JENRM, Vol. 4, No. 5, 32-35, 2017
Research Article

Acetylation of three Ghanaian hardwood species - Asanfena (*Aningeria robusta*), Dahoma (*Piptadeniastrum africanum*) and Kaku (*Lophira alata*)

Eric D. Marfo*

Abstract
The diffusion of chemicals and chemical reaction within the wood bulk are affected by many factors. One of these factors is the wood ultrastructure because the chemicals have to diffuse through the wood matrix to reach the sites where they will react. In this study three Ghanaian hardwood species with different densities were acetylated and the effect of the densities on the percentage hydrogen substitution and weight percentage gain as well as the effect of the modification on dimensional stabilization of the species were analyzed. The densities of the three wood species affected the percentage hydroxyl substitution as well as the weight percentage gain due to the modification. The results showed that the higher the density of the wood species, the lower the percentage hydroxyl substitution at the same condition of temperature, concentration of the reagent and time of reaction.

Keywords
Volumetric Swelling Coefficient–Anti-shrink Efficiency–Dimensional Stabilization.

* Department of Interior Design Technology, Takoradi Technical University, P. O. Box 256, Takoradi, Ghana. Email: emarfous@yahoo.co.uk.

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1. Introduction

Hardwoods belong to a group of angiosperm known as dicotyledons. Individual hardwoods have their specific problems like low durability, low modulus of elasticity and modulus of rapture and low density however; all wood species have dimensional changes as a problem. In Ghana, hardwoods are processed into lumber, moulding, plywood, flooring, profile boards, dowels, curls, doors and block boards for export. Examples of tropical hardwoods in Ghana are asanfena (*Aningeria robusta*) - a low density species (550kg/m^3), dahoma (*Piptadeniastrum africanum*) - a medium density species (700kg/m^3) and kaku (*Lophira alata*) - a high density wood species (1050kg/m^3). Asanfena is processed in sawmills into lumber, veneer, moulding, layons, furniture parts and flush doors for export. Dahoma is processed into lumber, boules and furniture parts for export and locally it is used by mines and railways as sleepers and it is also used for general construction purposes. Kaku is sawn into lumber, boules and sleepers for export. Generally kaku is used for heavy construction work, bridge building and decking.

Shrinkage and swelling of wood are affected by many factors such as moisture content, density, extractives and chemical composition. Acetylation has been considered as a method of protecting wood from absorbing moisture [1, 2, 3, 4]. The hydroxyl groups present in the polymers of wood cell wall absorb water by hydrogen bonding causing the wood to swell and lose water in an environment where the humidity is low causing shrinkage. These dimensional changes can cause degradation of wood product however; by blocking the hydroxyl groups in the cell walls, the absorption of water molecules into the cell wall by hydrogen bonding is reduced since the hydroxyl groups will be blocked and the acetyl groups formed will reduce the volume of space to be occupied by the water molecules. The changes in fibre saturation point of a chemically modified wood has been determined as a function of weight percentage gain (WPG) but not by the extent of hydroxyl substitution of the cell wall [5].

In chemical modification, the molecules of the reactant have to diffuse in the wood matrix into the sites where they will react to form covalent bonds [5]. At a particular time of reaction, concentration of the reagent and temperature, the extent of reaction of the reagent molecules with the accessible hydroxyl groups in the wood cell wall to form a covalent bond will depend on the density of the wood. The reaction of a reagent with wood has been considered to be dominated by two processes, namely surface and bulk effects [6]. What needs to be understood is whether the density of wood significantly affects the weight percentage gain and hence affects the improvement of dimensional stabilization. According to [7], there have been moves towards commercialization of chemical modification. Many companies are currently into the commercialization of wood acetylation, for example, DanAcell in Denmark and Sweden and Titan Wood in Holland. There are also commercial developments in the United States, North Wales, Malaysia, Sweden, Norway, Germany, The United Kingdom, and New Zealand Rowell [8].

In Ghana, natural durable wood species has reduced and the timber production area has reduced due to poor logging practices and over utilization of traditional species. There has been a strict control on extraction of some wood species from the Ghanaian forest. To be able to increase the life span of wood in service there is the need to research into improving properties such as dimensional stabilization of wood species. The study of this work was therefore to chemically modify three Ghanaian hardwood species with different densities so as to compare the effect of density on chemical modification of wood.

2. Materials and Methods

2.1 Experimentals

Kaku dahoma and asanfena logs were quarterly sawn into lumber and quickly kiln dried in a solar kiln at Takoradi Technical University 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). Two sets of samples were prepared with each set containing twenty replicates. One set was modified with acetic anhydride (AA). The modification process was repeated with the other set but de-ionized (DW) water was used which served as the control. The modified and the unmodified (control) samples were separately 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 stabilization was determined by estimating the volumetric swelling coefficient (%S) and anti-shrink efficiency (%ASE) using the repeated water-soaking/oven-dry method described by [9]. The modification processes and the other laboratory works were done in the chemistry laboratory of the Kwame Nkrumah University of Science and Technology in Kumasi in Ghana.

2.2 Modification

Method of modification as described by [10] was adopted. Samples 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^oC ($\pm5^oC$) and allowed to cool to ambient temperature over a silica gel. Samples were then weighed on a Satorious balance. Weighed samples (W_1) were vacuum impregnated with pyridine for one hour at 100^oC ($\pm5^oC$), followed by impregnation with a one molar solution of the acetic anhydride in a pyridine at 100^oC ($\pm5^oC$) for 8 hours. The modification processes were repeated but with de-ionized water which served as the control samples. At the end of the reaction samples were placed in ice-cold acetone to stop the reaction. Samples were again placed into the soxhlet apparatus for soxhlet extraction as detailed previously and samples were reweighed (W_2) after oven drying. From the results weight percentage gain due to modification (%WPG) and the percentage hydroxyl substitutions (%OH) were calculated using the method described by [11] as in equation 1.

$$\%OH = (N/H) \times 100.............. Equation \quad (1)$$

Where N = (weight increase due to modification/molecular weight). H = weight of untreated block.

2.3 Estimation of Dimensional Stabilization

The volumetric swelling coefficient %S was calculated as in equation (2)

$$\%S := (V_2 - V_1)/V_1 \times 100............ Equation \quad (2)$$

Where V_2 is the volume of wood after soaking and V_1 is the volume of wood before soaking. The ant-shrink efficiency (%ASE) was calculated as in equation 3

$$ASE(\%) := (Sr - St)/Sr \times 100...... Equation \quad (3)$$

Where Sr is the volumetric swelling coefficient of the unmodified samples, and St is the volumetric swelling coefficient of the modified samples.

2.4 Statistical Methods

Genstart 12 edition was used for the analytical analysis. The significance difference between modified and unmodified wood samples was evaluated using analysis of variance (ANOVA).

3. Results and Discussion

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

The results in Table 1 shows that the higher the density of the wood species the lower the %OH and %WPG. The molecules of the reagent have to diffuse through the wood matrix to reach the reaction sites and therefore when the density of the wood is high there is a low diffusion rate.

Table 1. Average (%WPG) and %OH of Wood Samples

Species	Density	%WPG	%OH
Asanfena	500kg/m^3	10.16^c	15.86^c
Dahoma	700kg/m^3	6.59 ^{b}	10.29^b
Kaku	1050kg/m^3	4.15^a	6.48^a

*Means with the same superscript are not significantly different at P < 0.05.

3.2 Estimation of Dimensional Stability of Modified and Unmodified Samples using Average %S

Table 2 shows the average percentage swelling coefficient values of five oven-dry/water-soak cycles of unmodified and modified samples. From the %S values of the unmodified samples(DW values not in parenthesis), kaku with the highest density had the least %S and asanfena with the lowest density had the highest %S. This shows that for the unmodified samples the higher the density of the wood species the higher the dimensional stability. For the modified samples (AA values not in parenthesis), there was no significant difference in dimensional stability between the dahoma and asanfena using the %S. The higher %OH and %WPG of both dahoma and asanfena accounted for the improvement in dimensional stabilization. Even though kaku had the least %OH and %WPG, it was more dimensionally stabilized than dahoma and asanfena after modification. This may be due to its high density. According to [12] there is a relationship between density of wood species and weight percentage gain (WPG) of treated wood samples. The average WPG of diazonium salt treated wood samples of batai, jelutong, pulai, terbulan and rubberwood were 6, 5.5, 5.3, 4.8 and 4 respectively [12]. It has been found that the WPG values of wood samples were dependent on the density of wood species [12]. The densities of these tropical wood species were 380, 450, 455, 480, and 650 kg/m3 for batai, jelutong, pulai, terbulan, and rubberwood, respectively and the amounts of diazonium salt penetration in wood were 2.0, 1.4, 1.3, 1.07 and 0.92 mg for batai, jelutong, pulai terbulan, and rubberwood respectively [12]. The amount of chemicals that can be introduced into wood is dependent on the density of wood species and this is expected, because lower density wood species gain higher amounts of chemical and vice-versa [13].

In Table 2, the %S values of unmodified dahoma and asanfena (DW values in parenthesis) were significantly higher than their modified (AA values in parenthesis) counterparts. This suggested that there was improvement in dimensional stability due to the bulking which reduced the space in the cell wall to be occupied by the water molecules to cause volume change. However there was no significant difference between the %S values (AA values in parenthesis) of the modified and unmodified (DW values in parenthesis) kaku. This was attributed to the low levels of the %OH substitution and the %WPG of the kaku modified samples. The higher the %OH and %WPG, the more reduction of sorbing water molecules into the wood cell wall. Once there was enough bulking, there was a limited amount of water molecules that was sorbed into the cell wall to cause dimensional changes. The reduction of S in modified samples corresponded to the moisture excluding capacity of the treatment [14]. The values in Table 2 also shows that, the %S of modified asanfena was lower than that of the unmodified dahoma which suggest that the dimensional stability of modified asanfena at %WPG of 10.16 and %OH of 15.86 is higher than the dimensional stability of unmodified dahoma. This means the bulking of the cell wall of asanfena samples with a higher (%WPG) as a result of blocking the hydroxyl groups (%OH) reduced the absorption of water by the modified asanfena samples, hence a better dimensional stabilization.

Table 2. Comparison of Average %S among three wood species. Values in parenthesis were comparing the modified and the unmodified samples of the same species. Values not in parenthesis were comparing %S among different wood species.

Species	%S (AA)	%S (DW)
Asanfena	7.43^a (7.43^a)	9.46^a (9.46^b)
Dahoma	7.60^a (7.60^a)	8.42^b (8.42^b)
Kaku	5.34^b (5.34^a)	5.44^c (5.44^a)

*Means with the same superscript are not significantly different at P < 0.05.

3.3 Estimation of Dimensional Stability of Modified and Unmodified Wood Samples using %ASE

In Table 3, the low %ASE value for kaku means that the dimensional stabilization of the modified kaku was not significantly different from the unmodified. This might be due to low levels of %WPG and %OH of the modified kaku. The %ASE value of asanfena showed that the modified samples were highly dimensional stabilized than its unmodified samples. The dahoma modified samples were also dimensionally stabilized than the unmodified samples. In Table 3, wood samples modified with acetic anhydride had improvement in %ASE compared to their corresponding unmodified wood samples since the %ASE values were positive. The highest %ASE was observed in asanfena followed by dahoma and kaku had the least. The particular interaction between wood and chemical is considered to effectively improve ASE [15, 16]

Table 3. Average %ASE of the Wood Samples of 5 cycles.

Species	%ASE
Asanfena	21.46
Dahoma	7.13
Kaku	1.83

4. Conclusion

Acetic anhydride was used in dry pyridine to form ester bonds in three wood species with different densities. The results indicated that, the wood with the highest density had the least %OH and %WPG. The densities of the wood species affected the diffusion of reagent molecules into the wood to react with accessible hydroxyl groups in the wood cell wall to form covalent bonds. Using the %S and %ASE, the low and medium density wood species had significant improvement in dimensional stability after modification. The high density wood species had no significance difference between its modified samples and the unmodified samples.

5. Recommendation

Further research is recommended to compare the tangential (T) to radial (R) ratio (T/R) of modified and unmodified samples of the different species. This will help to know if the improved dimensional stability of modified wood species with low dimensional stability will be improved to become a medium or high dimensional stability wood species.

References

[1] R. M. Rowell, (1983). Chemical Modification of wood. *Forest Product Abstract* Pp 6(12) 363-382.

[2] S. Kuma, (1994). Chemical modification of wood.Wood fibre Science, 26(2) 270-280

[3] M. Bongers, and E. P.J. Beckers (2003). Mechanical properties of acetylated solid wood treated on pilot plant scale. In: Proceedings of 1st European Conference on Wood Modification, 2-4 April 2003, Ghent, Belgium, 341-351.

[4] A. N. Papadopoulos, (2010). Modified wood composites. BioResources, 5(1): 499-5

[5] C. A. S. Hill, (2008). The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents. Holzforschung, Vol. 62, pp. 423–428

[6] C. A. S. Hill, and D. Jones, (1996). The dimensional stabilization of corsican pine sapwood by reaction with carboxylic acid anhydride, the effect of chain length. *Holzforschung,* 50(5): 475-462.

[7] A. D. Sheen, (1992). The preparation of acetylated wood on a commercial scale. FRI Bulletin, 176, Chemical Modification of lignocellulosics. Pp. 1-8

[8] R. M. Rowell, (2005). Chemical modification of wood. In: R. M. Rowell, ed, *Handbook of wood chemistry and wood composites.* Taylor and Francis, boca Raton, FL, Ch. 22,674 – 691.

[9] R. M. Rowell, and Ellis, W. D. (1978). "Determination of dimensional stabilization of wood using the water-soaked method,' *Wood Sci.* 13, 104-111.

[10] C. A. S. Hill, Hale, M. D., Ormondroyd, G. A., Kwon, J. H., and Forster, S. C., (2006). The decay resistance of anhydride-modified Corsican pine exposed to the brown Rot fungus Coniophoraputeana. *Holzforschung,* 60: 625-629

[11] C. A. S. Hill., D. Jones., (1996). The dimensional Stabilization of Corsican Pine Sapwood by Reaction with Carboxylic Acid Anhydride. Holzforschung 50(5) 457-462

[12] S. Islam., S. Hamdan, R. Mohammad., M. R. Rehman., S. Ahmed and M. A. M. M. Idrus., (2012). Dimensional Stability and Water Repellent Efficiency Measurement of Chemically Modified Tropical Light Hardwood. BioResources 7(1), 1221-12.

[13] M. G. S. Yap., L. H. L. Chia and S. H. Teoh, (1990). "Wood polymer composites from some tropical hardwood," J. Wood Chem. Technol. 10(1), 1-19.

[14] R. Rashmi, R., Devi, A. I. Ali, I and Maji, T. K. (2003). "Chemical modification of rubberwood with styrene in combination with a crosslinker: Effect on dimensional stability and strength property," *Bio Tech.* 88, 185-188.

[15] E. Baysal., S. K. Ozaki, and M. K. Yalinkilic (2004). "Dimensional stabilization of wood treated with furfuryl alcohol catalyst by borates," *Wood Sci.* Technol. 38,

[16] M. Deka., C. N. Saikia., and K. K. Baruah, (2002). "Studies on thermal degradation and termite resistant properties of chemically modified wood," *Bioresource Technol.* 84, 151-157.