UDS International Journal of Development [UDSIJD]
Volume 4 No. 2, December, 2017
http://www.udsijd.org
ISSN: **2026-5336**

DIMENSIONAL STABILIZATION OF *Celtis mildbraedii* (ESA FUFUO) A TROPICAL HARDWOOD SPECIES

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Abstract

Celtis mildbraedii (esa fufuo) is a high density hardwood; however esa fufuo has a medium dimensional stability. In this study, esa fufuo was chemically modified with acetic anhydride (AA) and propionic anhydride (PA) in dry pyridine to improve its dimensional stability. The dimensional stability of the modified samples was found to be superior to the unmodified samples. The average percentage volumetric swelling coefficient (%S) values of the modified and unmodified samples were AA = 5.09a, PA = 5.21b and De-ionized water= 7.28c.The average percentage water absorption coefficient (%WAC) values of the modified and unmodified samples according to the treatment were AA = 47.80a, PA = 48.01a, De-ionized water (DW) = 84.70b. The AA modified samples were better dimensionally stabilized when using %S followed by the PA modified samples and the DW samples which were the least stabilized. However, by using %WAC there was no significant difference in dimensional stabilization between AA and PA modified samples. The percentage anti-shrink efficiency (%ASE) of the AA modified samples was higher than that of the PA modified samples (AA = 29.26b, PA = 28.21a) indicating a superior dimensional stability for AA modified samples to that of PA. The water repellent efficiency (%WRE) of AA = 43.604a and PA = 43.458a, which indicated that there was no significant difference between the AA and PA modified samples.

Keywords: Dimensional Stability, Cellulose, Hemicelluloses, Lignin

Introduction

Polymers made up mainly of cellulose, lignin and hemicelluloses are found in the wood cell wall. Even though wood is used for many purposes due to its valuable properties, it also displays some disadvantages, such as poor dimensional stability and high moisture absorption (Deka *et al*., 2003). The cellulose, hemicelluloses and lignin contain hydrophilic hydroxyl groups (-OH) that can attract water molecules from the surrounding environment through hydrogen bonding when the environment is moist and can also give out water molecules into a dry surrounding environment (Islam *et al*., 2012). These changes in the moisture content which cause changes in dimension of the wood lead to shrinkage and swelling of wood. When covalent bonds of the accessible hydroxyl groups of the polymers in the wood cell walls are formed by appropriate chemical treatment, absorption of water into the cell walls is reduced and changes in the dimensions of the wood are also reduced (Schneider & Brebner, 1985; Haetely and Schneider 1993; Rowell 1983; Pandey, *et al*., 2009).

The disadvantage of wood materials such as dimensional changes in wood is pronounced in some wood species. There is abundance of these wood species in the Ghanaian forest and one of such species is esa fufuo. The acetylation of wood to improve its dimensional stability has been studied for over sixty years (Tarkow *et al*., 1946; Goldstein *et al*., 1961; Bongers & Beckers, 2003; Papadopoulos, 2010). The shrinkage values obtained in the study properties of 10 Ghanaian high density lesser-used-species of importance to bridge construction in which *Celtis mildbraedii* was among, were high and in heavy construction where shrinkage is important, knowledge of the dimensional changes is important

(Ofori *et al*., 2009)). The total longitudinal shrinkage of *Celtis mildbraedii* was between 0.2 - 0.3% and therefore attention should therefore be paid to structural design detailing in uses where longitudinal stability is important (Ofori *et al* 2009).

Wood species are used due to their inherent properties. While some of the properties of the lesser used species are known, some are yet to be determined. Those species with properties below the required properties needed for their use therefore needs to be looked into and ascertain how their properties could be improved. The objective of this work was to chemically modify *Celtis mildbraedii* using propionic anhydride and acetic anhydride to improve its dimensional stability.

Materials and methods

Sources of wood materials

The *Celtis mildbraedii* log used for the study was obtained from Pan African Engineering Company in Kumasi in Ghana. The log was felled from the Krokosua Hill forest located at Juaboso in the Bia District of the Western region of Ghana.

Preparation of wood samples

The log was quarter sawn at the Bandsaw Mill at Pan African Engineering Company in Kumasi. Samples free from sapwood, knots and other defects with no visible infections by mold, stain or fungi were cut from the heartwood. The freshly sawn samples were quickly dried in a kiln for two weeks to prevent infection. The kiln dried lumber was sawn and then sanded to a dimension of 20mm x 20mm x 10mm (tangential x radial x longitudinal) for the estimation of dimensional stability.

Experimental run

Celtis mildbraedii samples were subjected to 3 treatments, with each treatment containing 30 replicates. The treatments included: 1. The use of 1M acetic anhydride (AA), 2. The use of propionic anhydride (PA) and 3. The use of de-ionised water (DW), which also served as a control for the experiments. After the modification process, samples were soaked in de-ionized water for five days and then oven dried. Volumes and weights of the water saturated and oven dried samples were taken. The water soak/oven dry was repeated for five times. The degree of dimensional stability was determined by estimating the volumetric swelling coefficient (%S), anti-shrink efficiency (%ASE), water absorption coefficient % WAC and water repellant efficiency (% WRE) using the repeated water-soaking method described by Rowell, & Ellis, (1978).

Modification

The method of modification as described by Hill *et al.,* (2006) was adopted. Samples in sets were 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 substance. Samples were then dried for 12 hours in an oven at 105^0 C ($\pm 5^0$C) and allowed to cool to ambient temperature over a silica gel. Samples were weighed on a Sartorius balance. Weighed samples (W1) were vacuum impregnated with pyridine for one hour at 100^oC ($\pm 5^0$C), followed by impregnation with a one molar solution of the acetic anhydride in a pyridine at 100^oC ($\pm 5^0$C) for 8 hours. The modification processes were repeated but with propionic anhydride and then with de-ionized water for the control samples. At the end of the reaction samples were separately placed in ice-cold acetone to stop the reaction. Samples were again put into soxhlet apparatus for soxhlet extraction and samples were re-weighed (W2) after oven drying. From the results the weight percentage gain due to modification (%WPG) and the percentage hydroxyl substitutions (%OH) were calculated.

Determination of dimensional stability

The water absorption coefficient (%WAC), water repellent efficiency %WRE and anti-shrink efficiency %ASE were calculated as shown in equation (1), (2) and (3) respectively.

$\%WAC = (W_a - W_b)/ W_b \times 100$ (1)

Where W_b is the initial weight of an oven-dried sample before water soaking and W_a is the weight after water soaking for 5 days

$\%WRE = (W_r - W_t)/ W_r \times 100$ (2)

Where W_r is the water absorption of untreated wood sample, and W_t is the water absorption of treated wood samples (oven dry).

$\%ASE) = (S_r - S_t)/S_r \times 100$ (3)

Where Sr is the volumetric swelling coefficient of the untreated samples, and S_t is the volumetric swelling coefficient of the treated samples.

The volumetric swelling coefficient %S was calculated as in equation (4).

$$\%S = (V_2 - V_1)/V_1 \times 100 \quad (4)$$

Where V_2 is the volume of wood after soaking and V_1 is the volume of wood before soaking.

Fourier Transfer Infra-red spectroscopy (FTIR) measurement

FTIR spectra were obtained using a Perkin Elmer FTIR spectrometer. The surfaces of the modified and unmodified samples were removed and analyzed.

Statistical analysis

Genstart, 12th edition was used for the analytical analysis. The significant differences between the modified and unmodified wood samples were evaluated using analysis of variance (ANOVA).

Results and discussion

Weight percentage gain (%WPG) and percentage hydroxyl substitution (%OH)

After the modification the average %WPG of the AA and PA modified samples for the estimation of dimensional stabilization were found to be 20.414%a and 20.991%b respectively and the average %OH of the AA and PA modified samples were 32.602%a and 24.975%b respectively.

Estimation of dimensional stability of modified and unmodified samples using %S

From the averages of %S values in Table 1, the modified samples had lower %S values in all the cycles than the control samples indicating that the modification using the PA and AA did improve the dimensional stability of the samples. The PA modified samples had the least %S in cycle 1 indicating the best dimensionally stabilized followed by the AA modified samples and the unmodified (control) samples, the least dimensionally stabilized in cycle 1. In cycle 2 and 3 there was no significant difference in %S between the PA and AA modified samples indicating there was no difference in dimensional stabilization whilst in cycle 4 and 5 the AA modified samples had lower %S values indicating they were better dimensionally stabilized than the PA modified samples in those cycles.

The average %S values from the 5 oven-dry/water-soak cycles of the AA, PA modified samples and that of the control (DW) samples shows that at $P < 0.05$, there were significant differences in dimensional stability among the samples. The mean %S values of the AA modified samples had the lowest %S value therefore the highest dimensionally stabilized followed by the PA modified samples and the DW samples were the least dimensionally stabilized. The %OH substitution by the AA modified samples was higher than that of the PA modified samples hence blocked more of the hydroxyl groups of the cell walls of the AA modified samples. Again the %WPG of the AA modified samples was higher than that of the PA modified samples that reduced amount of water that was absorbed by the AA modified samples more than that of the PA modified samples. Higher bulking of the AA modified samples than the PA modified making the AA modified sorbed less water.

Table 1: Average %S values of the samples at each Cycle

Treatment/ Chemical	Cycles					
	1	2	3	4	5	Average
AA	4.89b	4.73a	5.14a	5.66a	5.40a	5.09a
PA	4.60a	4.81a	4.98a	5.59b	6.06b	5.21b
DW	6.91c	6.94b	7.41b	7.35c	7.58c	7.28c

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

Estimation of dimensional stability of wood samples using %ASE.

From the %ASE averages in Table 2, the PA modified samples had a higher %ASE values in cycles 1 and 3 indicating a better dimensionally stabilized than the AA modified samples in those cycles. In cycle 2, 4 and 5 the AA modified samples had a higher dimensional stabilization.

To compare the dimensional stabilization between PA and AA modified samples, the averages of the 5 cycles were compared as shown in Table 2. The AA modified samples had a higher value meaning they were better dimensionally stabilized than that of the PA modified samples. This may be due to the AA modified samples having a higher %OH substitution and hence a better blocking of hydroxyl groups (OH) in the cell wall to reduce sorbing of water molecules by hydrogen bonding than that of PA. Increased %ASE means the chemical did not only react with the hydroxyl groups of the wood component but also blocked water molecule movement pathways inside the wood cell wall as confirmed by Baysal *et al*.(2004).

Table 2: Average %ASE of PA and AA Treated *Celtis mildbraedii* Wood Samples at each Cycle.

Treatment/ Chemical	Cycles					
	1	2	3	4	5	Average
AA	29.20a	31.78b	30.61a	28.44b	28.74b	29.26b
PA	31.34b	30.72a	32.86b	23.99a	20.12a	28.21a

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

Estimation of dimensional stability of wood samples using %WAC

From Table 3, there was no significant difference in %WAC between the AA and PA modified samples in cycle 1 and 2 indicating the same amount of water was absorbed. In cycles 3 and 4, the AA modified samples were better stabilized than the PA modified samples due to a lower absorption of water in AA modified samples whilst in cycle 5 the PA modified samples were better stabilized than the AA modified samples. From cycle 1 to 5, the modified samples (AA and PA) had lower %WAC values than the unmodified samples indicating the modified samples were better dimensionally stabilized. Lower WAC means fewer water absorption sites remain, and this effect contributes to the reduction in water uptake (Gindl, & Gupta, 2002).

The averages of %WAC of 5 oven-dry/water-soak cycles in Table 3 shows that the PA and AA modified samples were not significantly different from each other. The AA and PA modified samples had lower water absorption co-efficiency than the untreated samples. Lower water absorption for the treated wood samples could be attributed to blocking of some sorption sites (i.e. hydroxyl groups) in the interior of wood cell lumens and the cell wall (Gindl & Gupta, 2002).

Table 3: Average %WAC of wood Samples at each cycle

Treatment/ Chemical	Cycles					
	1	2	3	4	5	Average
AA	40.29a	45.61a	48.90a	51.61a	52.60b	47.80a
PA	40.27a	45.53a	50.08b	51.61a	52.60b	48.01a
DW	78.16b	79.30b	81.812c	92.05c	92.17c	84.70b

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

Estimation of dimensional stability of wood samples using %WRE

In Table 4, cycles 1, 2 and 4, the AA modified samples had the same %WRE values as that of the PA modified samples. This indicated that the water absorption of the AA and PA modified samples was the same.

The average %WRE values from the 5 oven-dry/water-soak cycles in Table 4, shows that there was no significant difference between the AA and PA treated samples. The effect of the chemicals on dimensional stabilization of the wood samples was the same.

Table 4: Average %WRE of Wood Samples at each Cycle

Treatment/ Chemical	**Cycles**					
	1	**2**	**3**	**4**	**5**	**Average**
AA	48.45a	42.48a	40.23b	43.92a	42.93a	43.60a
PA	48.48a	42.59a	38.79a	43.41a	44.02b	43.46a

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

FTIR spectroscopic analysis of chemical modification of *Celtis mildbraedii*

FTIR spectroscopic analysis was used to confirm that there were covalent bonds formed between the reagents used for the modification and the hydroxyl groups of the polymers in the wood cell walls.

Figure 1 shows a spectrum of the control samples. It shows peaks marked at 3340cm^{-1}, 1231cm^{-1} and 1030cm^{-1}. Peak marked 3340cm^{-1} correspond to O-H (H-bonded). Peaks at1030cm^{-1}correspond to O-C phenols and peak at 1231cm^{-1}correspond to O-C of alcohol. The peak at 1231cm^{-1} corresponds to O-C stretching band (Saikia, Ali, Goswan, & Ghosh, 1995).

Spectrum graph

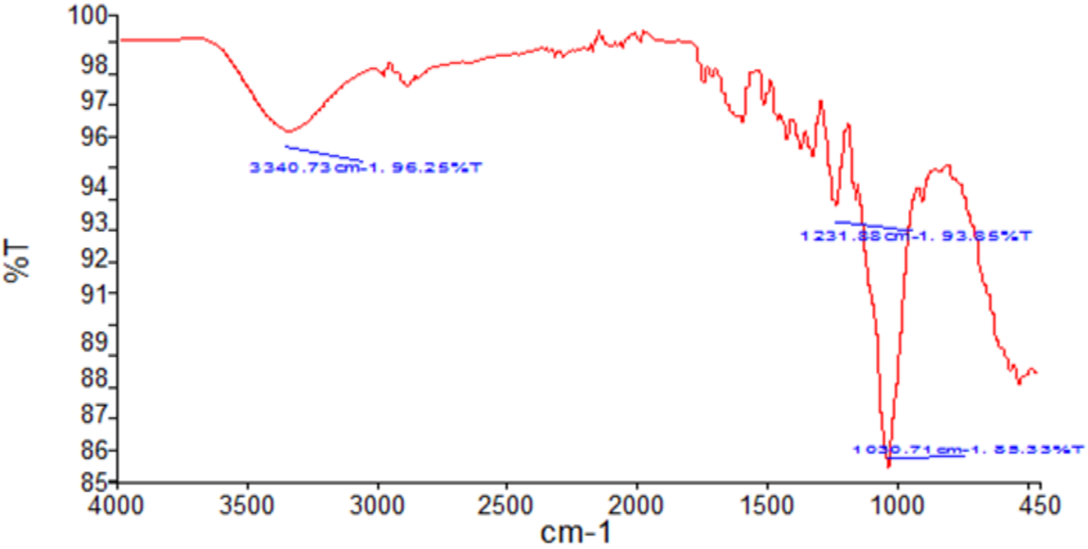

Figure 1: Spectrum of the unmodified *Celtis mildbraedii* wood samples

Figure 2 is a spectrum of AA modified samples. It shows peaks at 3338cm-1, 1716 cm-1, 1155 cm-1 and 1031cm-1. Peak marked 3338 cm-1 correspond to O-H (H-bonded). Peaks at 1030cm-1 correspond to O-C phenols. The peak marked 1716 cm-1 and 1155 cm-1 confirms ester formation.

Spectrum graph

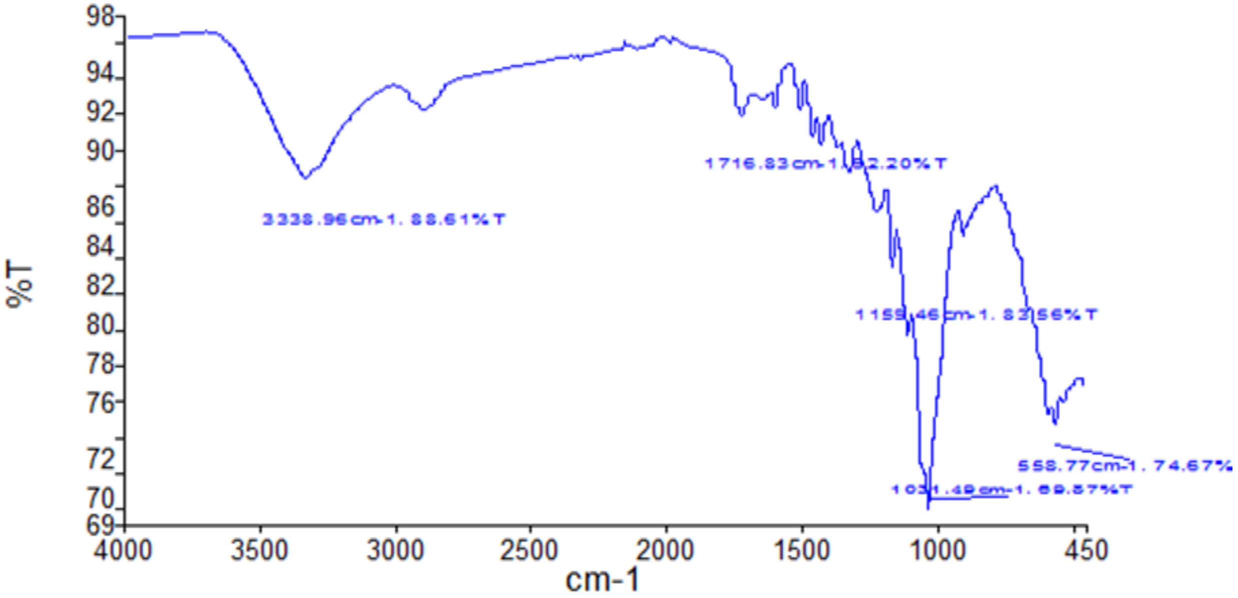

Figure 2: Spectrum of the acetic anhydride modified *Celtis mildbraedii* wood samples

According to Bellamy (1975); Saikia, Ali Goswan, & Ghosh (1995); Kuo, Lazakava & Reisev, (1988); Anderson, Pawlak, Owen, & Fiest (1991), the peak at 1726 $cm^{-1}$is attributed to the carbonyl groups C=O attached to the wood. The peak at 1723cm^{-1} is also attributed to C=O stretching vibration in conjugated ketones and ester carbonyl group esterification of hydroxyl groups (Kuo, McClelland, Chien, Walker, & Hse, 1988; Anderson *et al.,* 1991). Peaks at 1159 cm^{-1} indicate new ester groups are formed (Bodirkau, Carmen & Spiridon, 2009).

Conclusions

Using the average %S, dimensional stability of the AA, PA and the DW modified samples were in the increasing order DW < PA < AA with their %S in the order 7.23c < 5.20b< 5.08a respectively. The average %ASE also showed that the dimensional stabilization of the AA modified samples at $P < 0.05$ was superior to the PA modified samples (AA = 29.26b, PA = 28.21a).

From the average %WAC there was no significant difference between the AA and PA modified samples (AA = 47.80a, PA = 48.01a), however, the modified samples had a lower %WAC than the unmodified (DW = 84.70) indicating the modified samples were better dimensionally stabilized at $P < 0.05$. Using the %WRE there was no significant difference between the average of AA and PA modified samples (AA = 43.604a, PA = 43.458a).

From the average volumetric swelling coefficient %S, anti-shrink efficiency, water absorption capacity and water repellant efficiency, the dimensional changes of the modified *Celtis mildbraedii* was improved.

Acknowledgements

We are grateful to Mr. Gideon Amankwah of Soil Research Institute of CSIR- Ghana for his assistance on the statistical analysis, Mr. Brutse of Biochemistry Department, KNUST and Mr. Amankwah of Chemistry Department of Kwame Nkrumah University of Science and Technology, Kumasi, Ghana for their assistance for the laboratory works.

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