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Research Article

Chemical modification of *Petersianthus macrocarpus* (essia), to determine whether durability depends on bulking or hydroxyl substitution

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Abstract
Wood is a biodegradable material. Decay resistance of wood is improved when the wood is chemically modified. The decay resistance of a chemically modified wood is improved as the modification stabilizes the cell wall polymers against enzyme attack due to the blocking of accessible hydroxyl groups of the cell wall polymers which reduces the amount of water for hydrolysis. The improved durability of the modified wood as a result of reducing the amount of water molecules into the cell wall for hydrolysis will depend on either bulking or percentage hydroxyl substitution (%OH). *Petersianthus macrocarpus* (essia), a tropical hardwood species was chemically modified with acetic anhydride (AA) and pentanoic anhydride (PA) in dry pyridine to improve its decay resistance. Graveyard test was used to analyze the effect of the modification on the decay resistance of the wood in twelve weeks in-ground contact. Percentage weight loss and visual decay grades were used to evaluate whether the decay resistance depends on weight percentage gain or percentage hydroxyl substitution. The decay resistance of the modified samples were found to be dependent on bulking.

Keywords
Biodegradation–Carbohydrate polymers–Chemical modification–Wood–Termite Destruction.

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1. Introduction

1.1 Background

Wood cell wall contains three polymers, cellulose, hemicelluloses and lignin. Wood is degraded biologically by organisms which use the polymers as food sources mainly the carbohydrate polymers in the cell wall (Rowell et al. 2008). Termites contain in their hindguts certain flagellate protozoa which produce enzymes called cellulases that help to break down cellulose. Some termites also have bacteria for the breakdown of cellulose while some termites may also produce cellulase of their own (Tokuda & Watanabe, 2007). The hydroxyl groups in the three major wood polymeric components can be reacted with various reagents to form covalent bonds with useful properties (Rowell, 2012). When esters are formed in the wood cell walls, the hydroxyl (OH) groups are blocked thereby reducing the amount of water that are sorbed into the cell wall and therefore the amount of water needed for hydrolysis by decay causing organisms is reduced and decay resistance is improved. Chemical modification with carboxylic acid anhydride (CA) substitutes the hydroxyl groups in the cell wall polymers. The substitution blocks the hydroxyl groups from absorbing water molecules through hydrogen bonding thereby reducing amount of water molecules needed by decay causing organisms to cause decay. The substitutions also bulk the cell wall as well thereby reducing amount of water molecules that are sorbed into the cell wall. Decay resistance of chemically modified wood which reduces the amount of

water to be sorbed into the wood cell wall will depend much on OH substitution or bulking. According to Hill, Hale, Ormondroyd, Kwon & Forster (2006), acetylation works on the hypothesis of why acetylating protects wood from microbiological attack could not give a clear understanding of protection mechanism and there is clearly much work needed to understand fully this phenomenon. The purpose of this study is to chemically modify *Petersianthus macrocarpus* (essia) to investigate whether the decay resistance of chemically modified essia is as a result of percentage hydroxyl substitution or bulking. The study will contribute to the understanding of mechanism of decay resistance of chemically modified wood. *Petersianthus macrocarpus* is found in regions stretching from Guinea eastward to the Central African Republic and southward to DR Congo and northern Angola (Owusu, 2012, Louppe & Oteng-Amoako, 2016). In Liberia *Petersianthus macrocarpus* is common in moist semi-deciduous forest and uncommon in evergreen forest, but in Côte d'Ivoire and Ghana it is more abundant in evergreen forest and transitional zones between evergreen and moist semi-deciduous forest. In Central Africa it is reported to be found in the secondary forest. In southern Cameroon it is frequently found in agro forestry plantations of cocoa. According to Owusu, 2012; Louppe and Oteng-Amoako (2016), essia is used for construction, carpentry, furniture, canoes, mortars, tool handles, sliced veneer and plywood. It is suitable for flooring, mine props, vehicle bodies, railway sleepers, sporting goods, toys, novelties, agricultural implements and draining boards. It is valued as firewood and for charcoal production.)

2. Materials and Method

2.1 Preparation of Wood Samples

The log was quarterly sawn at the band mill. Samples were cut from the heartwood, free from sapwood, knots and other defects with no visible infections by mold, stain or fungi. The freshly sawn samples were quickly dried in a solar kiln to prevent infection. Dimension of samples were 12mm x 25mm x 125mm (Radial x Tangential x Longitudinal). Samples were randomly numbered. The sample sizes as given by ASTM D 1958 -06 were reduced to decrease the time for the field test and also to be able to extract the extractives using soxhlet.

2.2 Experimental

A set containing 150 replicates of *Petersianthus macrocarpus* samples was prepared and modified with acetic anhydride. The same number of replicates as described above was prepared for the pentanoic anhydride modification and another set for the de-ionized water (control). A total of 450 samples were prepared for the decay resistance estimation using the grave-yard test. In the estimation of decay resistance, percentage weight loss, visual decay grade and termite destruction grade, (ASTM D 1758 – 06) standards were used to analyze the impact of the modification on the durability of the modified wood.

2.3 Modification

Method of modification as described by Hill et. al., (2006) was adopted. Three sets of samples (each set contains 150 replicates) were separately modified using acetic anhydride, pentanoic anhydride and de-ionized as a control. Firstly, set of the samples containing 150 replicates was placed in a soxhlet extractor for solvent extraction using toluene/methanol/acetone (4:1:1 by volume) for eight hours in order to remove the extractive. Samples were then dried for 12 hours in an oven at 105^oC ($\pm 5^oC$) and allowed to cool to ambient temperature over a silica gel. Samples were then weighed on a Sartorius balance. Weighed samples (W1) were vacuum impregnated with pyridine for one hour at100^oC ($\pm 5^oC$), followed by impregnation with a one molar solution of the acetic anhydrides (AA) in a pyridine at 100^oC ($\pm 5^oC$) for 8 hours. The modification processes were repeated but with pentatonic anhydride (PA) and also with de-ionized water (DW) for the control samples. At the end of the reaction samples in sets were separately placed in ice-cold acetone to quench the reaction. Samples were allowed to stay in the acetone for one hour and then transferred to the soxhlet apparatus for soxhlet extraction as detailed previously, and samples were re-weighed (W2) after oven drying as detailed previously. From the results weight percentage gain due to modification (%WPG) and the percentage hydroxyl substitutions (%OH) were calculated.

2.4 Estimation of Durability by Grave-yard Test

The samples were exposed in a ground of active wood destroying fungi and termites. A natural area of fertile, fallow, level land of uniform character that was moist and well drain was selected. The test field was selected at Ayeduase near Kwame Nkrumah University of Science and Technology in Kumasi. According to Quartey (2009), the vegetation of Kumasi, the location for the field test is semi-deciduous forest. The town is within the plateau of south-west physiological region, which ranges between 250 and 350 metres above sea level. The metropolis has the wet sub-equitorial type of climate. Both temperature and humidity are moderate. The soil type is forest ochrosol(Obeng, 2000). According to Kumi-woode (1996), Kumasi has a high decay index with very high decay hazards. The soil of the test area is of medium to fine - texture with water holding capacity varying from 45 to 50% and PH varying from 4.5 to 5.0. The area is also home to a lot of termitarian mounts. The ecology of the termite species in Kumasi has been described by Usher and Ocloo 1980 and some of the species attacking timber as given by him are *Coptotermes intermidius Silvestri* from the family Rhinotermitidae (Coptermitinae), *Amitermes evuncifer* (Sjostedt) from the family Termitidae (Amitermitidae), *Ancistrotermes* spp. (mostly A

cruitifer(Sjostedt) but with the occassional *A. guineensis* (Silvestri) from the family Termitidae (Macrotermitinae) and *Macroterme* spp. (boyh *M. bilicosus* (Smeathman) and *M subhyalimus* (Rambur). Installing the stakes into the ground, test stakes were randomized. Thirty replicates from each of the modified and unmodified samples were picked after the first four weeks and then after every two weeks for analysis. Samples were cleaned and visual changes due decay and termite destruction were recorded. Samples were then oven dried and percentage weight lost (%WL) were recorded according to equation 1: The %WL = (Wb – Wa/ Wb) X100. . . . . Equation 1 Where Wb is weight of sample before ground contact, Wa is weight of sample after ground contact. The lower the %WL, the higher the resistance.

2.5 Statistical Methods

Genstart, 12 Edition was used for the analytical analysis. The significance of differences between untreated and treated wood samples was evaluated by a computerized statistical program (SPSS) composed of analysis of variance (ANOVA).

3. Results and Discussion

3.1 Weight Percentage Gain (%WPG) and Percentage Hydroxyl Substitution (%OH)

Table 1 shows the statistical differences in percentage hydroxyl substitutions (%OH) and weight percentage gains (%WPG) between the AA and PA modified samples. Values with the same letters were not significantly different from each other. There was no significant difference in %WPG between the AA and PA modified samples, however the %OH of the AA modified sample was higher than that of the PA modified sample. The AA having a lower molecular weight had the same %WPG as that of the PA modified samples due to its higher %OH substitution.

Table 1. Average %WPG and %OH of PA and AA Treated *Petersianthus macrocarpus* Wood samples

Chemical	%OH	%WPG
Acetic Anhydride	16.94a	11.28a
Pentanoic Anhydride	12.48b	11.28a

*Means with the same letters were not significantly different at $P < 0.05$

3.2 Estimation of Durability of Treated and Untreated *Petersianthus macrocarpus* Wood Samples using Average Percentage Weight Loss

The stakes (modified and unmodified) were installed in-ground in the selected area and the decay and termite destructions were inspected weighed and graded according to ASTM D 1758-06 standards. The installed samples were inspected after the first 4 weeks (to allow appreciable deterioration to begin) and then after every 2 weeks until 12 weeks as shown in Table 2.

Table 2. Statistical Differences in Percentage Weight Loss in 12 weeks in-ground contact of chemically modified *Petersianthus macrocarpus* wood samples using Pentanoic Anhydride (PA), Acetic Anhydride (AA) and De-ionized (DW).

Chemical	Weight Loss				
	4 Weeks	6 Weeks	8 Weeks	10 weeks	12 Weeks
AA	1.00a	1.21a	1.34a	1.45b	1.47b
PA	1.03a	1.32ab	1.38ab	1.50b	1.52b
DW	18.42a	20.60b	30.83c	40.66d	41.20e

*Means with the same letters were not significantly different at $P < 0.05$

In Table 2, the unmodified samples had very high weight loss during the 12 weeks in-ground contact than the modified samples. The weight losses of the unmodified samples were attributed to decay and destruction by termites. For the chemically modified samples, termites' nibbles were not found and therefore the weight loss was attributed to decay. There were very low weight losses of the modified samples indicating the modified samples were highly durable than the unmodified samples. From the analytical analysis there was no significant difference in decay resistance of the AA and PA modified samples during the twelve weeks. The improvement in decay resistance of the modified wood might be due to changing the conformation and configuration of the wood polymers and therefore might not be recognised by the decay causing organisms. The modification might have also blocked the hydroxyl sites and reduced the amount of water into the cell wall making the modified wood samples harder to be nibbled by the termites. There was no significant difference between the decay resistance of the AA and PA modified samples. A test for fungal and bacterial resistance has been done on acetylated composites with brown- white- and soft-rot fungi and tunneling bacteria in a fungal cellar. Control blocks were destroyed in less than 6 months whilst acetylated wood showed no attack after 1 year (Nilson et al., 1988; Rowell et al., 1989)

3.3 Estimation of Durability of the Modified and Unmodified *Petersianthus macrocarpus* Wood Samples against decay by Visual Grading (ASTM D 1758 – 06).

Samples of modified and unmodified were visually inspected and were graded according to AMST D 1758 – 06). Grade 10.0 being sound and 0.0 as a failure and the results shown in Table 3. In Table 3, the AA and PA modified samples had decay ratings between 10.00 at week four and decreasing to 9.95 at week twelve which means the modified samples were highly durable and there was no significant difference between the AA and

Table 3. Average decay grades of AA, PA and DW Treated *Petersianthus macrocarpus* Wood Samples in 12 weeks In-ground Contact.

Chemical	Decay Grade				
	4 Weeks	6 Weeks	8 Weeks	10 weeks	12 Weeks
AA	10.00	10.00	9.98	9.97	9.95
PA	10.00	10.00	9.97	9.97	9.95
DW	7.60	7.60	6.80	6.20	5.43

PA modified samples confirming the results of the decay grading using weight loss. The unmodified samples had a decay grade of 7.60 at week four and decreasing to a grade of 5.43 at week twelve indicating low durability. 10 = highly resistance, 0 = failure. The average decay resistance of the modified samples depended on bulking rather than %OH substitution. The PA modified samples had a lower %OH substitution than the AA modified samples (AA = 16.94a, PA = 12.48b). There was no significant different in %WPG values of the AA and PA modified samples AA =11.28a, PA = 11.28a), however the AA and PA modified samples had no significant difference in average decay resistance. If the determinant of durability was %OH, then the durability of AA modified samples should have been higher. According to Hill (2009), decay resistance of Corsican pine and European beech sapwood modified with anhydrides as determine by weight loss was a function of weight percentage gain (WPG) rather than the extent of hydroxyl (OH) substitution. The decreased in water molecules that were sorbed into the cell wall for the activities of decay organisms was bulking dependant rather than %OH substitution.

4. Conclusion and Recommendation

The modification improved the decay resistance of *Petersianthus macrocarpus*. There was OH substitution of the cell wall polymers and the substitution bulked the cell wall as well. Decay resistance of the modified wood as compared with the unmodified was due the covalent bond formed as a result of the substitution that made the modified wood more hydrophobic as compared to the unmodified. Comparing the %OH substitution and the %WPG, the improvement in durability due chemical modification depended on bulking rather than %OH substitution. Bulking of cell wall reduced amount of water that sorbed into the cell wall and therefore reduced amount of water required for the hydrolysis for the decay of wood. Further research is recommended to be carried out to determine decay using strength loss.

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