STRENGTH PROPERTIES, THERMAL STABILITY AND MICROSTRUCTURE OF ACETYLATED OBECHE

(Triplochiton scleroxylon K. SCHUM) WOOD

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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 the effect of acetylation on mechanical properties, thermal stability, and microstructural aspects of wood. Wood blocks, (each 20×20×60 mm) of Obeche wood 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.

Keywords: acetylation, compression strength, hardwood, microstructure, thermogravimetry

INTRODUCTION

Wood modification is the term used to describe the application of a chemical, biological or physical agent on wood, resulting in an improvement in the properties of the material.¹ There are several methods of wood modification, including thermal,^{2,3} fufurylation,^{2,4} impregnation⁵ and chemical modification, of which acetylation is the most studied and reported method.^{6,7} Convincingly, chemical modification of wood has been used to reduce number of hydroxyl groups, thus, improving the performance properties.⁸

In the last decade, acetylation has been the most promising method to enhance the economic and technical qualities of timber.⁹ It is a chemical reaction whereby acetic anhydride reacts with hydroxyl groups in the cell wall, thus forming a stable covalent bond.¹⁰ Hence, there is reduction in the number of hydrophilic hydroxyl groups that is responsible for moisture adsorption, thereby decreasing swelling and increasing decay

resistance.^{1,9,11,12} However, depending on the composition of the wood cell wall polymers, acetylation has a large influence on several wood properties, producing changes in color, density, stiffness, compressive strength, hardness and impact.¹³⁻¹⁵

Furthermore, there have been reports on modifications in physical and strength properties of wood when it is chemically modified, specifically, changes in moisture absorption,¹⁶ vibration,¹⁷ creep,¹⁸ acoustical properties, compression strength and hardness, and bending strength and shear strength.^{16,20} 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.²¹ The majority of chemical modification research on wood has been focused 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 the structural level of the acetylated obeche wood, which might possibly affect mechanical properties.

EXPERIMENTAL

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 dimensions of 20 mm \times 20 mm \times 60 mm (radial \times tangential \times longitudinal) were dried to a moisture content of ~7% before modification.

The wood blocks were impregnated with a mixture of acetic anhydride and acetic acid (m:m of 92:8), in a stainless-steel reactor by using vacuum and pressure, at a 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. The 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.¹⁴

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 the BS373 method.²² 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 \times 20 mm \times 10 mm) were examined under highresolution thermionic Scanning Electron Microscopy, using a Hitachi S3200N SEM. The cross-section of the wood surfaces was 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 charge 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 5-20 mg. Treated and untreated wood samples were subjected to heating under nitrogen atmosphere, at heating rate of 10 °C/min to 800 °C. 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 thermograms gives a clear indication of the number of stages of 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 1. The MCS//g and MOE ranged between 19.26-20.07 N mm⁻² and 855.26-1085.1 N mm⁻², respectively. The samples also acquired enhanced hydrophobicity. Reductions in the moisture content of acetylated samples after chemical modification can also lead to improving their mechanical properties.^{6,23} Yet, degradation of wood cell wall by modification may induce loss of strength. Some authors reported great strength modified loss of wood by dimethyloldihydroxyethylene urea (DMDHEU) because of acid degradation of the cell wall.^{1,24}

However, ANOVA result, as presented in Table 1, 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.^{16,20,25,26} However, a few studies have found a slight 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.*²⁷ reported that inconsistent changes in some mechanical properties of acetylated

samples depended on the type of wood, method of treatment and WPG. Sefc *et al.*²⁸ mentioned the average increase in compression strength for beech wood due to wood modification was insignificant. On the contrary, Hamdan and Islam²⁹ reported an increase in compressive modulus and decrease in modulus of rupture for 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 (Figs. 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 in pore size was seen 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 in changes in the mechanical properties of the wood.³⁰ The uptake of water by the cell wall will continue until the 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 occurs during water sorption.¹⁰

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.*,³⁰ who reported that swelling of the cell wall tissue after acetylation did not expand beyond the fiber saturation point; thus, the treatment caused no changes in the ultrastructure of the wood.

 Table 1

 Maximum compressive strength parallel to grain (MCS//g) and modulus of elasticity (MOE) of untreated and acetylated Obeche blocks

A actulation time (min)	Wood strength property (N mm ⁻²)				
Acetylation time (mm)	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)



(A) (B) Figure 1: SEM images of untreated *T. scleroxylon* wood at different magnifications; (A) 50×, (B) 250×



Figure 2: SEM images of 1h-acetylated T. scleroxylon wood at different magnifications; (A) 50×, (B) 250×



(A) (B) Figure 3: SEM images of 2h-acetylated *T. scleroxylon* wood at different magnifications; (A) 50×, (B) 250×



(A) (B) Figure 4: SEM images of 3h-acetylated *T. scleroxylon* wood at different magnifications; (A) 50×, (B) 250×



Figure 5: SEM images of 4h-acetylated T. scleroxylon wood at different magnifications; (A) 50×, (B) 250×



Figure 6: SEM images of 5h-acetylated T. scleroxylon wood at different magnifications; (A) 50×, (B) 250×

The likely reason is that the acetylation reaction takes place at a single site, with no occurrence of polymerization or cross-linking. The reduction in the pore sizes of acetylated wood samples 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.³¹ Furthermore, the kind of swelling that occurs in wood after the fiber saturation point has been reached, whereby the wood no longer absorbs water, is the same swelling that occurs during acetylation of wood. Hence, no obvious effect of acetylation was noticed on wood microstructure, even after long periods at elevated temperatures.

Thermal analysis

Thermal analysis of wood specimens is presented in Figure 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.³² In the second region, DTG curves are characterized by a peak just below 340 °C and a shoulder below 300 °C, which reflects the thermal degradation of cellulose and hemicelluloses. In the 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. 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.

The maximum weight loss and derivative temperature of thermal decomposition of untreated and acetylated wood specimens are given in Table 2. It can be seen that untreated wood samples have the highest weight loss of 1.32 at the derivative temperature of 335.03 °C, while the lowest weight loss of 1.18 at derivative temperature of 345.58 °C 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 of 5% and 10% occurred at 246 and 264 °C, respectively, for the untreated samples, whereas it shifted to a higher temperature for the acetylated samples, ranging between 260-267 °C and 279-285 °C, respectively. For 70% and 80% weight loss, the decomposition temperature for the untreated samples occurred at 350 and 447 °C, respectively, while for the acetylated samples, it occurred within the ranges of 348-369 °C and 420-487 °C, respectively. It has been confirmed from previous studies¹⁴ that the modification of wood with anhydrides etherifies hydroxyl groups with acetyl groups, leaving the surface more The higher hydrophobic. decomposition temperature of the acetylated samples, as compared to the non-acetylated sample, may be explained by the chemical changes in hemicelluloses and (to a lesser extent) cellulose. In comparison, the thermal stability of the 5hacetylated wood was higher than for other acetylated wood. This observation could be due to the greater weight gain observed in the blocks after acetylation, which may indicate a decrease in the number of hydroxyl groups as a result of etherification in the fiber walls.^{33,34}



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

 Table 2

 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. (°C)
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

CONCLUSION

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, considering that 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 with unmodified samples, which suggests an enhancement in thermal stability.

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REFERENCES

¹ C. A. S Hill, "Wood Modification: Chemical, Thermal and Other Processes", John Wiley & Sons, Chichester, 2006

² D. Sandberg, A. Kutnar and G. I. Mantanis, *iForest*, **10**, 895 (2017), https://doi.org/10.3832/ifor2380-010

³ D. Jones, D. Sandberg, G. Goli, and L. Todaro, "Wood Modification in Europe", University of Firenze, Italy, 2019, https://doi.org/10.36253/978-88-6453-970-6

⁴ G. I. Mantanis, *BioResources*, **12**, 4478 (2017), https://doi.org/10.15376/biores.12.2.4478-4489

⁵ L. Emmerich, S. Bollmus and H. Militz, *Wood Mat. Sci. Engr.*, **14**, 3 (2019), https://doi.org/10.1080/17480272.2017.1417907 ⁶ F. Bongers and S. J. Uphill, in *Procs.* 7th *International Scientific Conference on Hardwood Processing*, Delft, The Netherlands, August 28-30, 2019

⁷ S. L. Zelinka, G. T. Kirker, A. B. Bishell and S. V. Glass, *Forests*, **11**, 299 (2020), https://doi.org/10.3390/f11030299

⁸ R. M. Rowell, *For. Prod. J.*, **56**, 4 (2006)

⁹ A. Sandra, "Mechanical Properties of Chemical Modified Wood of Load-Bearing Constructions", Department of Structural Engineering Faculty of Engineering LTH, Sweden, 2016, pp. 1-153

¹⁰ R. M. Rowell, in "Handbook of Wood Chemistry and Wood Composites", edited by R. M. Rowell, Oxford, England, 1983, p. 363, https://doi.org/10.3139/9783446442504.022

¹¹ C. A. S. Hill and D. Jones, *Holzforschung*, **50**, 457 (1996), https://doi.org/10.1515/hfsg.1996.50.5.457

¹² F. G. Adebawo, O. Y. Ogunsanwo and S. O. Olajuyigbe, *J. For. Environ. Sci.*, **36**, 225 (2020)

¹³ Forest Products Laboratory (FPL), "Wood Handbook – Wood as an Engineering Material. General Technical Report FPL-GTR-190", Madison, Forest Products Laboratory, 2010, 508 p.

¹⁴ F. G. Adebawo, V. Naithani, H. Sadeghifar, D. Tilotta, A. L. Lucia *et al.*, *RSC Adv.*, **6**, 6571 (2016), https://doi.org/10.1039/C5RA19409A

¹⁵ R. M. Rowell, in "Chemical Modification of Lignocellulosic Materials", edited by D. N. S. Hon, Marcel Dekker, New York, USA, 1996, pp. 295-310

¹⁶ H. Akitsu, M. Norimoto, T. Morooka and R. M. Rowell, *Wood Fiber Sci.*, **25**, 250 (1993)

¹⁷ M. Norimoto, J. Grill and R. M. Rowell, *Wood Fiber Sci.*, **24**, 35 (1992)

¹⁸ M. Norimoto, J. Grill, K. Minato, K. Okamura, J. Mukudai *et al.*, *Wood Ind.* (*Japan*), **42**, 14 (1987)

¹⁹ H. Yano, M. Norimoto, T. Morooka and R. M. Rowell, *Wood Fiber Sci.*, **25**, 395 (1993)

²⁰ R. M. Rowell, in "Handbook on Wood and Cellulosic Materials", edited by D. N. S. Hon and N. Shiraishi, Marcel Dekker, Inc., New York, 1991, Chapter 15, pp. 703-756

²¹ S. F. James and M. O Bolade, *Maderas Cienc*. *Tecnol.*, **17**, 5 (2015)

²² British Standard 373: Methods of testing small clear specimens of timber. British Standards Institution, London, UK, 1957 ²³ H. Militz, *Holz Roh Werkst.*, **49**, 147 (1991)

²⁴ E. Nicholas and A. D. Williams, "Dimensional Stabilization of Wood with Dimethylol Compounds", Document No: IRG/WP 87-3412, International Research Group on wood Preservation, 1987

²⁵ P. Larsson and R. Simonson, *Holz Roh Werkst.*, **52**, 83 (1994)

²⁶ F. P. Liu, M. P. Wolcott, D. J. Gardner and T. G. Rials, *Comp. Int.*, 2, 419 (1994)
 ²⁷ X Yaniun F. Oiliang W. Oingwen X. Zefang and

 ²⁷ X. Yanjun, F. Qiliang, W. Qingwen, X. Zefang and M. Holger, *Eur. J. Wood Prod.*, **71**, 401 (2013)
 ²⁸ B. Šofo J. Tarihari, J. S. Sangara, J. Sangar

²⁸ B. Šefc, J. Trajković, T. Sinković, M. Hasan and I. Ištok, *Drvna Ind.*, **63**, 45 (2012) ²⁹ S. Hamdan and M. S. Islam, *Adv. Mater. Res.*, **576**, 314 (2012)

³⁰ C. Sander, E. P. J. Beckers, H. Militz and W. V. Veenendaeel *Wood Sci. Tech.*, **37**, 39 (2003), https://doi.org/10.1007/S00 226-002-0160-6

³¹ F. W. Karl, "Forestry Handbook", Society of American Foresters, 1984, pp. 616-623 ³² B. Wielang, T. Lourely, C. M. Karl, C. M. Karl, S. K. Karl

³² B. Wielage, T. Lampke, G. Mark, K. Nestler and D. Starke, *Thermochim. Acta*, **337**, 169 (1999) ³³ F. G. Adebawo, H. Sadeghifar, D. Tilotta, H.

³³ F. G. Adebawo, H. Sadeghifar, D. Tilotta, H. Jameel, Y. Liu *et al.*, *Starch - Stärke*, 1900086 (2019), https://doi.org/10.1002/star.201900086

³⁴ K. Hung, W. Tung-Lin, C. Yong-Long and W. Jyh-Horng, *Cons. Build. Mater.*, **108**, 139 (2016)