



## EVALUATING THE DEPENDENCE OF DIMENSIONAL STABILISATION OF CHEMICALLY MODIFIED *CELTIS MILDBRAEDII* (ESA FUFUO)

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### Abstract

*Wood absorbs moisture from the surrounding environment and releases moisture according to the temperature and the relative humidity of the surrounding environment leading to dimensional changes. Changes in dimensions can be reduced by chemical modification. The reduced dimensional changes of chemically modified wood depends on either the degree of blocking the hydroxyl groups of the wood polymers in the cell walls and/or bulking the cell wall to reduce the amount of water that can be absorbed into the wood cell wall. However, there is a conflicting result in literature concerning the dependence of absorption of water molecules into the cell wall. In this study, *Celtis mildbraedii* (esa fufuo), a tropical hardwood species was chemically modified and the dependence of dimensional stabilisation of the chemically modified esa fufuo has been evaluated. The dimensional stability of the modified samples was found to be dependent on bulking at a weight percentage gain below 20%.*

**Keywords: Bulking, Hydroxyl Substitution, Weight Percentage Gain, Hydrogen Bonding, Cell Wall Polymers**

### Introduction

The hydroxyl groups present in the polymers of a wood cell wall absorb water from the surrounding environment with high humidity causing the wood to swell and lose water in an environment where the humidity is low causing shrinkage (Islam, et al. (2012). Changes in the moisture content of wood will lead to variations in the dimensions of wood and the changes in wood dimensions limit its uses in certain applications (Obataya, and Minato, 2006). Dimensional changes of wood can be reduced by chemical modification and chemically modified woods have high dimensional stability and low moisture absorption (Rowell, 2005; Hill, 2006).

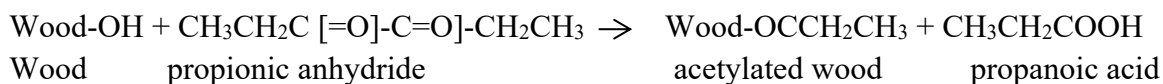
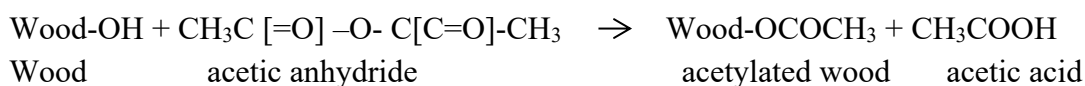
Absorption of moisture into the cell wall is by hydrogen bonding (Wang, Mukhopadhyaya and Moris, 2012) between the hydroxyl groups of polymers in the cell wall and water molecules and therefore by blocking the hydroxyl groups in the cell walls, the absorption of water molecules into the cell wall by hydrogen bonding is reduced since the hydroxyl groups will not be exposed. The hydroxyl

groups in the cell wall are responsible for the absorption of moisture from the surrounding environment resulting in dimensional changes (Kocaefe, Haung and Kocaefe, 2015). If carboxylic acid anhydride is used to modify wood, ester bonds are formed (<http://link.springer.com>) between the hydroxyl groups in the cell wall and the acetyl groups of the anhydride. The bonded acetyl groups bulk the cell wall (Hosseinpourpia, Adamopoulos and Mai, 2015) and reduce the volume of space to be filled by water molecules. The degree of acetyl groups formed can be determined by the weight percentage gain. The ester bonds formed between the wood and carboxylic anhydride modifies the hydroxyl groups. Bulking of the cell wall with the reacting chemical brings the wood back nearly to its green volume (Rowell, 2006) and the wood hydrophilicity also changes during the modification with the reacting chemical interfering with the normal hydrogen bonding (Rowell, 2009). The dimensional stabilisation is linked with the changes of wood from

hydrophilic to hydrophobic (Wang, Piao and Lucas, 2011). Reducing the moisture absorption into a chemically modified wood will therefore depend on the percentage hydroxyl substitution of the cell wall polymers and/or the extent of bulking the cell wall which can be determined, according to Marfo, Wereko and Larbi (2018) by the weight percentage gain due to modification. However, there is a conflicting result in the literature concerning the dependent of moisture absorption into the cell wall. According to Hill, (2008), the changes in the fibre saturation point of a chemically modified wood was determined and the correlation between fibre saturation point and weight percentage gain was not due to a cell wall bulking phenomenon. This finding, Hill (2008) and Rowell (2006) indicates, contrasts his earlier work that indicated cell wall bulking by bonded acetyl is directly correlated with the reduction in the capacity of the cell wall to accommodate water molecules. According to Rowell, Ibach, McSweey, and Nilson (2009), studies have shown that acetylation of pine with up to 20% weight percentage gain has a positive effect on its dimensional stability (<http://link.springer.com>), resulting in an anti-shrink efficiency of up to 70%. However, modification levels of weight percentage gain of 22% and above did not result in an additional increase in the anti-shrink efficiency (Rowell, 2005), indicating that the bulking effect of acetylation reaches a maximum at approximately weight percentage gain of 20%. According to Papadopoulos and Pougoula (2010) and Papadopoulos and Hill

(2003), improvements in dimensional stability are influenced by the chemical structure of the anhydrides used. At a comparable weight percentage gain, the levels of water sorption for pine treated with linear chain carboxylic acid anhydrides are the same, with substituent groups having different molecular sizes. This shows that improved dimensional stability correlates with the cell wall bulking, rather than with the degree of hydroxyl substitution level (Papadopoulos and Pougoula, 2010; Papadopoulos and Hill, 2003). A conflicting result suggests that dimensional stabilities were not equal for rubber woods, which were modified with acetic and hexanoic anhydrides below a weight percentage gain of 10% (Kacaefe et al., 2015). According to Minato, Takazawa and Ogura (2003), decrease in hygroscopicity depends on the degree of acetylation but there is also the possibility that the dimensional stabilising effect of acetylation mainly originates from the bulking effect (Minato, Takazawa and Ogura, 2003). There is therefore the need for further investigation to clarify whether dimensional stabilization of chemically modified wood depends on percentage hydroxyl substitution or weight percentage gain.

When acetic anhydride forms an ester bond with hydroxyl group, the bonded acetyl will be  $^+COCH_3$  and when propionic anhydride forms an ester bond with hydroxyl groups the bonded acetyl will be  $^+COCH_2CH_3$ .



Because the bonded acetyl from the propionic anhydride has a longer carbon chain and hence a higher molecular mass (57g/mol.) than that of acetic anhydride (43g/mol.), at equal weight percentage gain, the  $^+COCH_3$  will have a higher degree of hydroxyl substitution than  $^+COCH_2CH_3$  and therefore if sorption of moisture is reduced by degree of hydroxyl substitution, then wood samples modified with the acetic anhydride will have a lower moisture sorption.

The objective of this research is therefore to chemically modify *Celtis mildbraedii* using two carboxylic acid anhydrides with different carbon chain lengths to determine whether the dimensional stabilization of the

chemically modified *Celtis mildbraedii* depends on percentage hydroxyl substitution and or weight percentage gain.

## Materials and Methods

### Materials

#### *Wood Resource*

The *Celtis mildbraedii* log was obtained from Pan African Engineering Company in Kumasi in Ghana. The log was felled from the Krokosua Hill forest at Juaboso located in the Bia District of the Western region of Ghana. *Celtis mildbraedii*, locally called esa fufuo in Ghana, is a tropical hardwood species (Ofori et al., 2009; Marfo et al., 2018) abundant in the Ghanaian forest and can be used for bridge construction, but its shrinkage value is high (Ofori et al., 2009). *Celtis mildbraedii* is medium weight (Ofori et al., 2009; Marfo et al., 2018) and has a density of 600 -785kg/m<sup>3</sup> at moisture content of 12% (Oyen, 2012). In Ghana esa fufuo is used for furniture, plywood, handles veneer, mouldings, and flooring.

#### *Chemicals*

The chemicals/reagents used for the study included the following: Acetic anhydride, propionic anhydride, methanol, acetone, ethanol, pyridine, silica gel.

#### *Wood sample Preparation*

The log was quarter sawn at the Band-saw Mill at Pan African Engineering Company in Kumasi in Ghana. Samples free from sapwood and defects were cut from the heartwood. The 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 20 mm x 20 mm x 10 mm (tangential x radial x longitudinal). Twelve (12) sets of samples of *Celtis mildbraedii* were prepared and each set contained 30 replicates.

#### *Experimental run*

Four sets: set 1, set 2, set 3 and set 4 were treated with 1M acetic anhydride solution and the times used for the treatment (the impregnation with the anhydride solution) were 5, 6, 7 and 8 hours respectively. The next four (4) sets: set a, set b, set c

and set d were treated with 1M propionic anhydride solution and the times used for the treatment were 5, 6, 7 and 8 hours, respectively. The last four sets: set I, set II, set III and set IV were treated with de-ionised water, and this set served as control. The respective treatment times 5, 6, 7, 8 hours in a set are real times the samples were impregnated with the corresponding anhydride solution and the de-ionized water in the case of control.

#### *Treatment*

The treatment method as described by (Hill et al., 2006; Marfo et al., 2018) was adopted. Samples were placed in a Soxhlet extractor for solvent extraction using toluene/methanol/acetone (in the ratio: 4:1:1 by volume) for eight hours in order to remove the extractive substance. Samples were then oven dried for 12 hours at 105° C (±5°C) and allowed to cool to ambient temperature over a silica gel. Samples were weighed on a Sartorius balance and recorded as ( $w_b$ ). Weighed samples ( $w_b$ ) were vacuum impregnated with pyridine for one hour at 100°C (±5°C), and then impregnation with 1M solution of the anhydride in a pyridine at 100°C (±5°C) for 5 hours. After the treatment, samples were placed in ice-cold acetone to stop the reaction. Samples were again placed in Soxhlet apparatus for Soxhlet extraction and re-weighed and recorded as ( $w_a$ ) after oven drying. The experimental processes were repeated three times but the time for treating the wood samples were 5, 6, 7 and 8 hours. Propionic anhydride and deionised water (control) were used for the treatment of samples through the same process as that of the acetic anhydride.

#### *Determination of the weight percentage gain due to modification (%wpg) and the percentage hydroxyl substitutions (%OH)*

The weight percentage gain due to modification (%wpg) and the percentage hydroxyl substitutions (%OH) were then calculated using the equations 1 and 2 below:

$$\%wpg = (w_a - w_b/w_b \times 100 \quad (\text{Marfo, et al., 2018}) \quad (1)$$

$w_a$  = weight after modified and  $w_b$  is the weight before modified

$$\%OH = (N/H) \times 100 \text{ (Hill and Jones, 1996).} \quad (2)$$

$N$  = (weight increased due to modification)/mol. Weight of modificant (Hill and Jones; 1996, Hill and Mallon, 1998).

$H$  = weight of unmodified block  $\times$  0.0149. (The factor 0.0149 represents the number of moles of hydroxyl groups per gram of wood (Hill and Jones, 1996).

***Determination of the Percentage Volumetric Swelling Coefficient, Percentage Anti-Shrink Efficiency and Percentage Water Absorption Coefficient***

The degree of dimensional stabilisation can be determined using the percentage volumetric swelling coefficient, anti-shrink efficiency and the water absorption coefficient (Marfo, et al., 2018). When the percentage volumetric swelling coefficient is low it means the dimensional changes are low, when the percentage anti-shrink efficiency is high it means the dimensional changes are low and when percentage water absorption coefficient is low it means water absorption is low and therefore dimensional changes are low. Volumes of oven dry modified and control samples were measured using digital Vernier Calipers and recorded as  $V_o$  and the oven dry samples were weighed and recorded as  $W_o$ . The wood samples were then soaked in de-ionized water for five days and the water saturated volumes were measured and recorded as  $V_s$  and the saturated samples were weighed and recorded as  $W_s$ . The oven dry / water saturated processes were repeated for five cycles and the average volumes were measured.

The percentage volumetric swelling coefficient (%S), anti-shrink efficiency %ASE and the water absorption coefficient (%WAC) were calculated as shown in equation (3), (4) and (5) respectively (Marfo et al., 2017)

$$\%S = (V_s - V_o) / V_o \times 100 \quad (3)$$

Where  $V_s$  is the volume of wood after soaking and  $V_o$  is the volume of wood before soaking (Marfo, et al., 2018)

$$\%ASE = (S_r - S_t) / S_r \times 100 \quad (4)$$

$S_r$  is the volumetric swelling coefficient of the untreated samples, and  $S_t$  is the volumetric swelling coefficient of the treated samples (Islam, et al., 2011)

$$\%WAC = (W_s - W_o) / W_o \times 100 \quad (5)$$

Where  $W_o$  is the initial weight of an oven-dried sample before water soaking and  $W_s$  is the weight after water soaking for five days (Marfo et al., 2018)

***Statistical analysis***

Genstat, 12<sup>th</sup> 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**

***Comparing the Dimensional Stabilisation for Control and the Modified Samples using Percentage Volumetric Swelling Coefficient and Water Absorption Coefficient***

Table 1 shows percentage volumetric swelling coefficient and water absorption coefficient of the control and modified samples at different treatment times of five, six, seven and eight hours. The percentage volumetric swelling coefficient and percentage water absorption coefficient values in Table 1 were calculated using equations 3 and 5 respectively. Values of percentage volumetric swelling coefficient and water absorption coefficient of control samples are in braces, that of acetic anhydride modified samples are in parentheses and that of propionic anhydride samples are in brackets. Volumes and weights of the samples were respectively measured and weighed at the Chemistry Department laboratory of Kwame Nkrumah University of Science and Technology in Kumasi, Ghana. The percentage volumetric swelling coefficient and percentage water absorption coefficient values of control, acetic anhydride and propionic anhydride modified samples having the same superscripts were not significantly different from each other whilst those having different superscripts were significantly different from each other at  $P < 0.05$ . The control samples had significant higher percentage volumetric swelling coefficient and percentage water absorption coefficient values

than their modified counterparts at all the treatment times of 5, 6, 7 and 8 hours. The percentage swelling coefficient and percentage water absorption coefficient values of the control samples were comparatively higher than their modified counterparts at the same time of heating which means that the shrinkage of the modified samples was lower than the unmodified samples and also the modified samples had lower water absorption. This is because there had been hydroxyl substitution and cell walls bulking of the acetic anhydride and propionic

anhydride chemically modified samples (Marfo et al., 2018). The bulking and hydroxyl substitution reduced the amount of water molecules that were sorbed into the cell wall of the chemically modified samples. The control samples had higher percentage volumetric swelling coefficient and percentage water absorption coefficient values. This might be due to the fact that there was no hydroxyl substitution and therefore no bulking of the cell walls since deionized water was used

**Table 1: Values of Percentage Volumetric Swelling Coefficient and Percentage Water Absorption Coefficient of Control, Acetic Anhydride and Propionic Anhydride Modified Samples**

Time for Treatment/Hours	Percentage volumetric swelling coefficient	Percentage water absorption coefficient
5.00	{6.90} <sup>c</sup> [5.60] <sup>a</sup> (5.80) <sup>b</sup>	{80.30} <sup>c</sup> [52.60] <sup>a</sup> (53.61) <sup>b</sup>
6.00	{7.00} <sup>b</sup> [5.40] <sup>a</sup> (5.42) <sup>a</sup>	{83.91} <sup>b</sup> [51.68] <sup>a</sup> (51.62) <sup>a</sup>
7.00	{7.10} <sup>b</sup> [5.10] <sup>a</sup> (5.12) <sup>a</sup>	{84.30} <sup>b</sup> [51.61] <sup>a</sup> (50.60) <sup>a</sup>
8.00	{7.12} <sup>b</sup> [5.02] <sup>a</sup> (5.00) <sup>a</sup>	{84.31} <sup>b</sup> [50.60] <sup>a</sup> (50.70) <sup>a</sup>

Values with different superscript are significantly different at  $P < 0.05$ .

***Evaluating Dimensional Stabilisation Relationship with Percentage Hydroxyl Substitution and Weight Percentage Gain using Percentage Volumetric Swelling Coefficient***

Table 2 shows percentage hydroxyl substitutions, weight percentage gain and the percentage volumetric swelling coefficient of the acetic anhydride and propionic anhydride modified samples. The percentage hydroxyl substitution and the weight percentage gain were calculated using equations 2 and 1 respectively. Values of the acetic anhydride modified samples are in parentheses and propionic anhydride values in brackets.

The unmodified samples had no percentage hydroxyl substitution and weight percentage gain since there was no hydroxyl substitution.

**Table 2: Values of Percentage Hydroxyl Substitution, Weight Percentage Gain and Percentage Volumetric Coefficient of Acetic Anhydride and Propionic Anhydride Modified Samples**

Time for Treatment/Hours	Percentage hydroxyl substitution	Weight percentage gain	Percentage volumetric swelling coefficient
5.00	[22.30] <sup>a</sup> (30.12) <sup>b</sup>	[19.90] <sup>b</sup> (19.40) <sup>a</sup>	[5.60] <sup>a</sup> (5.80) <sup>b</sup>
6.00	[22.86] <sup>a</sup> (31.80) <sup>b</sup>	[19.91] <sup>a</sup> (19.90) <sup>a</sup>	[5.40] <sup>a</sup> (5.42) <sup>a</sup>
7.00	[23.00] <sup>a</sup> (32.20) <sup>b</sup>	[20.46] <sup>a</sup> (20.40) <sup>a</sup>	[5.12] <sup>a</sup> (5.10) <sup>a</sup>
8.00	[24.98] <sup>a</sup> (32.60) <sup>b</sup>	[20.90] <sup>b</sup> (20.61) <sup>a</sup>	[5.02] <sup>a</sup> (5.00) <sup>a</sup>

Values with different superscript are significantly different at  $P < 0.05$

In Table 2, as the heating time increased, the percentage hydroxyl substitution and the weight percentage gain of both the acetic anhydride and propionic anhydride modified samples increased. This was because as heating time of samples in the propionic anhydride and acetic anhydride solutions increased, the substitution of hydroxyl groups in the wood samples increased and therefore weight percentage gain increased. As the percentage hydroxyl substitution and weight percentage gain increased, the percentage volumetric swelling decreased. Increase in percentage hydroxyl substitution reduced the exposed hydroxyl and therefore reduced hydrogen bonding by the hydroxyl groups in the cell wall, hence the amount of water molecules to be absorbed into the wood cell wall decreased and the volumetric shrinkage decreased. The acetic anhydride modified samples had a higher percentage hydroxyl substitution than that of propionic anhydride modified samples at all the different times of treating the wood samples as shown in Table 2, but there were no significant difference in the weight percentage gain of the acetic anhydride and propionic anhydride modified samples at the heating times of 6 and 7 hours at  $P < 0.05$  are shown in Table 2. The propionic anhydride modified samples had a higher weight percentage gain at heating times of 5 and 8 hours. However, the propionic anhydride modified samples had a lower percentage volumetric swelling coefficient at the treatment time of 5 hours where the acetic anhydride modified samples had a significant higher percentage

hydroxyl substitution at  $P < 0.05$ . If dimensional stabilisation of the modified samples depends on percentage hydroxyl substitution, then the percentage volumetric swelling coefficient values of the acetic anhydride modified samples with a higher percentage hydroxyl substitution should have been lower. However, since the percentage volumetric swelling coefficient of the propionic anhydride modified samples with a lower percentage hydroxyl substitution, had a lower percentage volumetric swelling coefficient value at a treatment time of 5 hours and there were no significant difference in percentage volumetric swelling coefficient values at heating times of 6, 7 and 8 hours between the propionic anhydride modified samples and the acetic anhydride modified samples values, then the dimensional stabilisation depended on weight percentage gain.

*Evaluating Dimensional Stabilisation Relationship with Percentage Hydroxyl Substitution and Weight Percentage Gain using Percentage Anti-Shrink Efficiency*

Table 3 shows the percentage hydroxyl substitution, weight percentage gain and anti-shrink efficiency of the acetic anhydride and propionic anhydride modified samples. The percentage anti-shrink efficiency values were calculated using equation 4. Values of acetic anhydride modified samples are in parentheses and that of propionic anhydride in brackets.

**Table 3: Values of Percentage Hydroxyl Substitution, Weight Percentage Gain and Percentage Anti-Shrink Efficiency of Acetic Anhydride and Propionic Anhydride Modified Samples.**

Time for Treatment/Hours	Percentage hydroxyl substitution	Weight percentage gain	Percentage anti-shrink efficiency
5.00	[22.30] <sup>a</sup> (30.12) <sup>b</sup>	[19.90] <sup>b</sup> (19.40) <sup>a</sup>	[18.84] <sup>b</sup> (15.94) <sup>a</sup>
6.00	[22.86] <sup>a</sup> (31.80) <sup>b</sup>	[19.91] <sup>a</sup> (19.90) <sup>a</sup>	[22.86] <sup>b</sup> (22.57) <sup>a</sup>
7.00	[23.00] <sup>a</sup> (32.20) <sup>b</sup>	[20.46] <sup>a</sup> (20.40) <sup>a</sup>	[28.17] <sup>b</sup> (27.89) <sup>a</sup>
8.00	[24.98] <sup>a</sup> (32.60) <sup>b</sup>	[20.90] <sup>b</sup> (20.61) <sup>a</sup>	[29.49] <sup>b</sup> (29.76) <sup>a</sup>

Values with different superscript are significantly different at  $P < 0.05$ .

In Table 3, propionic anhydride modified samples had higher percentage anti-shrink efficiency values than that of acetic anhydride modified samples. When the percentage anti-shrink efficiency is high, then the dimensional

stabilisation is high. Higher percentage anti-shrink efficiency 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 Basal, Ozaki and Yaliakilic (2004). The propionic anhydride modified samples with lower percentage hydroxyl substitution at all the different heating times had a higher percentage anti-shrink efficiency values than that of the acetic anhydride modified samples. This indicated that the percentage anti-shrink efficiency depended on weight percentage gain and therefore dimensional stabilisation of the modified samples

did not depend on percentage hydroxyl substitution but rather on weight percentage gain.

*Evaluating Dimensional Stabilisation Relationship with Percentage Hydroxyl Substitution and Weight Percentage Gain using Percentage Water Absorption Coefficient*

Table 4 shows the percentage hydroxyl substitution, weight percentage gain and percentage water absorption coefficient values of the acetic anhydride and propionic anhydride modified samples. Values of acetic anhydride modified samples are in parentheses and that of propionic anhydride modified samples in brackets.

**Table 4: Values of Percentage Hydroxyl Substitution, Weight Percentage Gain and Percentage Water Absorption Coefficient of Acetic Anhydride and Propionic Anhydride Modified Samples.**

Time for Treatment/Hours	Percentage hydroxyl substitution	Weight percentage gain	Percentage water absorption coefficient
5.00	[22.30] <sup>a</sup> (30.12) <sup>b</sup>	[19.90] <sup>b</sup> (19.40) <sup>a</sup>	[52.60] <sup>a</sup> (53.61) <sup>b</sup>
6.00	[22.86] <sup>a</sup> (31.80) <sup>b</sup>	[19.91] <sup>a</sup> (19.90) <sup>a</sup>	[51.68] <sup>a</sup> (51.62) <sup>a</sup>
7.00	[23.00] <sup>a</sup> (32.20) <sup>b</sup>	[20.46] <sup>a</sup> (20.40) <sup>a</sup>	[51.61] <sup>a</sup> (50.60) <sup>a</sup>
8.00	[24.98] <sup>a</sup> (32.60) <sup>b</sup>	[20.90] <sup>b</sup> (20.61) <sup>a</sup>	[50.60] <sup>a</sup> (50.70) <sup>a</sup>

Values with different superscript are significantly different at  $P < 0.05$

In Table 4, apart from the treatment time of 5 hours where the acetic anhydride modified samples had a higher percentage water absorption coefficient, there was no significant difference in percentage water absorption coefficient values between the acetic anhydride and propionic anhydride modified samples at different heating times of treatment. A higher percentage water absorption coefficient means sorption of water molecules into the cell wall is high. Reducing water absorption into the cell wall of chemically modified wood samples will depend on the degree of hydroxyl substitution to reduce the absorption of water molecules by hydrogen bonding or bulking the cell wall to reduce the volume of the cell wall space. In Table 4, at a heating time of 5 hours, acetic anhydride modified samples had a higher percentage hydroxyl substitution value of 32.12 than propionic anhydride modified samples

with percentage hydroxyl substitution value of 22.30. Even though propionic anhydride modified samples had higher weight percentage gain value of 19.90 than the acetic anhydride modified samples with weight percentage gain value of 19.40, the acetic anhydride modified samples had a higher percentage water absorption coefficient value of 53.61 as compared to that of propionic anhydride modified samples of percentage water absorption coefficient value of 52.60 at  $P < 0.05$ . This means the absorption of water by the acetic anhydride modified samples with a higher percentage hydroxyl substitution value was higher. However, at the weight percentage gain value of 19.90 and above, for both acetic anhydride and propionic anhydride modified samples as shown in Table 4, there was no significant difference in percentage water absorption coefficient between the acetic anhydride and

propionic anhydride modified samples. This is in agreement with the comparison of results by Rowell et al. (2009); and Rowell (2005) that showed the acetylation of pine with up to 20% weight percentage gain has a positive effect on the dimensional stability. However, modification levels of 22% weight percentage gain and above did not result in an additional increase in the anti-shrink efficiency as shown by Rowell (2005), indicating that the bulking effect of acetylation reaches a maximum at approximately 20% weight percentage gain. At heating times of 6, 7 and 8 hours for the treatments, even though the acetic anhydride modified samples had a higher percentage hydroxyl substitution than that of propionic anhydride modified samples, there was no significant difference in percentage water absorption coefficient between the acetic anhydride and propionic anhydride modified samples which indicated that the percentage water absorption coefficient depended on weight percentage gain up to approximately 20%.

#### ***Comparing the Effect of the Chain Length of the Acetic Anhydride and Propionic Anhydride as the Bulking Effect on Dimensional Stabilisation***

Propionic anhydride has a longer chain length with a higher molecular mass than acetic anhydride. At a comparative weight percentage gain of 19.91 and 19.90 of propionic anhydride and acetic anhydride modified samples respectively at treatment time of 6 hours as shown in Table 2, there was no significant difference between percentage volumetric swelling coefficient values of 5.40 and 5.42 for propionic anhydride and acetic anhydride modified samples respectively. There was also no significant difference between percentage water absorption coefficient values of 51.68 and 51.62 for propionic anhydride and acetic anhydride modified samples respectively at a treatment time of 6 hours as shown in Table 1. However, the acetic anhydride modified samples had a significantly higher percentage hydroxyl substitution value 31.80 as compared to a lower percentage hydroxyl substitution value of 22.86 for propionic anhydride modified samples as shown in Table 2. This means the dimensional stability of the modified *Celtis mildbraedii* depended on bulking rather than percentage hydroxyl substitution. This also means that at the same weight percentage gain of acetic anhydride (19.90) and propionic anhydride

(19.91) modified samples the bulking effect did not depend on the size of structure of the bonded acetyl, but rather the weight percentage gain. According to Papadopoulos and Pougoula, (2010); and Papadopoulos and Hill, (2003) improvement in dimensional stability are influenced by the chemical structure of the anhydrides used but at a comparable weight percentage gain, the levels of water sorption for pine treated with linear chain carboxylic acid anhydrides are the same, with substituent groups having different molecular sizes. This shows that improved dimensional stability correlates with the cell wall bulking, rather than with the degree of hydroxyl substitution level (Papadopoulos and Pougoula, 2010; Papadopoulos and Hill, 2003).

#### **Conclusion**

Chemically modified wood decreases the amount of water that can be absorbed into the wood cell wall. Using the percentage volumetric shrinkage and anti-shrink efficiency, dimensional stabilisation of chemically modified *Celtis mildbraedii* wood samples was found to depend on weight percentage gain. However, using percentage water absorption coefficient the dimensional stabilisation was established to depend on weight percentage gain but only when the value is below 20% weight percentage gain.

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