Research Square

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Strength Properties, Thermal Stability, and Microstructure of Acetylated Obeche (Triplochiton Scleroxylon K. Schum) Wood

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Abstract

Acetylation is a well-established process to improve dimensional properties of wood and resistance to fungi attack. This study was carried out due to limited studies on its effect on mechanical properties, thermal stability, and microstructural aspects of wood. Wood blocks, (each 20×20×60 mm) of Obeche were acetylated with acetic anhydride at 120°C for 60, 120, 180, 240 and 300 minutes. The microstructure and thermal stability of acetylated and unmodified wood blocks were assessed using SEM and TGA, respectively. The Maximum compressive strength (MCS//g) and Modulus of Elasticity (MOE) of the wood specimens were also determined. The SEM indicated no visible damage or defect in the microstructure of all the acetylated wood and no significant differences in the strength properties compared to untreated wood. Acetylated wood showed an increased thermal stability compared to unmodified wood.

Introduction

Wood modification is the term used to describe the application of a chemical, biological or physical agent on wood resulting to improvement in the property of the material (Hill 2006). There are several methods of wood modification including thermal (Sandberg et al. 2017; Jones et al. 2019), fufurylation (Mantanis 2017; Jones et al. 2019), impregnation (Emmerich et al. 2019), and chemical modification of which acetylation is the most studied and reported method (Bongers and Uphill 2019; Zelinker et al. 2020). Convincingly, chemical modification of wood has been used to reduce number of hydroxyl groups, thus, improving the performance properties (Rowell 2006).

In the last decade, acetylation has been the most promising method to enhance the economic and technical qualities of timber (Sandra 2016). It is a chemical reaction whereby acetic anhydride reacts with hydroxyl groups in the cell wall, thus forming a stable covalent bond (Rowel 1983). Hence, there is reduction in the number of hydrophilic hydroxyl groups that is responsible for moisture adsorption thereby decreasing swelling and increasing decay resistance (Hill and Jones 1996; Hill 2006; Sandra 2016; Adebawo et al. 2020). However, the acetylation, depending on the composition of the wood cell wall polymers, has a large influence on wood several wood properties such as changes in color, density, stiffness, compressive strength, hardness and impact (FPL 2010; Adebawo et al. 2016; Rowell 1996).

Furthermore, there have been reports on modifications in physical and strength properties of wood when it is chemically modified such as changes in moisture absorption (Akitsu et al. 1993), vibration (Norimoto et al. 1992), creep (Norimoto et al. 1987), acoustical properties (Yano et al. 1993), compression strength and hardness (Hillis 1984), and bending strength and shear strength (Rowell 1991; Akitsu et al. 1993). However, few reports are available on the changes in the physical and mechanical properties of tropical hardwoods after acetylation.

One of the few studies on tropical hardwood, Obeche (*T. scleroxylon*) confirmed that heat treatment could increase the dimensional stability and increase glass transition temperature (Fabiyi and Ogunleye 2015). The majority of chemical modification research on wood has been on enhancing dimensional instability

and resistance to biological deterioration. Information on the microstructure of the acetylated tropical hardwood Obeche and the effect on strength, microstructure and thermal properties has also not been well documented. This study was carried out to ascertain if there is any alteration at structural level of the acetylated obeche wood, which might possibly affect mechanical properties.

Materials And Methods

Wood blocks preparation and Acetylation Process

Sapwood from plantation grown Obeche (*T. scleroxylon*) taken at breast height was used for this study. The planks were sawn and 75 blocks with dimension 20 mm × 20 mm × 60 mm (radial × tangential × longitudinal) were dried to a moisture content of ~ 7% before modification.

The wood blocks were impregnated with mixture of acetic anhydride and acetic acid (m:m of 92:8), in a stainless-steel reactor by using vacuum and pressure at temperature of 25°C and 10–15 bar of pressure for 30 minutes to saturate the wood. The internal temperature was controlled with the introduction of Nitrogen gas as the inert medium. Acetylation reaction was carried out for varying periods of time (1, 2, 3, 4 and 5 h) to achieve different degrees of impregnation while the temperature was fixed at 120°C. The acetylated samples were then washed, stored in acetone for 60 minutes, and then allowed to air dry for a week. A total of fifteen (15) samples were treated for each acetylation time (Adebawo et al. 2016).

Evaluation of selected mechanical properties of unmodified and acetylated Obeche

The maximum compressive strength parallel to grain (MCS//g) and modulus of elasticity (MOE) of the blocks (20 mm x 20 mm x 60 mm) were determined following BS373:1957 method. Using a 4kN computer-controlled MTS-SANS CMT 5000 Universal testing machine, the strength properties were measured. The untreated and acetylated samples were examined at a crosshead speed of 0.635 mm/min, with ten replicates of each treatment utilized.

Microstructure examination of unmodified and acetylated Obeche wood samples.

The microstructures of the cross-sections of untreated and acetylated Obeche wood blocks (20 mm × 20 mm × 10 mm) were examined under high resolution thermionics Scanning Electron Microscope (SEM) - Hitachi S3200N. The cross- section of the wood surfaces were examined to verify possible changes in wood structure. The VP-SEM used in the microscope allowed direct observation (without precoating) as the atmosphere conductivity prevents electrical change accumulation at low magnifications.

Thermal Analysis

Wood samples that had already been acetylated for each treatment as well as untreated samples were ground to a size of 40 mesh. Thermogravimetric analysis (TGA) of acetylated and untreated wood samples was carried out using a thermogravimetric analyzer (TA Q500). The samples were evenly and

loosely distributed in an open sample pan, and the initial sample weight was between 5-20mg. Treated and untreated wood samples were subjected to heating under nitrogen atmosphere at heating rate of 10^0C/min to 800^0C. Weight loss against temperature was recorded. The variation of the mass of the sample allows drawing the TG (variation of the mass in function of the temperature) and TGD (derivative of loss of mass versus the time) thermograms. The combination of these two thermo grams gives a clear indication of number of stages of the thermal degradation

Results And Discussion

Maximum compressive strength (MCS//g) and Modulus of Elasticity (MOE)

The maximum compressive strength parallel to the grain (MCS//g) and Modulus of Elasticity of untreated and acetylated samples are presented in Table I. The MCS//g and MOE ranged from 19.26–20.07 N mm^{-2} and 855.26 -1085.1 N mm^{-2}, respectively. The samples also acquired enhanced hydrophobicity. Reductions in moisture content of acetylated samples after chemical modification can also lead to improving its mechanical properties (Militz 1991; Akitsu et al. 1993). Yet, degradation of wood cell wall by modification may induce loss of strength. Some authors reported great strength loss of wood modified by dimethyloldihydroxyethylene urea (DMDHEU) due to acid degradation of the cell wall (Nicholas and Williams 1987; Hill 2006).

Table I. Maximum compressive strength parallel (MCS//g) to grain and Modulus of Elasticity (MOE) of untreated and acetylated Obeche blocks.

	Wood strength property (N mm^{-2})	
Acetylation time (Min)	**MOE**	**MCS//g**
Untreated	855.26 (79.56)a	19.26 (1.18)a
60	950.3 (274.23)a	20.06 (0.19)a
120	1085.1 (320.28)a	19.79 (0.56)a
180	1060.7 (58.06)a	20.07 (0.83)a
240	1061.6 (21.85)a	19.38 (0.87)a
300	991.4 (186.91)a	19.62 (0.73)a

Each value is a mean of ten replicates (standard deviation in parentheses)

However, ANOVA result as presented in Table I demonstrated that all MCS//g and MOE of the acetylated wood samples showed no significant difference when compared to the unmodified samples despite the slight increase in mean values.

The results are generally in line with previous findings reporting a negligible effect of acetylation on strength properties (Akitsu et al., 1993; Larsson and Tillman, 1989; Larsson and Simonson 1994; Liu et al. 1994; Rowell, 1991). However, a few studies have found slightly reduction in the mechanical properties. This may be due to reduction in the amount of fiber per volume as a result of lignocellulose hydrolysis. Yanjun et al. (2013) reported inconsistent changes in some mechanical properties of acetylated were depending on the type of wood, method of treatment and WPG. Sefc et al. (2012) mentioned the average increase of compression strength for beech wood due to wood modification was insignificant. On the contrary, Hamdan and Islam (2012) reported an increase in compressive modulus and decrease in modulus of rupture of modified five different tropical hardwoods- Jetulang (*Dyera costulata*), Terbulan (*Endospermum diadenum*), Batai (*Paraserianthes moluccana*), Rubberwood (Hevea brasillensis), Pulai (*Astonia pnematophora*) - after treatment.

Scanning Electron Microscopy of Acetylated wood

The acetylation treatments of Obeche showed no obvious defects and damage in the microstructure of the wood for all the acetylated wood (Fig. 1–6). However, slight alterations in color of the acetylated samples occurred when compared with the unmodified specimens. Also, the large pore sizes seen on the micrographs of the untreated samples reduced after acetylation. The highest reduction was seen in pore sizes in the 240 min and 300 min acetylated Obeche wood samples.

During acetylation, the use of elevated temperatures and acetic acid could lead to swelling of the cell wall which could have changed or damaged cell wall tissues resulting to changes in the mechanical properties of the wood (Sander et al. 2003). Uptake of water by the cell wall will continue until fiber saturation point is reached leading to bulking of the cell wall, but, repeated swelling and shrinking will possibly lead to structural deformation. Acetylation gives a lasting bulking effect contrary to reversible swelling that occur during water sorption (Rowell 1983). In the present study, SEM revealed no obvious damages in the microstructure of the acetylated Obeche wood; the cell walls remained intact with no visible defects or deformation, which are in line with the findings of (Sander et al. 2003) who reported that swelling of the cell wall tissue after acetylation did not expand beyond the fiber saturation point; thus, the treatment gave no changes to the ultrastructure of the wood. The likely reason is because acetylation reaction takes place at a single site with no occurrence of polymerization or cross-linking. The reduction in the acetylated wood samples pore sizes may be attributed to etherification at the hydroxyl groups by bulky acetyl groups, thereby reducing pore sizes. It has been found that wood species with large vessels and pores such as Obeche are usually light weight with coarse texture (Karl 1984). Furthermore, the kind of swelling that occurs in wood after fiber saturation point has been reached whereby the wood no longer absorb water is the same swelling that occurs during acetylation of wood. Hence, no obvious effect of acetylation on wood microstructure still after long periods at elevated temperatures.

Thermal Analysis

Thermal analysis of wood specimens is presented in Fig. 7. Thermal analysis of all the wood specimens revealed three distinct regions. In the first region, the peak produced by the derivative curves between 20°C and 160°C, relates to water evaporation from the intercellular space and there was no material degradation up to 160°C. When the temperature exceeded 160°C, decomposition occurred, and thermal stability decreased progressively (Wielage et al. 1999; Ruxanda et al. 2012). In the second region, DTG curves is characterized by a peak just below 340°C and a shoulder below 300°C, which reflects the thermal degradation of cellulose and hemicellulose. In third thermogravimetric region, char formation and loss of gases took place. The untreated and acetylated wood samples show a main one-stage degradation within the range of 250–480°C, in which all the carbohydrates decomposed (Ruxanda et al. 2012). Due to rapid decomposition of cellulose, a narrow peak having a long tail is observed.

The thermal decomposition of untreated wood specimen began at temperatures between 200 and 250°C and increased until 335°C which is the maximum rate loss of the material. For all the acetylated counterparts, the thermal decomposition began to occur at temperatures above 260°C and increased with higher temperatures until 346°C for maximum rate loss of the wood.

Table II. Thermogravimetric analysis of untreated and acetylated wood of *Triplochiton scleroxcylon.*

Reaction Time (Min).	$T_{5\%}$	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{70\%}$	$T_{80\%}$	Max weight loss	Der. Temp (ºC)
Untreated	246.15	263.56	307.58	331.43	349.85	446.90	1.32	335.03
60	260.74	279.07	311.41	331.35	347.69	456.25	1.31	337.94
120	265.41	283.07	315.92	338.19	354.67	419.58	1.29	344.35
180	267.4	285.32	318.26	339.36	355.6	443.25	1.29	346.85
240	264.23	283.32	317.92	339.86	355.94	453.42	1.21	345.10
300	263.15	282.48	317.08	340.78	359.99	487.27	1.18	345.58

The maximum weight loss and derivative temperature of thermal decomposition of untreated and acetylated wood specimens are given in Table II. It could be seen that untreated wood samples have the highest weight loss of 1.32 of derivative temperature of 335.03°C while the lowest weight loss of 1.18 at derivative temperature of 345.58 was observed in the 5h-acetylated samples.

It can be seen that the acetylated samples showed distinct degradation stages from untreated samples. The decomposition temperature for the weight loss at 5% and 10% occurred at 246 and 264°C, respectively, for the untreated samples, whereas shifted to a higher temperature for the acetylated samples ranging from 260–267°C and 279–285°C, respectively. At 70% and 80% weight loss, the decomposition temperature for the untreated samples occurred at 350 and 447°C, respectively, while the

acetylated samples at occurred within the range of 348–369°C and 420–487°C, respectively. It has been confirmed from previous studies (Adebawo et al. 2016) that modification of wood with anhydrides etherify hydroxyl groups with acetyl groups, leaving the surface more hydrophobic. The higher decomposition temperature of the acetylated samples as compared to the non-acetylated sample may be explained by the chemical changes in hemicellulose and (to a lesser extent) cellulose. In comparison, thermal stability of the 5h- acetylated wood was higher than other acetylated wood. This observation could be due to greater weight gain observed in the blocks after acetylation which may indicate decrease in hydroxyl groups as a result of etherification in the fiber walls (Adebawo et al. 2019; Hung et al. 2016).

Conclusions

The study presented the upshot of acetylation on microstructure, selected strength properties (MOE and compression parallel to the grain), and thermal stability of Obeche (*T. scleroxylon*). Acetylation at different levels of wood modification did not have any negative effect on the compression parallel to the grain and bending stiffness of the wood; thus, the wood became a good engineering material because substantial reductions in mechanical properties greatly limit its application. Likewise, acetylation did not alter the microstructure of the wood; in fact, there was only reduction in the large pore sizes of the wood owing to replacements of hydroxyl groups with bulky acetyl groups. Thermogravimetric analysis supported that weight loss at varying reaction times was lower by comparison to unmodified samples which suggests an enhancement in thermal stability.

Declarations

Acknowledgments

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Figures

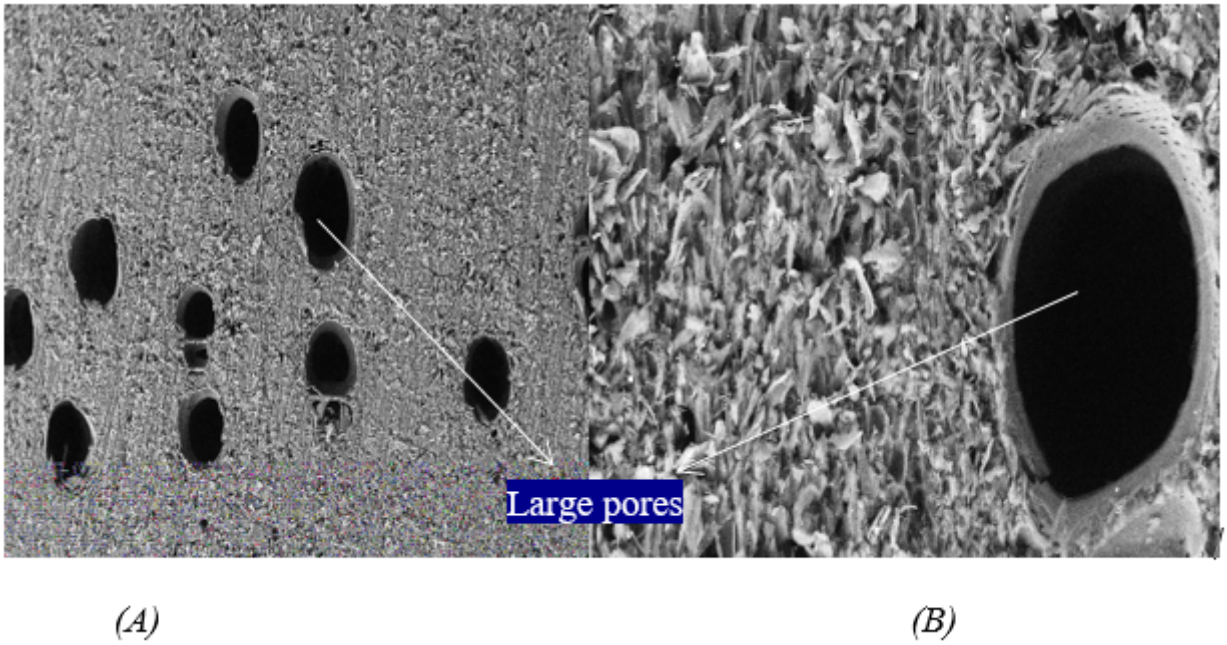


Figure 1

SEM Image of untreated T. scleroxylon wood at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

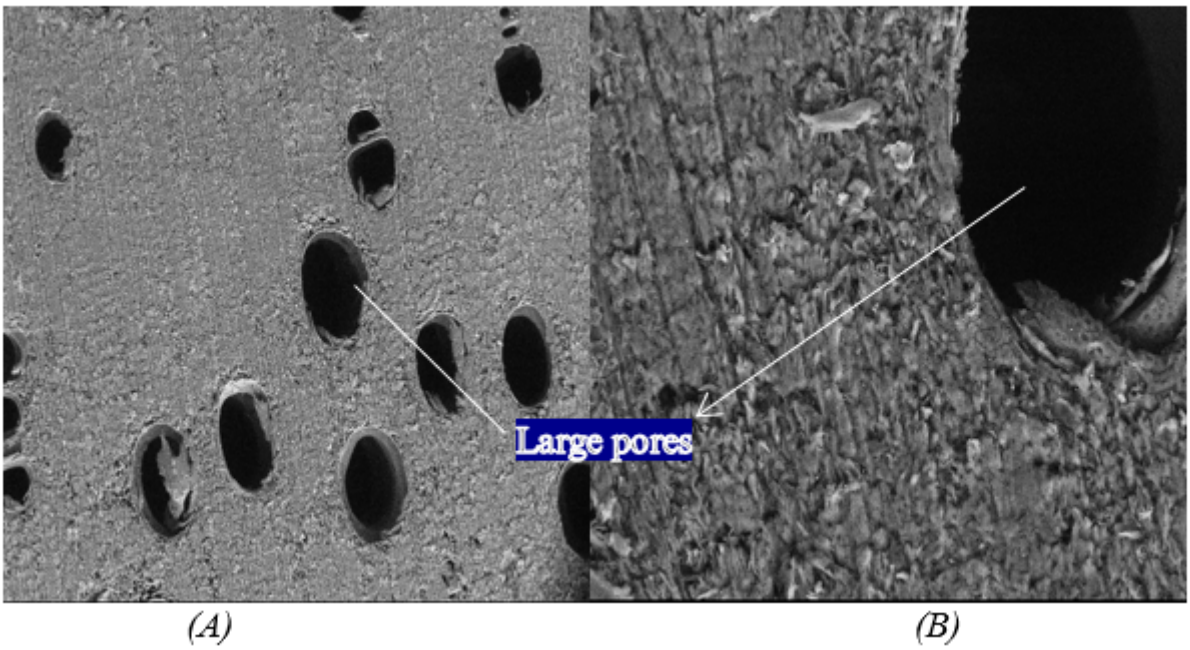


Figure 2

SEM Image of 1h-acetylated T. scleroxylon wood sample at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

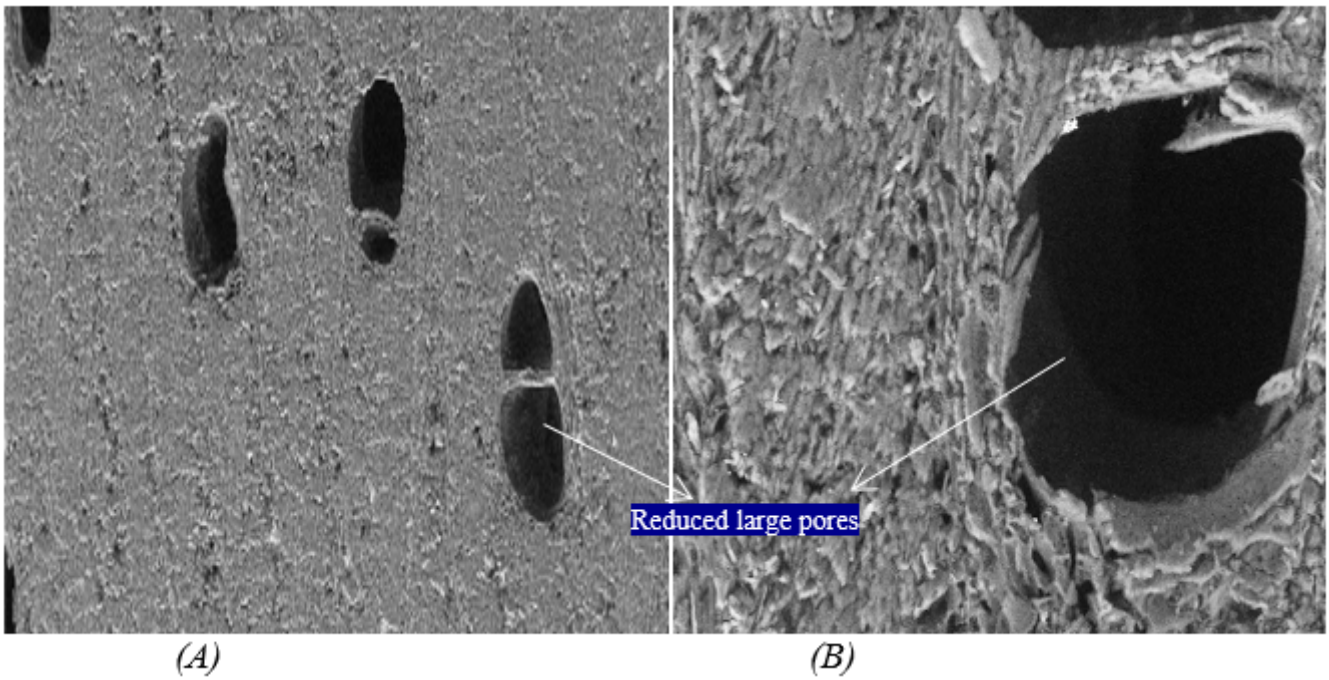


Figure 3

SEM Image of 2h-acetylated T. scleroxylon wood sample at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

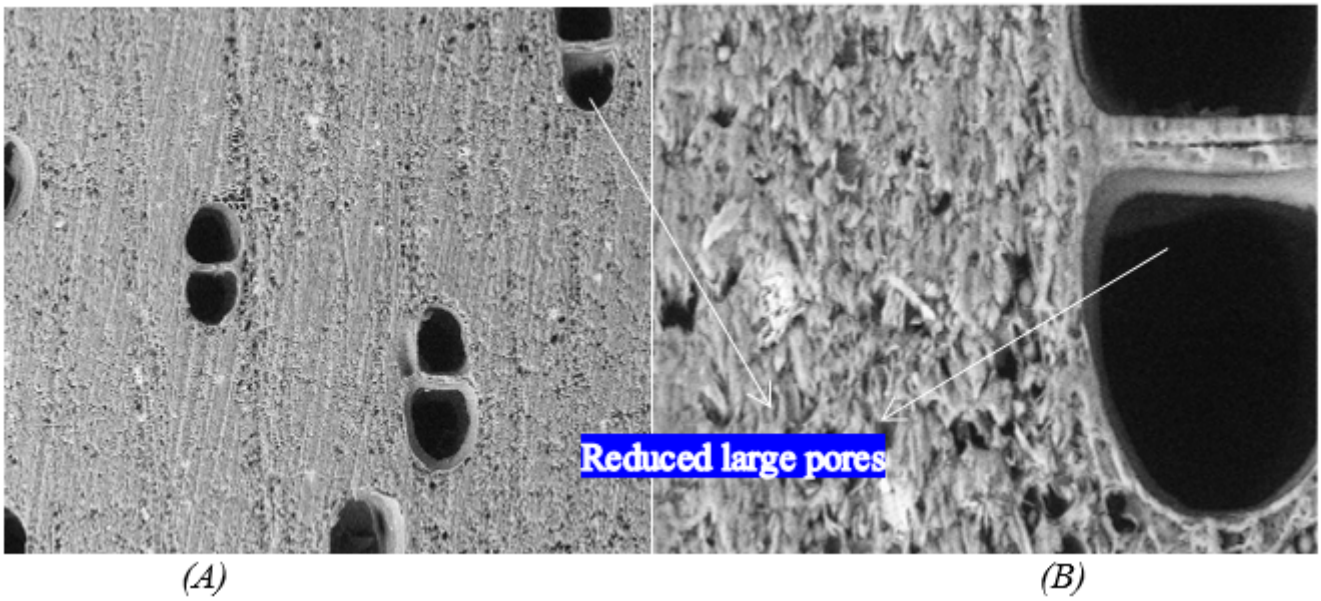


Figure 4

SEM Image of 3h-acetylated T. scleroxylon wood sample at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

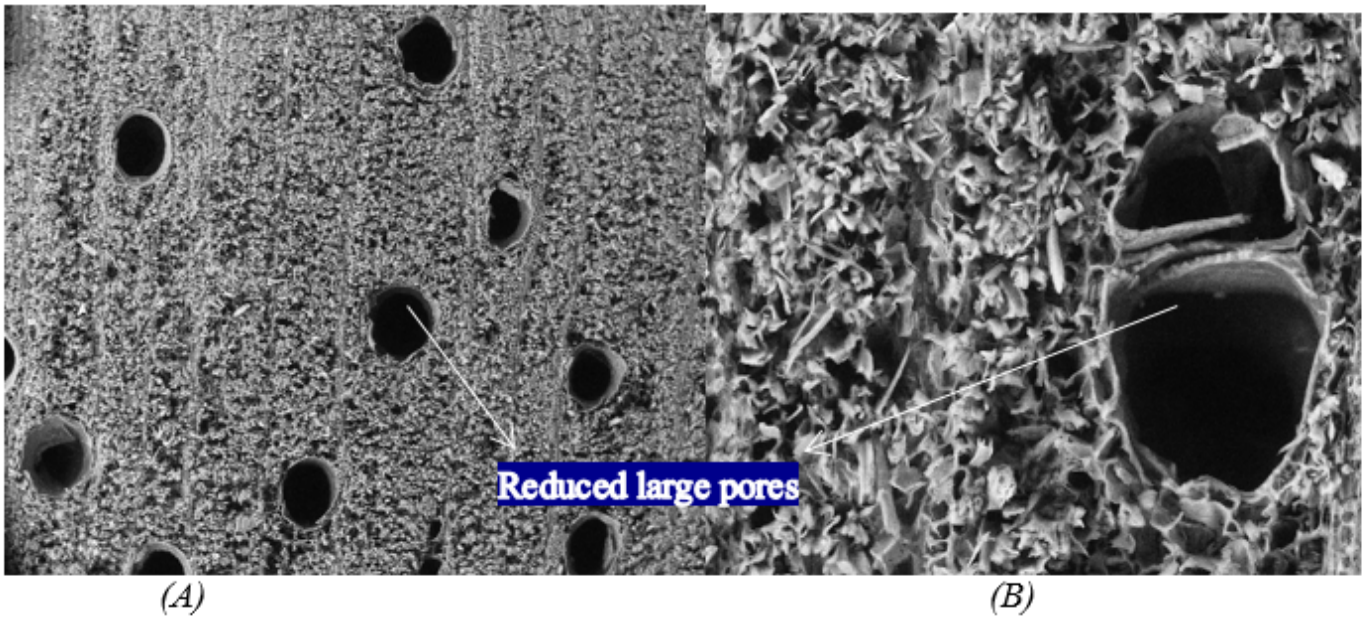


Figure 5

SEM Image of 4h- acetylated T. scleroxylon wood at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

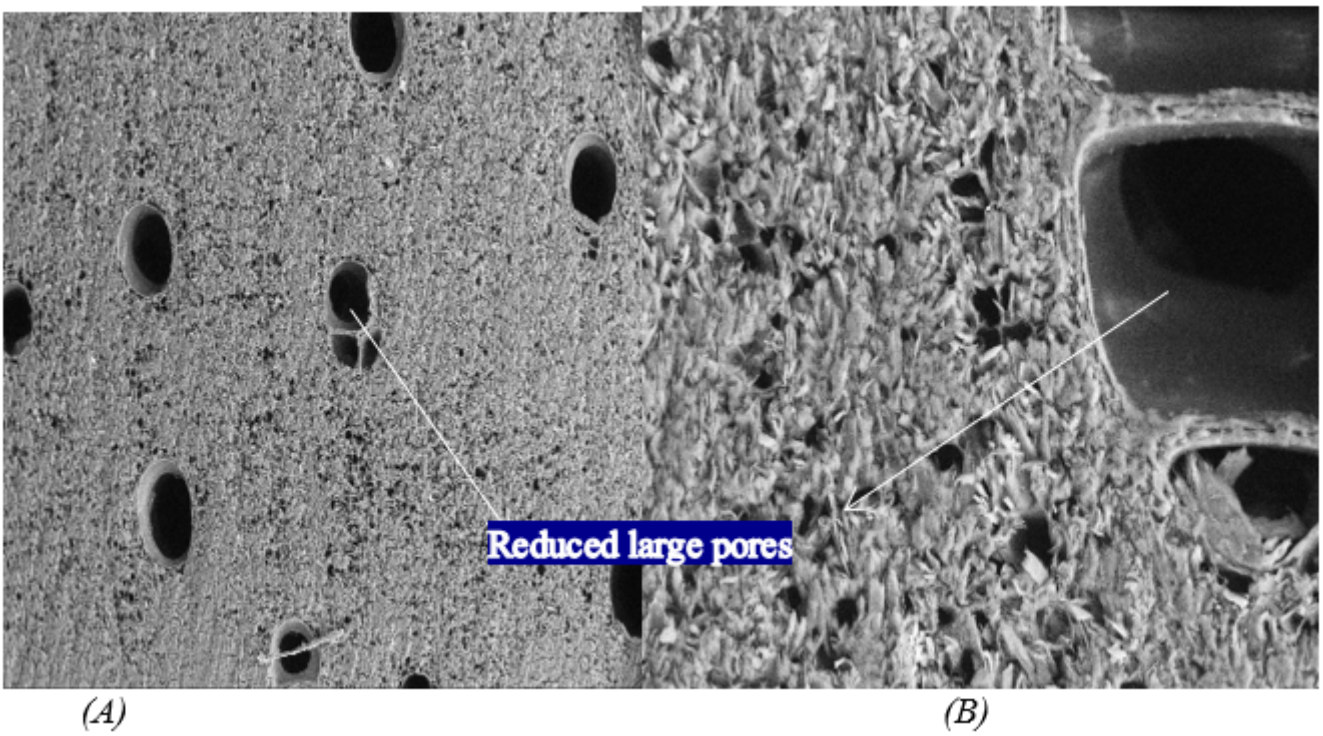


Figure 6

SEM Image of 5h- acetylated T. scleroxylon wood at different magnifications

(A) Mag. 50 × (B) Mag. 250 ×.

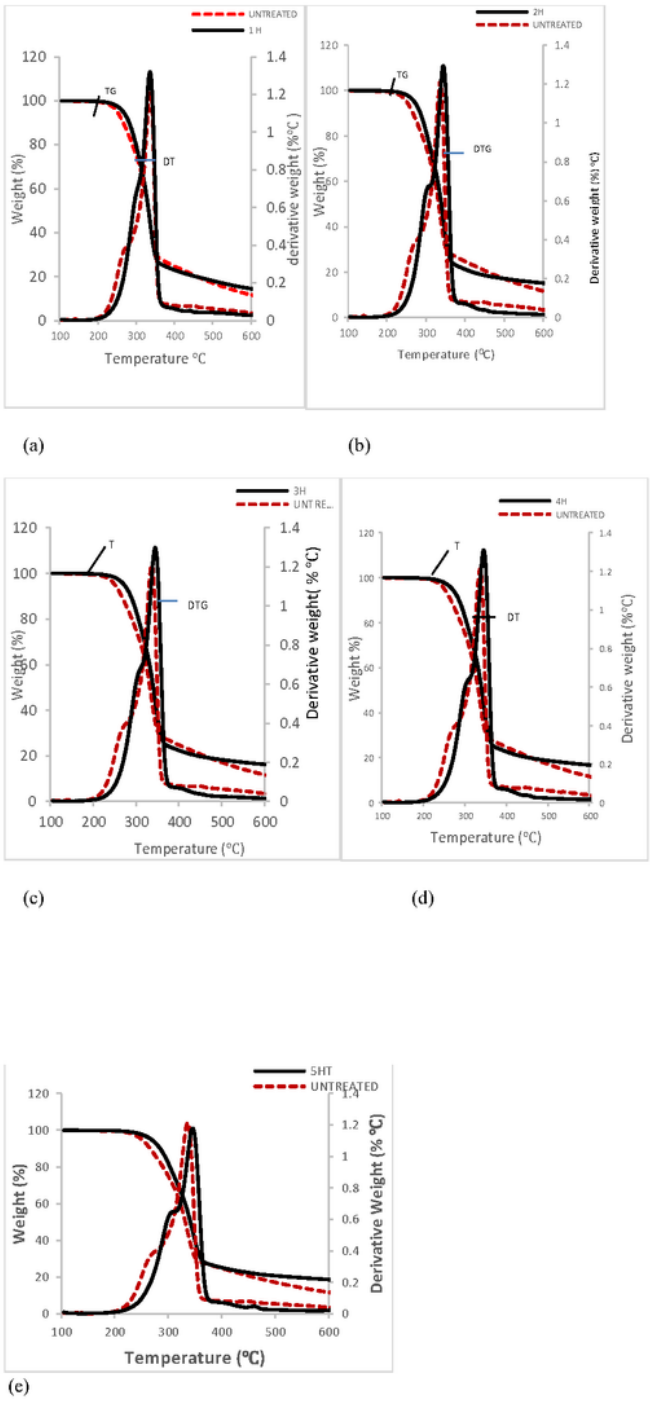


Figure 7

Thermogravimetric and differential thermogravimetric of untreated and acetylated Obeche wood. (a) untreated and 1h-acetylated samples (b) untreated and 2h- acetylated samples. (c) untreated and 3h-acetylated samples. (d) untreated and 4h-acetylated samples (e) untreated and 5h- acetylated samples.