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MID-INFRARED SPECTROSCOPY AND DYNAMIC MECHANICAL ANALYSIS OF HEAT-TREATED OBECHE (*Triplochiton scleroxylon*) WOOD

James S. Fabiyi [1,♠], Bolade M. Ogunleye[1]

ABSTRACT

The chemical structure change and rheological behaviour of heat-treated Obeche (*Triplochiton scleroxylon*) wood were investigated. Wood samples were treated at 160 and 200°C for 30, 60 and 120 minutes. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and dynamic mechanical analysis (DMA) were employed to characterize the chemical structure and rheological property of the heat-treated wood, respectively. Infrared data showed that there was a reduction in the number of hydroxyl groups (one of the factors normally attributed to water absorption) of heat treated wood relative to the control samples. The relative cellulose crystallinity increased slightly which may be one of the factors contributing to the stiffness of the heat-treated wood. The latter increases with increasing treatment temperature and time. The rheological properties of the wood samples were tested while submerged in N-methyl-2-pyrrolidone solvent under saturated conditions. DMA results showed that the increasing heat treatment time caused an increase in the glass transition temperature relative to the control sample, irrespective of the treatment temperature. Therefore, heat treatment at moderately high temperatures (160 and 200 °C) showed an interesting potential which could be used to reduce water absorption and improve flexural modulus of Obeche wood.

Keywords: Chemical structure, dynamic mechanical analysis, glass transition temperature, heat-treated wood, infrared spectroscopy, rheological properties.

INTRODUCTION

Wood is an ancient renewable natural resource that has many applications especially in construction industry. However, wood has some disadvantages over its competitors such as steel, plastic and concrete. Wood is dimensionally unstable under changing moisture and temperature conditions. Additionally, it is degradable, weatherable and flammable; the former properties are more pronounced in the presence of moisture. The challenges facing wood industries in Nigeria are not limited to the aforementioned disadvantages but also the problems of over-exploitation and deforestation. Over-exploitation and deforestation have left Nigerian forests with young and small diameter trees which are mostly composed of a high proportion of juvenile wood as well as lesser known or underutilized timber species. These trees contain less chemical extractives that could make wood naturally durable. Therefore, construction industries are faced with finding solution to the problem of wood degradation and instability. Improvement on the inherent properties of wood polymers and their structures is achieved through various wood modification techniques such as thermal, hydrothermal, chemical, mechanical (densification) and plasma modifications (Hill 2006).

Thermal modification known as heat treatment causes the number of hydroxyl groups of cellulose and hemicelluloses to decrease thereby resulting in the decrease of the adsorption of water (Mitsui *et al.* 2008). Enhancement of the dimensional stability of wood occurs because volume swelling caused by water absorption is under control in consequence for the reduction in the number of water accessible hydroxyl sites and unknown mechanisms. Heat treatment of wood has been suggested to cause irreversible creation of new hydrogen bonds in the amorphous regions of cellulose and hemicelluloses (Kato and Cameron 1999); a phenomenon known as hornification in which a decrease of water retention value of fibres occurs due to structural changes in the cell wall during drying (Laivins and Scallan 1993).

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Additional mechanisms or factors that are yet to be identified have been suggested to contribute to the water absorption and equilibrium moisture content of heat-treated wood (Rautkari *et al.* 2013). An illustration of the hydroxyl groups' reduction is shown in Figure 1. Previous studies revealed that heat treatment reduces the equilibrium moisture content, water absorption, thickness swelling and wettability of wood (Pétrissans *et al.* 2003, Hakkou *et al.* 2005). Heat treatment at high temperature also induces darkening of wood (Brischke *et al.* 2007).

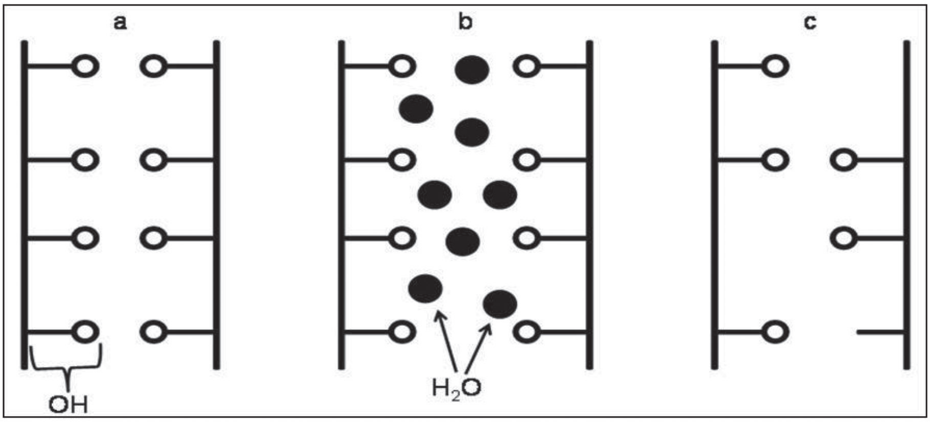


Figure 1. Schematic illustration of (a) untreated cell wall polymers with OH-groups, (b) cell wall polymers filled with water molecules and (c) cell wall polymers with removed OH-groups and cleaved chains.

In addition, other important wood properties such as surface color, durability and hardness are changed capable of enhancing efficient utilization of lesser known or underutilized timber species especially those of low economic and constructional values. Dimensional instability, flammability, biodegradability, and degra¬dation caused by acids, bases, and ultraviolet radiation are due to the chemical degradation reactions of wood which can be prevented or, at least, slowed down if the cell wall chemistry is altered (Rowell and Konkol 1987, Kumar 1994).

The growing interest in the application of heat-treated wood is due to (i) concern about environmental impact of chemical wood preservatives, (ii) cost of chemical modification, (iii) availability of chemical modification equipment, and (iv) availability of small diameter logs with a larger proportion of juvenile wood. Over the last two decades, markets for heat-treated wood have developed considerably and becoming the most successful among many other wood modification methods (Hill 2006). Heat-treated wood lack residual treatment chemicals thereby resulting in a lower environmental impact at the end of life contrary to that of chemically treated wood. Therefore, heat-treated wood can be used for garden, kitchen and furniture, cladding on wooden buildings, bathroom cabinets, floor material, musical instruments, ceilings, inner and outer bricks, doors and window joinery, and a variety of other outdoor and indoor applications (Syrjanen and Oy 2001). Most heat treatments of wood are conducted at various temperatures ranging from 140 to 260 °C with the time of duration from 30 minutes to several hours in an environment with low oxygen content (Homan and Jorissen, 2004, Ates *et al.* 2009). Temperatures over 150 °C alter the physical and chemical properties of wood permanently (Korkut *et al.* 2009). Temperatures below 140 °C are insufficient to cause significant change in wood properties and a temperature above 260 °C results in severe degradation of the wood material (Hill 2006, Korkut and Kocaefe 2009).

Several studies have been conducted on the effects of heat treatment on wood color change, moisture sorption and dimensional stability, durability and mechanical properties (Rowell and Konkol 1987, Temiz *et al.* 2006, Hakkou *et al.* 2005, Korkut and Kocaefe 2009). However, research on the effects of heat treatment on the rheological behaviour and surface chemistry of Nigeria native trees is scanty. An understanding of the chemical structure of wood is essential to determine the influence of thermal treatment on the wood polymers' functional groups, because almost all properties of wood depend upon its chemical composition. The viscoelastic behaviour of heat-treated wood is of a great importance because it is influenced by the temperature setting that such wood can tolerate (under which condition degradation would not occur) during some processing operations. These operations include board manufacturing and surface hardening of woods for furniture and interior materials (Uhmeier *et al.* 1998). During thermoforming, softening temperature makes wood malleable and helps optimization of steam bending (Redman 2010). The most important viscoelastic property associated with these processing operations is the glass transition temperature, *Tg*, (softening temperature). The temperatures at which wood polymers would reach their *Tg* when wood is in its dry state would be far above the temperature that could cause destruction (char). Therefore, saturating wood with a solvent plasticizer such as water, ethylene glycol and N-methyl-2-pyrrolidone would lower the *Tg* and helps maintain the integrity of the wood (Salmén 1984).

Therefore the aim of this study was to investigate the compositional analysis using infrared spectroscopy and dynamic viscoelastic properties of heat-treated Obeche (*Triplochiton slecroxylon*) wood.

MATERIALS AND METHODS

All specimens (10 mm × 20 mm × 20 mm) were cut from a single piece of commercial Obeche (*Triplochiton scleroxylon*) sapwood lumber (900 mm × 1200 mm × 3600 mm) obtained from a local sawmill in Akure, Ondo state, Nigeria. The lumber was randomly selected from the base position (0 to 30% of the merchantable height) of a 23 year old tree. Forty defect-free specimens were randomly selected in order to deal with the biological variability of wood; then divided into 8 treatment groups. The specimens were oven-dried at 105 °C until constant weight was achieved; then cooled in a desiccator over silica gel. Untreated samples were referred to as control.

The heat treatment was conducted in a closed process vessel, a Muffle furnace, with a temperature controlled heating unit. The oven-dried samples were thermally treated at temperatures of 160 and 200 °C for 30, 60 and 120 min under anhydrous nitrogen gas. The temperature of the furnace was kept at the treatment temperature for 5 min before introducing the wood samples. At the end of each treatment, the heat-treated samples were removed from the furnace, cooled in a desiccator over silica gel.

Compositional analysis

The effect of heat treatment on the surface chemistry of Obeche wood was determined using Attenuated total reflectance Fourier transform infrared spectroscopy. Infrared measurements were performed at room temperature with a Thermo-Nicolet Avatar 370 FTIR spectrometer operating in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal with 2 mm diameter sampling area). Thin slices (50 µm) were cut at 4 mm below the wood surface using a microtome, vacuum dried and subjected to FTIR analysis. Two replicate specimens per treatment were analysed. Each spectrum was taken as an average of 64 scans at a resolution of 4 cm^{-1}. Moderate pressure (the knob of the ATR was controlled until the pressure read 12) was applied to the specimen during the measurement to ensure good contact with the ATR crystal, which is essential to achieve high quality results. A separate single channel sample spectrum was automatically divided by the single channel background (from the clean ATR crystal) spectrum for each sample. Six spectra per wood treatment sample were collected and averaged to one spectrum, which was thereafter ATR and baseline corrected following spectra analysis procedure from Omnic software v 7.3. The spectra were shifted parallel to the wavenumber-axis so that the minimum between 2000 and 1800 cm^{-1} was equal to zero, as suggested by Zavarin *et al.* (1990). Spectra used for the calculation of crystallinity index and lignin relative content were baseline-corrected using the rubber-band method whereby more than two reference points were used. There is no absorbance scale provided in the figures presented in this study because the spectra are shifted parallel to the wavenumber axis as presented in a study conducted by Schwanninger *et al.* 2004).

Determination of rheological properties

Wood specimens (cylindrical discs, 8 mm diameter, 5 mm thickness) for the dynamic viscoelastic properties determination were taken from each heat-treated wood using a commercially available ‘‘plug-cutter’’. The experiment was conducted with a TA Instruments 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). 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). Note, the positioning of the growth rings within the specimen geometry was random.

A modified testing procedure of Fabiyi *et al.* (2011) was adapted. Specimens were saturated with N-methyl-2-pyrrolidone (NMP, C_5H_9NO, pH: 7,7 to 8,0 (10%, aqueous), flash point: 93 °C) at room temperature. Solvent-submersion analysis was conducted with a modified 8 mm diameter parallel-plates fixed into a stainless steel cup that maintained specimen immersion and was then covered to reduce evaporative losses. During analysis, specimens were maintained under a 20 N compressive force to prevent plate slippage but less than the required force to cause crushing. Anhydrous N2 gas is 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).

The dynamic mechanical analysis of all the heat-treated wood was conducted under cooling scans. They were equilibrated at 130 °C for 20 min, and then cooled from 130 to 0 °C at 3 °C/min under the frequency of 1 Hz. Two specimens were analyzed within each subsample. Average storage modulus, loss modulus, and tan δ traces were created using OriginPro software version 8.0.63 (OriginLab, Northampton, MA, USA). The Tg of each cooling scan curve was determined following data analysis procedure from TA Rheology Advantage software by finding the maximum peak. Statistical analysis was performed in SPSS v17 software using analysis of variance (ANOVA) for the tan δ maximum of the modified wood.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The effects of heat treatment on the polysaccharides (cellulose and hemicelluloses) and lignin of Obeche wood were examined using FTIR spectroscopy. Infrared spectra were recorded from untreated (control) and heat-treated Obeche samples (Figures 2, 3, 4). The fingerprints of the functional groups of the untreated Obeche wood are labelled in figure 2. Similar functional groups were observed in the spectra of the heat-treated wood and the summary of IR assigned bands is presented in table 1. IR spectra of heat-treated Obeche wood considerably changed relative to the control samples. The intensity of the C-H stretching vibration around 2897 cm^{-1} for the 160 °C and 200 °C treated wood only decreased significantly relative to control samples for 120 min treatment time (Figure 3 and Figure 4). The number of hydroxyl group at 3341 cm^{-1} significantly decreased with a prolonged treatment for heat-treated wood at 160 °C (Figure 3). At 200 °C, the number of hydroxyl groups decreased with increasing treatment time without a significant difference among them (Figure 4). The decrease in the intensity of stretching vibrations of hydroxyl groups at 3341cm^{-1} showed that some hydroxyl group sites have been lost because of heat treatment. This reduction of the hydroxyl group can be used to explain as the usually observed high dimensional stability of heat-treated wood (Tuong and Li 2010). The ratio of the peak heights at 1506 cm^{-1}/897cm^{-1} was used to calculate the relative lignin content of the heat-treated Obeche wood as adapted from Schwanninger *et al.* (2004). The lignin proportion increased with increasing temperature and treatment time (Table 2). Esteves and Pereira (2009) and de Moura *et al.* (2012) also observed increased lignin contents with increasing treatment temperature. The increase in relative lignin content could be due to the degradation of the hemicelluloses and the apparent thermally stable lignin (de Moura *et al.* 2012).

Table 1: Summary of IR bands observed in untreated and treated Triplochiton scleroxylon wood.

Wavenumber (cm^{-1})	Peak assignment	Structural polymer	Reference
853	C–H out-of-plane in position 2, 5 and 6 of G units	-	Faix (1992)
897	C_1-H deformation of glucose ring	Cellulose	Fengel and Ludwig (1991)
1030	C–O stretching of primary alcohol	Cellulose and hemicelluloses	Faix (1992)
1055	C–O stretching of secondary alcohol	Cellulose and hemicelluloses	Pandey (1999)
1101	aromatic skeletal and C–O stretch	Polysaccharides and Lignin	Pandey (1999)
1155	C–O–C asymmetric valence vibration	Cellulose and hemicelluloses	Pandey (1999)
1227	C–C plus C–O plus C=O stretch; G condensed > G etherified	Lignin	Faix (1992)
1263	G ring plus C=O stretch	Lignin	Faix (1992)
1319	C-H_2 rocking vibration	Cellulose	
1369	C–H_2 deformation vibration	Cellulose and hemicelluloses	Faix (1992)
1421	C-H in-plane deformation with aromatic skeletal vibrations	Lignin	Pandey (1999)
1454	Asymmetric C–H bending from methoxyl group	Cellulose	Fengel and Ludwig (1991)
1507	aromatic skeletal vibration (C=C), guaiacyl > syringyl	Lignin	Faix (1992)
1593	Aromatic skeletal vibrations plus C=O stretch; S > G; G condensed > G etherified	Lignin	Faix (1992)
1656	C=C *cis* stretching of unsaturated acids or sterols	Tannin	Sun and Tomkinson (2002)
1733	C=O valence vibration of acetyl-	Xylan in hemicelluloses	Fengel and Ludwig (1991), Lionetto *et al*. (2012)
2897	C-H stretching in methyl and methylene groups		Faix (1991)
3342	OH stretching	Wood polymers	Hergert (1971)

Despite the various functional groups changes observed in the spectra of the heat-treated wood, only those that have direct influence on the mechanical and dimensional stability were considered for discussion in this study. Changes in cellulose crystallinity and the wood polymer hydroxyl group affect the mechanical property and dimensional stability. Mo *et al.* (1994) stated that the physical and mechanical properties of polymers depend significantly on the degree of crystallinity. The amorphous and crystallised cellulose have been characterized using the assigned peak for cellulose at 1421 cm^{-1} and 1369 cm^{-1} for CH_2 and CH bending mode, respectively; 1155 cm^{-1} and 897 cm^{-1} for C-O-C stretching and C-H deformation, respectively, 1319 cm^{-1} for CH_2 rocking, which distinguished between amorphous and crystallised cellulose, and 2897 cm^{-1} for C-H stretching vibrations (Fackler *et al.* 2011, Temiz *et al.* 2006). Based on this information, the determination of relative cellulose crystallinity index using the ratios of absorbance of 1319 to 2897 cm^{-1} and 1421 to 897 cm^{-1} have been widely employed (Ferrús and Pagés 1977, Hassan *et al.* 2000, Akgül *et al.* 2007, Ates *et al.* 2009, Tuong and Li 2010). Therefore, some regions of interest are considered (Figure 2 and Figure 3).

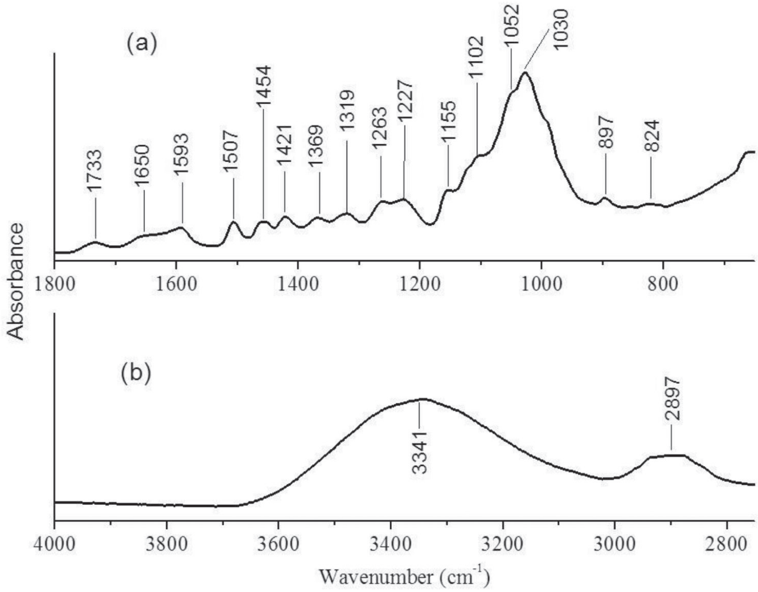


Figure 2. Infrared spectra of untreated *Triplochiton scleroxylon* wood sample. (a) spectra of wood in the range of 1800 to 650 cm^{-1} and (b) of 4000 to 2750 cm^{-1}. No absorbance scale provided in the figure because they are shifted parallel to the wavenumber axis.

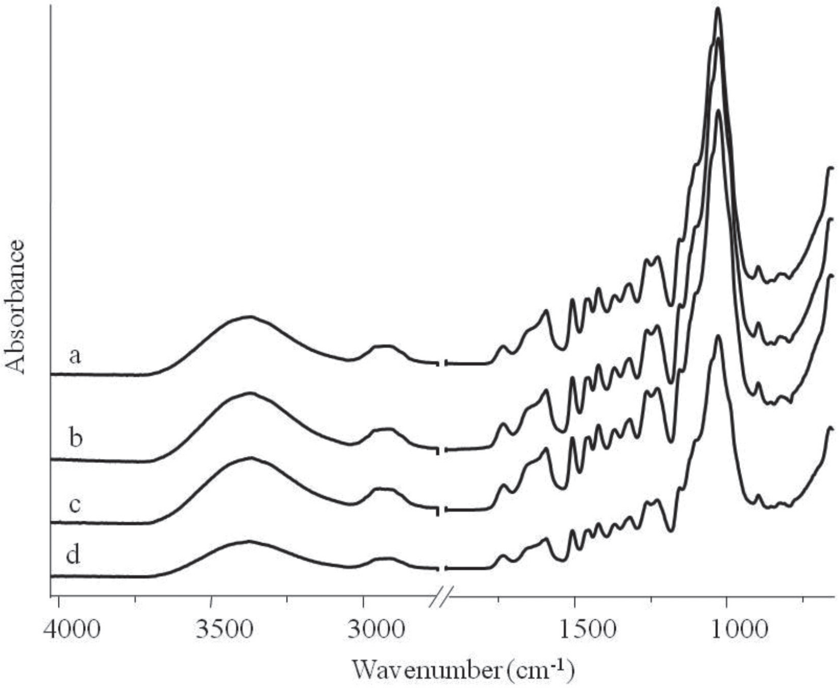


Figure 3. Infrared spectra of *Triplochiton scleroxylon* wood samples (a) control, (b) treatment at 160 °C for 30 min., (c) treatment at 160 °C for 60 min., and (d) treatment at 160 °C for 120 min. No absorbance scale provided in the figure because they are shifted parallel to the wavenumber axis.

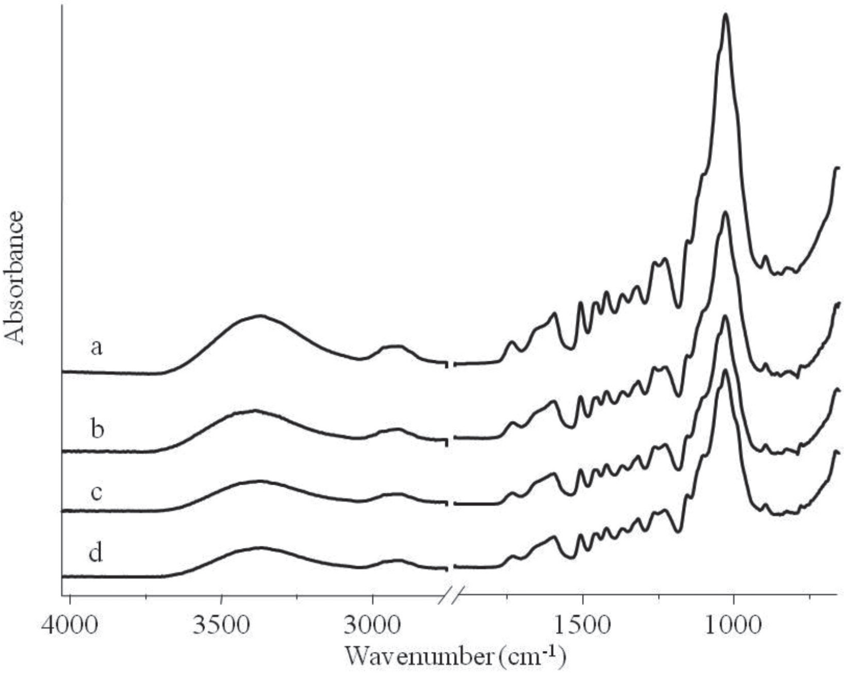
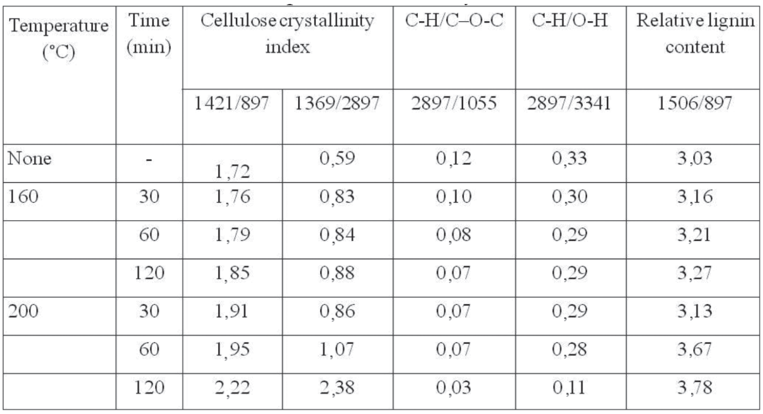


Figure 4. Infrared spectra of *Triplochiton scleroxylon* wood sample (a) control, (b) treatment at 200 °C for 30 min., (c) treatment at 200 °C for 60 min., and (d) treatment at 200 °C for 120 min. No absorbance scale provided in the figure because they are shifted parallel to the wavenumber axis.

Table 2 shows that an increase in treatment temperatures and times caused a slight increase in the crystallinity index relative to the control sample. A similar trend was found by Tuong and Li (2010). The increase in the crystallinity has been suggested to be due to the crystallization in the "quasi"-crystalline amorphous regions caused by rearrangement or re-orientation of cellulose molecules inside the amorphous regions (Bhuiyan *et al.* 2000). In addition, an increase in crystallinity could be attributed to degradation/rearrangement of amorphous cellulose content (Hill 2006). Heat treatment of wood causes decomposition of hemicelluloses, ramification of lignin and crystallisation of cellulose (Kocaefe *et al.* 2008); these changes result in reduction of swell of heat-treated wood (Calonego *et al.* 2011). In an early study conducted by Tjeerdsma *et al.* (1998), significant reduction in water adsorption of heat-treated wood was attributed to the increase in the relative proportion of the crystalline cellulose, in which the hydroxyl groups are not easily accessible to water molecules. Tsuchikawa and Siesler (2003) concluded that the diffusion of solvent (penetrant) into the amorphous region of wood was faster than that into the semi-crystalline or crystalline regions irrespective of wood species.

Table 2. Relative crystallinity index, ratio of C-H to C-O-C and relative lignin content of heat treated *Triplochiton scleroxylon* wood.



Temperature (°C)	Time (min)	Cellulose crystallinity index		C-H/C–O-C	C-H/O-H	Relative lignin content
		1421/897	1369/2897	2897/1055	2897/3341	1506/897
None	-	1,72	0,59	0,12	0,33	3,03
160	30	1,76	0,83	0,10	0,30	3,16
	60	1,79	0,84	0,08	0,29	3,21
	120	1,85	0,88	0,07	0,29	3,27
200	30	1,91	0,86	0,07	0,29	3,13
	60	1,95	1,07	0,07	0,28	3,67
	120	2,22	2,38	0,03	0,11	3,78

Rheological properties

Temperature dependencies of the storage modulus and loss modulus for heat-treated Obeche wood specimen at 1 Hz with heating rate of 3 °C/min are shown in Figure 5. The storage modulus increased with decreasing temperature from 130 to 0 °C due to the stiffening of the NMP fully saturated wood and maintained in a plasticiser. The storage modulus represents the ability of any material to store mechanical energy and resist deformation (Hrabalova *et al.* 2010). This could be used to evaluate the rigidity or stiffness of the material. Heat treatment at 160 °C and 200 °C for 120 min. caused significant increase in the storage and loss moduli of modified Obeche wood whether at glassy or rubbery state. This implies that heat treated Obeche wood at 160 °C and 200 °C for 120 min. are more flexible than the untreated wood. From the glassy state (0 °C) to the rubbery state (130 °C), heat treated wood at 200 °C for 120 min has the highest stiffness. Boonstra *et al.* (2007) observed that thermally treated Scots pine and radiata pine at 165 °C had a 10 and 13% increase in the modulus of elasticity, respectively. They further remarked that the increase of the MOE (26%) of the radiata pine occurred when the hydro-thermolysis treatment temperature was raised to 175 °C. Boonstra *et al.* (2007) suggested that because wood polymers are inter-related and networked, a heat treatment method which affects the individual wood components and their interaction is bound to affect the mechanical properties of wood. Hirai et al. (1972) observed that the wood dynamic elastic modulus slightly increased after about 100 hours' heating at the relatively low temperature of 100 °C, corresponding to the increase in the cellulose crystallinity. The effect of heat treatment on the tan δ intensity and tan δ maximum (the point where transition between the glassy to rubbery state occurs) is shown in Figure 5. Tan δ intensity decreased with increasing in heat treatment duration except for 160 °C at 60 min. The glass transition temperatures are heat treatment duration dependent; increasing the treatment time from 30 to 120 mins at 160 °C and 200 °C caused increase in the *Tg* (Figure 6). Increase in the heat treatment time results in increase in *Tg* irrespective of the temperature at which the wood samples were treated relative to control.

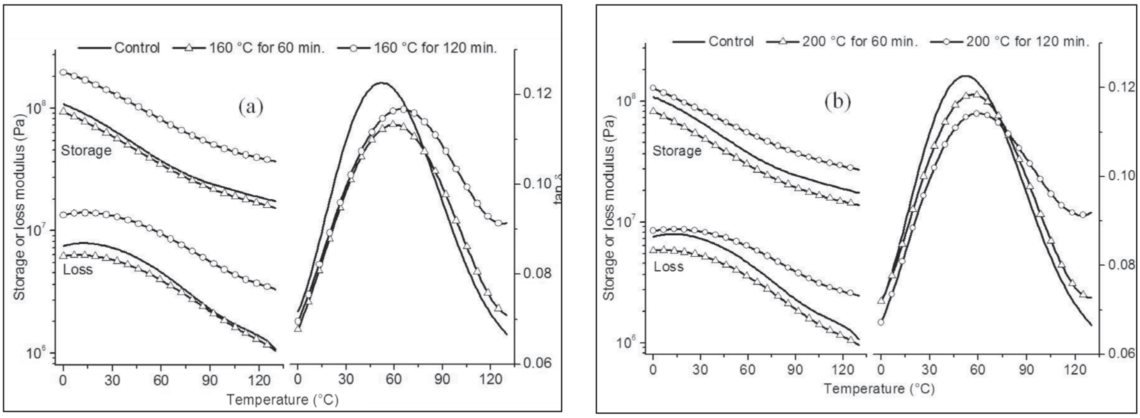


Figure 5. Average compressive-torsion cooling scans of heat-treated at (a) 160 °C and (b) 200 °C for 60 and 120 min. *Triplochiton scleroxylon* wood (saturated and immersed in NMP, 3 °C/min, 1 Hz).

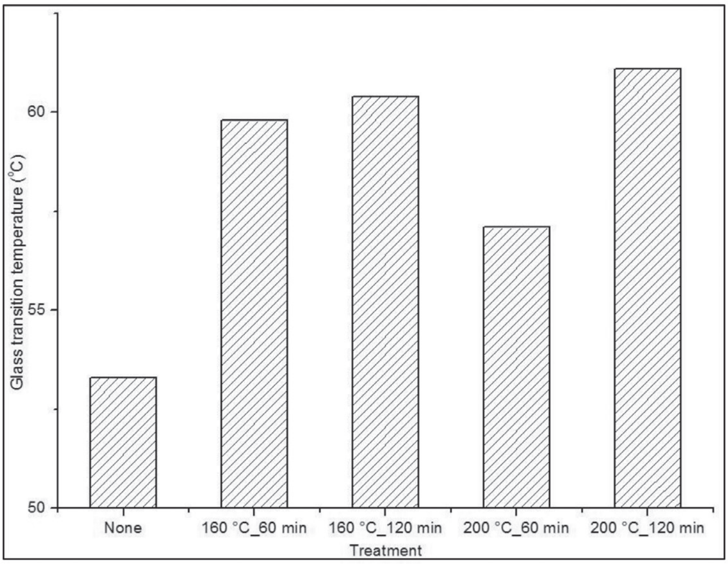


Figure 6. Glass transition temperature of heat (at 160 and 200 °C for 60 and 120 min.) treated *Triplochiton scleroxylon* wood (3 °C/min, 1 Hz, each mean, n = 2).

CONCLUSIONS

In this study Obeche (*Triplochiton scleroxylon*) wood samples were subjected to heat treatment at two different temperatures (160 and 200 °C) and three different duration levels (30, 60 and 120 min). The effect of heat treatment on the rheological behaviour and surface chemistry was investigated. The higher the treatment temperature and the longer the treatment time, the lower the number of hydroxyl groups and the higher the relative crystallinity index, which would result in improving the dimensional stability and stiffness of the heat-treated wood. The glass transition temperature increased with increase in the heat treatment time relative to the control at any given heat treatment temperature (160 or 200 °C). Therefore, heat treatment of Obeche wood at moderately high temperature is a promising approach towards its properties improvement.

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