reported during cellulose thermal treatment (Zawadzki and Wisniewski, 2002), could be at the origin of the increase of crystallinity.

FTIR analysis are more difficult to interpret due to the similarities of the spectra before and after treatments. However some small modifications can be observed indicating the same tendencies as previously observed by NMR. The O–H absorption band at 3350 cm^{-1} decreased compared to all other bands. Characteristic C–O absorption band of polysaccharidic components at 1058 cm^{-1} corresponding to C–O stretching vibrations decreases slightly comparatively to lignin characteristic band at 1600, 1510 and 1450 cm^{-1} confirming the degradation of hemicelluloses.

Microscopic analysis of *G. robusta* wood before and after heat treatment is presented in Fig. 4.

Microscopic analysis indicates that anatomical structure of wood was only slightly affected during treatment (Fig. 4). Vessels, fibers, parenchyma and rays are still obvious after heat treatment. The main differences was presence



Before heat treatment After Heat treatment
(white arrows indicates the extractives deposited in the vessels)

Fig. 4. Transverse sections of *Grevillea robusta* wood.

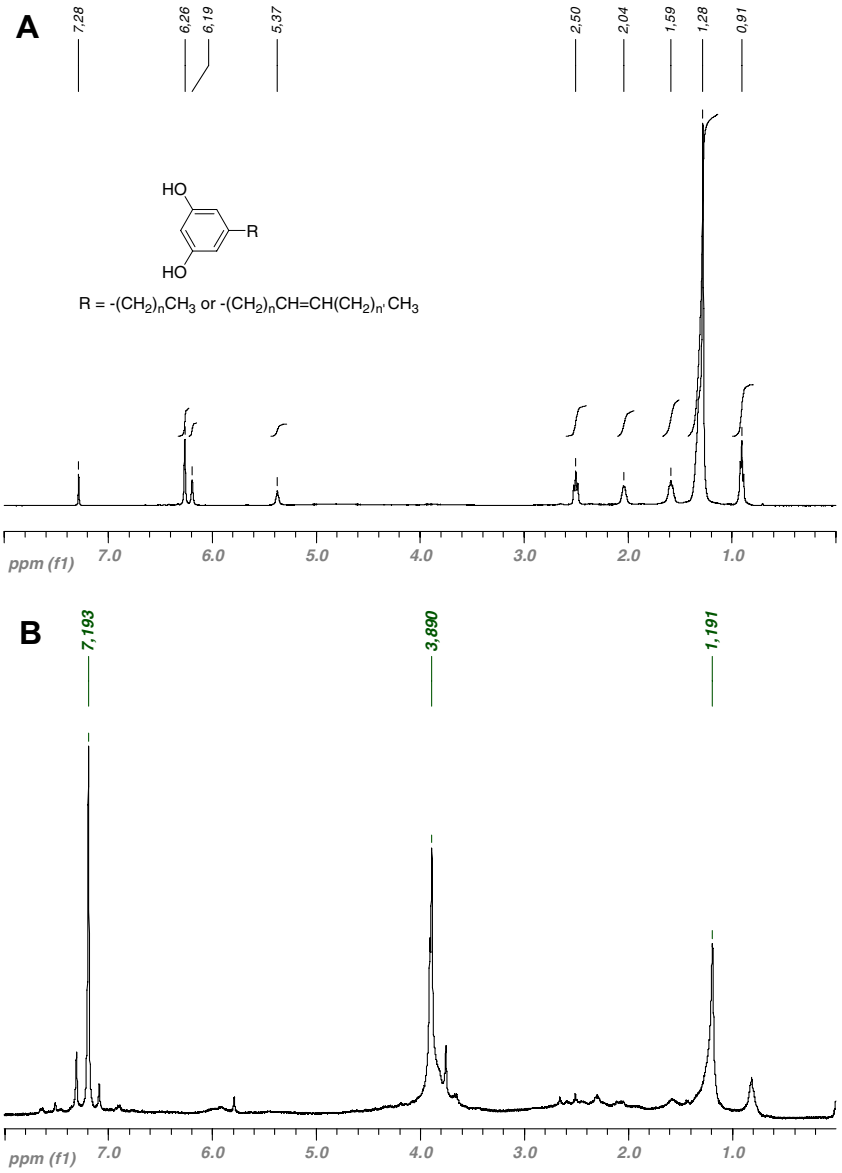


Fig. 5. [1]HNMR spectra of dichloromethane extractives of *Grevillea robusta* wood before (A) and after thermal treatment at 250 °C during 7 h (B).

of important quantities of extractives deposited in the vessels, which disappear after thermal treatment. ^{1}H NMR analysis of extractives of untreated and heat treated *G. robusta* after Soxhlet extraction with dichloromethane indicated an important degradation of these latter ones (Fig. 5). Before heat treatment, extracts are mainly constituted of *n*-alkyl and alkenyl resorcinols. Chemical shifts of aromatic protons appears as two singlets at 6.19 and 6.26 ppm characteristic respectively of the proton between the two hydroxyl groups and of the two other protons. Signal at 5.37 ppm is attributed to vinylic protons of ethylenic double bond. Signals at 2.50 and 2.04 ppm are characteristic of benzylic and allylic protons, while signals at 1.59, 1.28 and 0.91 correspond to methylene and methyl groups of fatty alkyl chain. Proton of phenolic hydroxyl group appears as a singlet at 7.28 ppm. ^{1}H NMR spectra is strongly modified after heat treatment indicating a total disappearance of characteristic chemical shifts of extracts initially present in wood. Signals of aromatic and ethylenic hydrogen atoms totally disappeared, while those of fatty alkyl chain are still obvious but present important modifications. The assignment of the NMR signals of extractives after heat treatment are not clearly identified at present. In the same time, quantity of extractives decreased from 5.2% before heat treatment to 1.6% after heat treatment confirming the degradation observed by NMR. Heat treatment result also in some shrinkage. Due to the anisotropy of wood, the shrinkage depends on the orientation. Tangential shrinkage is of approximately 6%, while radial shrinkage is of approximately 2% as measured with a veneer calliper.

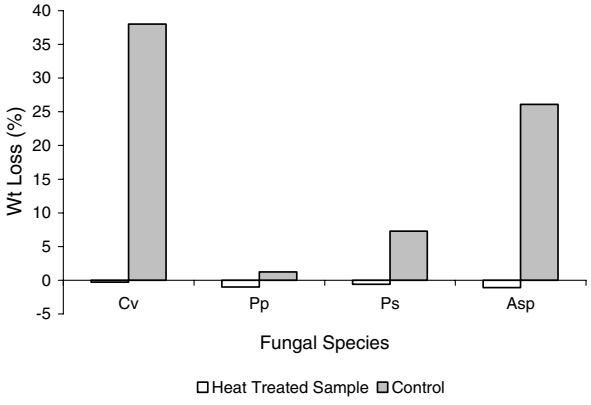
Effect of time of heat treatment performed at 250 °C on the durability to the white rot fungus *C. versicolor* is reported in Table 1. The results shows that heat treatment considerably improves wood durability. Different levels of wood degradation corresponds to different weight losses after varying the treatment time. It was observed that the ability of *C. vericolor* to degrade wood was reduced after modification by heat treatment. Durability against fungus increased with treatment time with optimum resistance reached after 20% mass losses. At the same time, untreated *G. robusta* control and beech wood control virulence were severely degraded by the fungus showing validity of the experiment. Decrease of wood wettability demonstrated by the higher contact angles measured after treatment has in a first time no or limited effects on the high moisture content recorded after biological test confirming results previously reported indicating that hydrophobic character conferred to wood after thermal treatment was not at the origin of the improvement of durability (Kamdem et al., 2002; Gosselink et al., 2004; Hakkou et al., 2005, 2006).

Durability of *G. robusta* heat treated wood was then investigated with different brown rot and white rot fungi. Tests were carried out with two European species (*C. versicolor* and *P. placenta*) and two tropical species (*P. sanguineus* and *Antrodia* sp.). Results are presented in Fig. 6. In all cases heat treated *G. robusta* was resistant to fungal attack. However, these results must be moderated according to the tested fungus. Indeed, while untreated *G. robusta* samples are strongly degraded by *C. versicolor* and *Antrodia* sp., heat treated samples show no degradation showing the efficiency of the treatment. Results are not significant in the case *P. placenta* and *P. sanguineus*, for which untreated samples like heat treated ones were not or only slightly

Table 1
Effect of time of treatment at 250 °C on durability of *Grevillea robusta* wood after three months exposure to *Coriolus versicolor*

Sample	θ (°)	ML (%)	MC (%)	WL (%)[a]
Grevillea robusta heat treated 0.5 h	113	12	111	3.6 ± 0.5
Grevillea robusta heat treated 1 h	116	16	104	2.2 ± 0.6
Grevillea robusta heat treated 5 h	113	20.5	88	0
Grevillea robusta heat treated 7 h	118	22	78	0
Grevillea robusta heat treated 15 h	111	26	49	0
Grevillea robusta control	31	–	97	25.8 ± 11.2
Fagus sylvatica control	–	–	53	33.5 ± 3.4

[a] Average value on four replicates.



Coriolus versicolor (Cv), *Poria placenta* (Pp), *Pycnoporus sanguineus* (Ps), *Antrodia sp.*(Asp)

Fig. 6. Weight losses of *Grevillea robusta* heat treated or not for 7 h at 250 °C after three months exposure to different fungi.

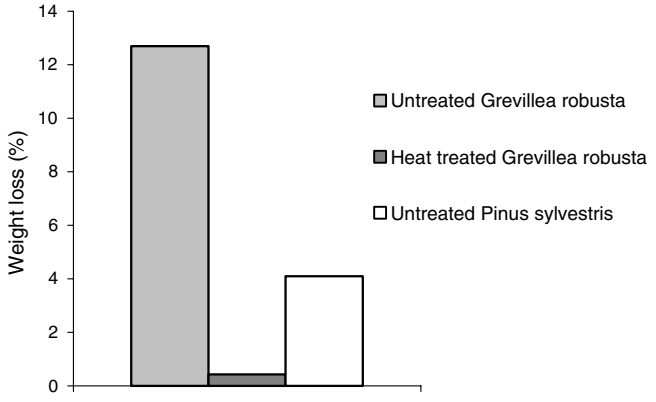


Fig. 7. Weight losses of *Grevillea robusta* heat treated for 7 h at 250 °C and controls tested against termites in laboratory conditions for 28 days.

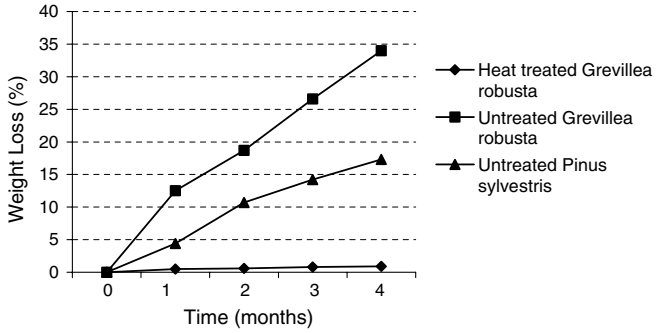


Fig. 8. Weight losses of *Grevillea robusta* heat treated for 7 h at 250 °C and controls tested against termites in field conditions.

attacked. Such a behaviour could probably be explained by water logging of the wood blocks hence not allowing the development of the fungi.

Results concerning resistance to termites after 28 days in laboratory conditions are presented in Fig. 7. Heat treated *G. robusta* showed insignificant termite attack, while untreated samples were severely attacked (compare weight losses of less than 1 for control to weight losses comprised between 11% and 14% for heat treated samples). Untreated *G. robusta* is more susceptible to termites than untreated *P. sylvestris*. Survival rate of termites was high in the controls. Mortality rate was high in the treated samples as the result of feeding on treated wood or inability to feed on it hence starve to death. After three weeks, all the termites in the treated sample containers were noted to have died. These results were confirmed under field test conditions (Fig. 8). There was significant difference between attacks on the heat treated *G. robusta* samples and the controls when exposed to termites in the natural environments. Attack on all samples increased with exposure time.

4. Conclusion

This study shows that heat treatment of *G. robusta* increases its durability against basidiomycetes and termites. The decay resistance depends of the treatment condition and is total for treatments performed at 250 °C for 7 h. Wettability changes observed after the heat treatment cannot be used to explain wood enhanced durability. Similarly to studies reported on non durable European wood species, chemical modifications seems to be the most plausible hypothesis to explain wood durability improvement. Mass losses, ^{13}C MAS NMR and FTIR analysis indicate important degradation of hemicelluloses. Moreover, NMR analysis indicate the presence of degradation products within the wood polymeric components due to a beginning of degradation of cellulose. Microscopic analysis indicate that wood anatomy was slightly affected and that some shrinkage occurred after treatment. All these results show that heat treatment could be a valuable alternative to toxic chemicals used actually to treat *G. robusta* wood in Kenya. This is confirmed by improved durability against fungi and termites in the laboratory and in the field. However, our results needs further investigations to validate laboratory results on larger scale and to study the effect of heat treatment on mechanical properties.

Acknowledgement

This work was supported by grant from the French government through the Embassy in Nairobi.

References

Alen, R., Kotilainen, R., Zaman, A., 2002. Thermochemical behaviour of Norway spruce (*Picea abies*) at 180–225 °C. Wood Sci. Technol. 36, 163–171.

Cannon, J.R., Chow, P.W., Fuller, M.W., Hamilton, B.H., Metcalf, B.W., Power, A.J., 1973. Phenolic constituents of *Grevillea robusta* (Proteaceae). Structure of robustol, a novel macrocyclic phenol. Aust. J. Chem. 26 (10), 2257–2275.

Gosselink, R.J.A., Krosse, A.M.A., van der Putten, J.C., van der Kolk, J.C., de Klerk-Engels, B., van Dam, J.E.G., 2004. Wood preservation by low-temperature carbonisation. Ind. Crops Prod. 19, 3–12.

Hakkou, M., Petrissans, M., El Bakali, I., Gerardin, P., Zoulalian, A., 2005. Wettability changes and mass loss during heat treatment of wood. Holzforschung 59 (1), 35–37.

Hakkou, M., Petrissans, M., Gerardin, P., Zoulalian, A., 2006. Investigation of the reasons for fungal durability of heat treated beech wood. Polym. Degrad. Stab. 9 (2), 393–399.

Hill, C., 2005. The Use of timber in the twenty-first century. In: Wood Modification, Chemical Thermal and other Processes, Wiley Series in Renewable Resources, pp. 1–18, ISBN-10 0-470-02172-9.

Kamdem, D.P., Pizzi, A., Jermannaud, A., 2002. Durability of heat-treated wood. Holz als Roh- und Werkstoff 60, 1–6.

KFMP, Kenya Forest Master Plan, 1994. Development Programmes, Ministry of Environment and Natural Resources, Government of Kenya.

Mouras, S., Girard, P., Rousset, P., Permadi, P., Dirol, D., Labat, G., 2002. Propriétés physiques de bois peu durables soumis à un traitement de pyrolyse ménagée. Ann. Forest Sci. 59, 317–326.

Nuopponen, M., Vuorinen, T., Jasma, S., Viitaniemi, P., 2004. Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies. J. Wood Chem. Technol. 24 (1), 13–26.

Patzelt, M., Stingl, R., Teischinger, A., 2002. Termische Modifikation von Holz und deren Einfluß auf ausgewählte Holzeigenschaften, In: Modifiziertes Holz Eigenschaften und Märkte, LIGNOVISIONEN Band 3, pp. 101–149, ISSN 1681–2808.

Ridley, D.D., Ritchie, E., Taylor, W.C., 1968. Chemical studies of the Protaceae II. Constituents of *Grevillea robusta*; the synthesis of *n*-tridecylresorcinol (grevillol) and related substances. Aust. J. Chem. 21 (12), 2979–2988.

Ritchie, E., Taylor, W.C., Vautin, S., Protaceae, I., 1965. Grevillea robusta and Orites excelsa. Aust. J. Chem. 18 (12), 2015–2020.

Santos, J.A., 2000. Mechanical behaviour of eucalyptus wood modified by heat. Wood Sci. Technol. 34, 39–43.

Sivonen, H., Maunu, S.L., Sundholm, F., Jämsä, S., Viitaniemi, P., 2002. Magnetic resonance studies of thermally modified wood. Holzforschung 56, 648–654.

Standard method laboratory for evaluation to determine resistance to subterranean termites, 1997. American Wood Preserver's Association Standard, E1-97, p. 4.

Standard method of evaluating wood preservatives by field tests with stakes, 1993. American Wood Preserver's Association Standard, E1-97, p. 9.

Tjeerdsma, B.F., Boonstra, M., Pizzi, A., Tekely, P., Militz, H., 1998. Characterisation of the thermally modified wood: molecular reasons

for wood performance improvement. Holz Roh-Werkstoff 56, 149–153.

Unsal, O., Ayrilmis, N., 2005. Variations in compression strength and surface roughness of heat treated Turkish river gum (*Eucalyptus camaldulensis*) wood. J. Wood Sci. 51, 405–409.

Weiland, J.J., Guyonnet, R., 2003. Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. Holz Roh-Werkstoff 61, 216–220.

Wikberg, H., Maunu, S.L., 2004. Characterisation of thermally modified hard- and softwoods by ^{13}C CPMAS NMR. Carbohyd. Polym. 58, 456–461.

Yildiz, S., Gezer, E.D., Yilditz, U.C., 2006. Mechanical and chemical behavior of spruce wood modified by heat. Build. Environ. 41, 1762–1766.

Zawadzki, J., Wisniewski, M., 2002. ^{13}C NMR study of cellulose thermal treatment. J. Anal. Appl. Pyrolysis 62, 11–121.