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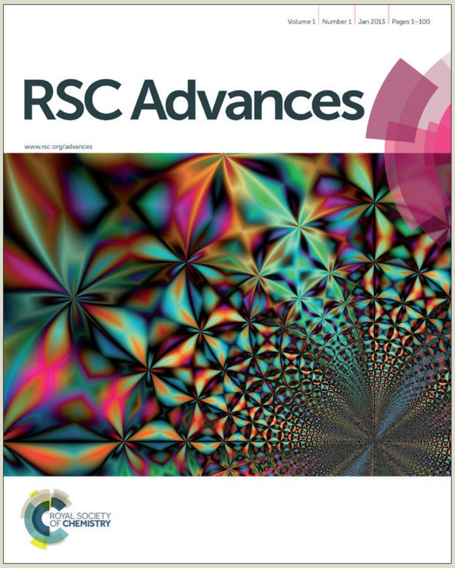

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

MORPHOLOGICAL AND INTERFACIAL PROPERTIES OF CHEMICALLY-MODIFIED TROPICAL HARDWOOD

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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ABSTRACT

Chemical modification of wood with acetic anhydride is an environmentally friendly process to sustain and improve wood properties over a longer term than naturally allowed. Such an approach offers many potential and attractive product avenues for the wood industry. In this study, Obeche tropical hardwood (*Triplochiton scleroxylon*) was acetylated with acetic anhydride to improve its mechanical and interfacial properties relative to unmodified wood; specifically, dimensional stability in terms of anti-swelling efficiency (ASE), water repellent efficiency (WRE), and hydrophobicity were the target properties of interest. The chemical modification was carried out at 120 °C with five varying reaction times (1-5 h) to optimize the reaction based on weight percent gain (WPG). It was found that as the reaction time increased, the WGP and hydrophobicity increased, but the percentage of water absorption and volumetric swelling diminished. In total, acetylation provided the hardwood with good dimensional stability. The chemically-modified wood was characterized by Fourier Transform-Infrared (FT–IR), dynamic contact angle, and an Owens-Wendt surface energy analysis.

Keywords: *Acetylation, Dimensional Stability, Hydrophobicity, Anti-Swelling Efficiency, Water Repellent Efficiency*

Introduction

Wood is a natural and renewable raw material that not only possesses a low processing energy demand, but it is both recyclable and biodegradable.[5,30] It is characterized by a porous network structure composed of cell walls made up mainly of biopolymers, i.e., polysaccharide polymers (cellulose and hemicelluloses) and phenolic polymers (lignin). This cellular structure endows wood with a high strength-to-weight ratio to obtain high-quality wood suitable for use as a structural material.[32] Wood has been used for construction, tools, furniture and artistic medium for thousands of years due to its high strength-to-weight ratio, unique porous structure, and aesthetic characteristics.[3]However, wood components are easily degraded by microorganisms, particularly at high moisture levels.[12] In terms of moisture absorption and

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See biological degradation, hemicelluloses play a key role. Hemicellulose polymers are accessible, hygroscopic, and contain sugar residues that may be the recognition point for microorganisms to start wood degradation[27.] Additionally, the most abundant functional group in the wood cell wall is the hydroxyl group which in general possesses a hygroscopic character which subsequent to water exposure results in wood with poor dimensional stability. In other words, wood shrinks as it dries and swells when it wets. These fluctuations and instabilities limit the application of wood as a high-quality material.[2]

Many methods have been used to minimize the dimensional instabilities in wood, but wood modification has proven effective. Various types of wood modification are possible, e.g., thermal, resin impregnation, surface modification, and chemical modification, [13] specifically acetylation.

Chemical modification of wood typically requires the formation of chemical bonds between the reagent and the wood cell wall polymers. The reaction occurs between the hydroxyl groups of the polymers and the reagent molecules and leads to a change in the chemical and physical properties of the wood.[29] There are many types of chemical modifications, but acetylating with acetic anhydride is considered one of the most promising ways of enhancing wood properties.[12,13] The hydroxyl groups (-OH) of wood (principally the carbohydrates) would each be chemically bound to one acetate (CH3COO) residue from an acetic anhydride molecule $(CH3CO)_2O$. This substitution reaction reduces the hydrophilicity of the wood, or more specifically, the number of free hydroxyl groups to interact with water molecules thus reducing hygroscopicity.

It has been already established that reductions in hygroscopicity and improved dimensional stability of acetylated wood depend on successful esterification of the accessible hemicelluloses in the cell wall to reduce hydrogen bonding with water and thus bulking the cell wall to its green volume.[23, 26]Chemical modification of the cell wall polymers of wood has proven to be an extremely effective approach to increase dimensional stability, hydrophobicity, UV resistance, and biological resistance. [7, 13, 17, 18, 30, 35]

The bulk of research on wood acetylation has been on softwoods[11, 15, 23, 24, 44] that are not native to the tropics where the harvesting of wood, primarily hardwoods, is rising exponentially. Several accounts of acetylation of hardwood species have been reported although a number of hardwood species tend to be durable and dimensionally stable, [10, 20] however, there are several tropical hardwood species that are less durable and dimensionally unstable and hence less desirable for timber harvesting. However, such species cannot be overlooked because for many tropical forested regions, they represent the sole harvesting opportunity. A few reports have surfaced for the acetylation of hardwood species of tropical origin.[4, 36.]

Thus, in this study, a fast growing tropical hardwood species, found in West Africa, *viz*., *Triplochiton scleroxylon* K. Schum, was the subject of the current study to improve its harvesting and timber prospects. It is known in Nigeria as Obeche, one of the most profitable and successful indigenous tree species in the Nigerian timber market.[9] It is a versatile raw material with a huge volume supply because it can also be grown under plantation management.[21] However, it has low durability and is prone to wood decay as a result of fungal attack; yet, when treated with preservatives, it responds favourable over a long term window.[1] Once the rate at which this particular wood absorbs moisture is reduced, hydrophobicity and dimensional stability increases, and consequently biological durability is improved.

MATERIALS AND METHODS

Wood preparation and modification procedures

Wood bolts were obtained from a 22 year old Obeche (*Triochiton scleroxylon*) and sectioned to 20 × 20 × 300 mm (radial x tangential x longitudinal) coupons. The resultant coupons were further converted to specimens with dimensions of 20 × 20 × 60 mm (radial × tangential × longitudinal) of which sixty samples with no defects were selected. The specimens were weighed and their masses recorded, oven dried at 105±2°C, cooled over silica gel in a desiccator, and then weighed again to determine their moisture content before modification.

Slightly modified literature methods were used for their acetylation.[19, 37, 38] Wood samples of approximately 8% moisture content were added to a stainless steel pressure reactor vessel containing acetic anhydride and acetic acid (92:8) after which the temperature was set to 25 °C and 10-15 bar of pressure was applied for 30 minutes to impregnate the wood. Excess acetylation fluid was removed from the vessel and nitrogen gas was introduced as the inert medium to control the internal temperature of the wood. The reaction's temperature was fixed at 120 °C for various periods of time (1, 2, 3, 4 and 5 h) to attain different impregnation levels. When the temperature of the circulating fluid reached approximately 60 °C, the acetylation of the wood began. This was shown by an increasingly rapid rise in temperature as measured by thermocouples in the reaction vessel. Heat generated by the circulating fluid increased the temperature inside the wood to about 130-135 °C for ~ 15minutes. It was necessary to condense the acetic acid – acetic anhydride vapour to control the pressure and temperature inside the reaction vessel before reaching 120 °C. At the end of the acetylation reaction, the reaction was quenched by cooling the reactor in an ice bath; the wood samples were washed several times, and then soaked in distilled water for 24 h. The wood samples were then air dried and oven dried at 105±2 °C for 24 h to remove remaining acetic acid. The average weight percent gain (WPG) was calculated for each batch of experimental samples

Weight Percent Gain

The weight percent gain (WPG) of the wood samples after the treatments was measured on an oven dry basis. The specimens were weighed, dimensions measured with a digital calliper, and then oven-dried at 105±2 °C before and after treatment until a constant weight was achieved. They were cooled over a silica gel desiccators and weighed at an accuracy of ±0.001 g. WPG was calculated according to equation 1 which gives an averaged relative change in the oven-dry weight and volume of the tested specimens from the treatments. Ten (10) replicates of treated and untreated specimens were used to determine the WGP.

$$\text{WPG (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

Where,

W_1 = Oven-dry weight of samples before treatment, (g)

W_2 = Oven-dry weight of samples after treatment, (g)

Estimation of Dimensional Stability

Anti-swell efficiency (ASE) and water repellent efficiency (WRE) for both modified and unmodified samples were measured according to ASTM-1037 (1999). Five oven-dry specimens for each treatment with dimensions 20 × 20 ×10 mm were soaked in a water bath at a temperature of 20±1 °C for 168 h; weight and dimension of specimens were determined before and after soaking.

Anti-swell efficiency was calculated according to equations (2) and (3)

$$\text{ASE (\%)} = \left(\frac{S_u - S_m}{S_u}\right) \times 100 \qquad (2)$$

Where,

ASE = Anti-Swell Efficiency

S_u = Volumetric swelling coefficient of unmodified wood samples

S_m = Volumetric swelling coefficient of modified wood samples

Volumetric swelling coefficient (S) was calculated as follows:

$$\text{S (\%)} = \frac{V_2 - V_1}{V_1} \times 100 \qquad (3)$$

Where,

V_1 = volume of wood before soaking

V_2 = volume of wood after soaking

Water repellent efficiency was calculated according to equations (4) and (5):

$$\text{WRE (\%)} = \left(\frac{W_u - W_m}{W_u}\right) \times 100 \qquad (4)$$

Where,

W_u = Water absorption of unmodified samples

W_m = Water absorption of modified samples

Water absorption (WA) was calculated as follows:

$$\text{WA (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (5)$$

Where,

W_2 = weight of specimen after water soaking

W_1 = weight of specimen before water soaking

Surface Free Energy Determination

The surface free energy of the solid and its polar components was determined through contact angles of liquids against the solid using a form of the Young equation[42], given as equation (6):

$$\gamma_L \text{Cos}\, \theta = \gamma_S - \gamma_{SL} \qquad (6)$$

Where, γ_S is the surface free energy of a solid, γ_L is the surface tension of the test liquid, γ_{SL} is the solid-liquid interfacial tension and θ is the contact angle.[43]

According to Owen-Wedt-Kaeble, [41] the surface free energy of a solid can be divided into respective dispersive and polar components whereas the summation of the components is approximately equal to the surface free energy of the solid, as given by

γ^0_S (surface free energy) = γ^d_S (dispersive component) + γ^p_S (polar component).

The free energy of interface between the liquid and the solid can be further refined according to the following equation:

$$\gamma_{SL} = \gamma_L + \gamma^0_S - 2(\gamma^d_S \gamma^d_L)^{1/2} - 2(\gamma^p_S \gamma^p_L)^{1/2} \qquad (7)$$

Where, γ_{SL} is the free energy interface between a liquid and a solid; γ_L is the surface free energy of the liquid; γ^0_S is the surface free energy of the solid; γ^d_S is the dispersive component of the surface free energy of the solid; γ^p_S is the polar component of the surface free energy of solid; γ^d_L is the dispersive component of the surface free energy of the liquid; γ^p_L is the polar component of the surface energy of the liquid .Combining equation 6 and 7, the following equation is obtained

$$\gamma_L(1+\text{Cos}\, \theta) = 2[\sqrt{\gamma^d_L \gamma^d_S} + \sqrt{\gamma^p_L \gamma^p_S}] \qquad (8)$$

In equation 8, only γ^d_S and γ^p_S are unknown and can be calculated using the contact angles of two test liquids whose γ^d_L and γ^p_L are known. Water and Diiodomethane were chosen as the test liquids. The adhesion parameters of these liquids are given in Table 1.

Table 1: Adhesion parameters for several test liquids.

Test Liquid	γL	γL^d	γL^p
		(mJ/m2)	
Water	72.8	21.8	51
Diiodomethane	50.8	50.8	0

Measurement of Dynamic Contact Angle

The contact angles of the reference liquids on the acetylated and untreated wood specimens were determined using a Phoenix 300 Contact Angle Analyser. Deionized water and diiodomethane were used as the probe fluids. The specimens were of dimension 20 × 20 × 10 mm and the cross section was sanded to obtain a smooth surface. Measurement of contact angle was done with a water droplet of 4µm in volume. The system was equipped with a camera capable of taking pictures as the water drops on the specimen.

FT-IR

The acetylated and unmodified samples were ground in a Wiley Mill machine and sieved to a 40-mesh particle size. Extractives-free wood samples were prepared using acetone and hot water following a standard method (TAPPI T264 CM97, Oct.2007) for FT-IR spectrophotometry. The IR spectra of the acetylated and unmodified samples were obtained using an ATR technique using a Perkin-Elmer FT-IR Frontier spectrophotometer by accumulation of 64 scans with a resolution of 4 cm-1 at 600- 4,000 cm -1.

Statistical analysis

Data obtained in the study were analysed using analysis of variance (ANOVA). Treatment means were separated using the Duncan Multiple Range test at α= 0.05.

RESULTS AND DISCUSSION

Weight percent gain from acetylation as a result of reaction time for *Triplichiton scleroxylon* is shown in figure 1. Not unexpectedly, the WGP increased with increasing reaction time. The highest WGP was found to be 22.74% when the samples were acetylated for 300 minutes. The WGP of other acetylated woods were found to be 10.37, 14.09, 18.37 and 19.06% at 60, 120, 180, and 240 minutes, respectively. This is in line with what has been reported in the literature[49], where it was reported that an increase in WPG for wood sawdust was found after 5 h of treatment with organic anhydride. This latter result was attributed to morphological and structural characteristics and degradation of the wood samples. Esterification of the hydroxyl groups in wood and acetic anhydride was supported by IR spectroscopy as shown in Figure 2. The increase of the number of acetyl groups can be easily observed in the IR spectra. Three major strong peaks were observed in the acetylated samples compared to their controls. The relevant peaks are: carbonyl (C=O) stretch region occurring at (1738–1730 cm-1), carbon–hydrogen (C- H) bond occurring ~1375-1370 cm-1, and carbon-oxygen (C–O) stretch occurring at (1245–1000cm-1) [6, 15, 31].

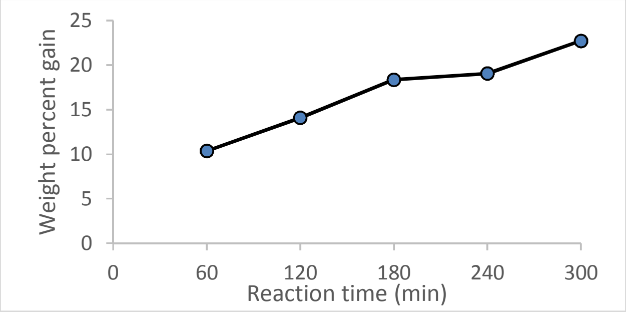

Figure 1: Degree of acetylation of *Triplochiton scleroxylon* as a function of reaction time.

The strong band of the carbonyl group at 1738-1730 cm-1 in all of the treated samples strongly suggested that hydroxyl functional groups (-OH) in the wood were acetylated. The intensity of these peaks increased with an increase in acetylation times in accordance with what has been previously reported.[14,19,22] The C-H at 1370 in acetylated wood is from methyl group (of the acetyl unit) vibrations in cellulose and hemicellulose.[8,34] There was an increase in this band from acetylation. The (C–O) stretch that occurred at (1245–1000cm-1) is due to carbonyl deformation in the ester bonds in lignin and xylan during the acetylation that also increases with reaction time.[4, 19, 34]

The data obtained also showed that acetylated samples had a higher IR transmission than the control (figure 3). The ratio of the IR transmission of the carbonyl group at 1738-1730 $cm^{-1}$for the control and acetylated sample (300 min) is 1: 3.44 and for other acetylated samples are 2.05, 2.13, 2.77, and 2.90 for 60, 120, 180, and 240 min, respectively.

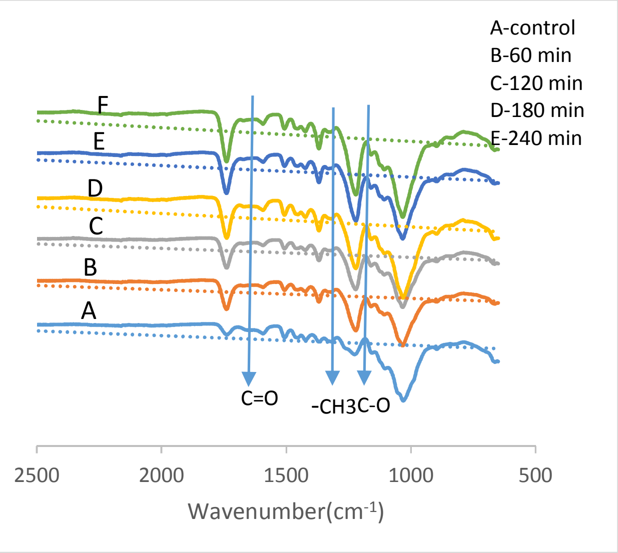

Figure 2: FT-IR (ATR) spectra of acetylated and non-acetylated wood.

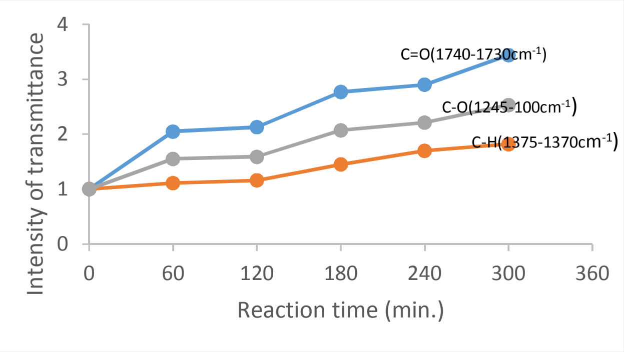

Figure 3: Intensity of the transmittance at different reaction times.

The IR transmission in acetylated wood samples (300 min) at frequencies occurring at 1245-1000 $cm^{-1}$was found to be 2.53 times higher than the control samples and for other acetylated samples it was also ~2 times higher than the control samples. It can be concluded from the results that the acetylation rate increases as the reaction time increases.

Results of volumetric swelling, Anti Swell Efficiency (ASE) and water absorption, water repellent efficiency (WRE), of acetylated and untreated (control) specimen are presented in Figures 4 and 5, respectively, to provide information on the dimensional stability of the samples. The water absorption and volumetric swelling values decreased linearly with an increase in WPG; also WRE and ASE increased with an increase in WPG. Volumetric swelling of WPG 22.74, 18.37, 10.37% and control samples was 2.18, 3.2, 5.28, and 10.01%, respectively, and their ASE was 78.22, 67.43 and 37.97%, respectively, for the treated samples. Also, water absorption of WPG 22.74, 18.37, 10.37% and control samples was 82, 107, 170, and 213%, respectively, and their WRE was 61.5, 49.77 and 20.18%, respectively, for acetylated wood samples. Based on these results, it is evident that acetylation has an adverse effect on the water absorption and volumetric swelling of the wood. As the acetylation time increases, WPG naturally increases, but water absorption and volumetric swelling does not because as already shown, the hydroxyl groups in the wood are replaced by acetyl groups, thus reducing the rate at which the wood absorbs water and swells. Anhydrides react with wood cell wall components and consequently bulk the cell wall. During acetylation, the wood is nearly swelled to its original volume due to replacement of the (-OH) groups with acetyl groups. There is an increase in wood volume proportional to weight gain. [16, 28] When such wood comes in contact with water, however, there will only be a slight increase in weight due to swollen state of the cell wall, thereby making it is difficult for acetylated wood to absorb water compared to its controls. Because the wood is already swollen to its original volume, it is dimensionally stable.[26]

The results of the contact angles (CAs) for reference liquids of water and diiodomethane of acetylated samples under different acetylating levels for the samples relative to their controls are presented in Table 2.

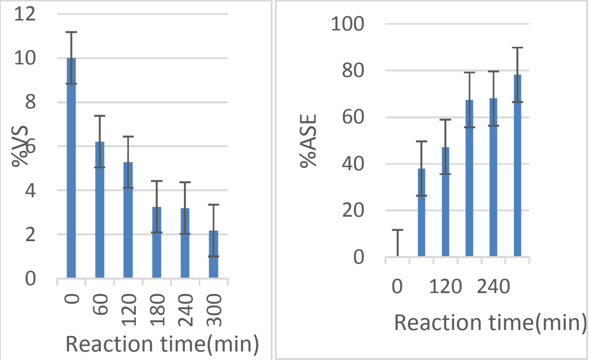

Figure 4: Volumetric swelling (VS) and Anti swell efficiency (ASE)

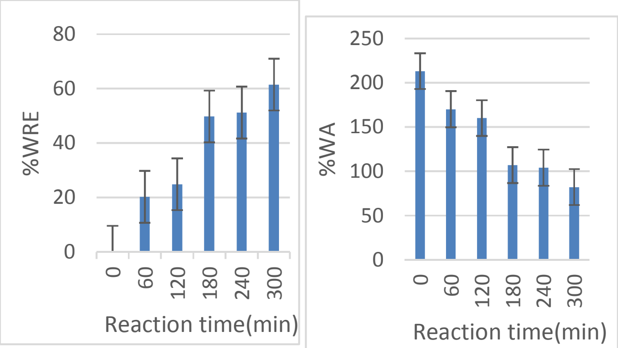

Figure 5: Water absorption and Water repellent efficiency (WRE).

The results showed that the contact angles of water and diiodomethane on the control samples were 62.25° and 22.01°, respectively. A significant increase in these contact angles were observed after acetylation indicating that acetylation induced changes in the surface polarity of the wood samples. For all the acetylated samples, the contact angles increased with increasing degree of acetylation. The contact angles increased gradually with longer reaction time thus, the 300 min acetylated samples had the highest contact angles of 93.31° and 53.57° for water and diiodomethane, respectively, followed by 240, 180, 120 and 60 min. acetylated samples as presented in Table 2.

Table 2: Contact angles for the acetylated and untreated *Triplochiton scleroxylon* wood.

Specimen	Contact Angles, degrees	
	Water	Diiodomethane
Control	62.25(9.6)^{a}	22.01(1.8)^{a}
60 min	80.90(5.8)^{b}	30.23(0.7)^{b}
120 min	86.35(1.5)^{b,c}	36.68(2.6)^{c}
180 min	88.08(0.5)^{b,c}	40.03(0.3)^{cd}
240 min	91.98(1.6)^{c}	42.46(1.4)^{d}
300 min	93.31(2.76)^{c}	53.56(4.7)^{e}

Standard deviations are in parentheses. Means with the same superscript letters in the same column are not significantly different at α = 0.05 using the Duncan Multiple Range Test.

The highest contact angles, i.e., the highest levels of hydrophobicity, were found in samples with high WPGs indicating that reaction time has a significant effect on the contact angles. Higher reaction times gave rise to higher WPGs, consequently higher contact angles. This is due to incorporation of acetyl groups into the cell walls thereby making the wood surface hydrophobic. These results are similar to the results of other authors[48,] who reported that reaction time affects the contact angles of acetylated nanofibrillated cellulose. Different contact angles of untreated and modified wood samples at different reaction times can be attributed to the physical properties of wood surfaces. Contact angle is a function of the interfacial surface tension of wood. When the forces of attraction (surface tension) that make up the liquid are overcome by the surface energy of the wood, then the liquid spreads on the wood to wet it. If the force of surface tension is not able to overcome adhesion, the liquid droplets will maintain their spherical shape that is manifested as an increase in contact angle.

In addition, and not surprisingly, there was significant difference in the results for the total free surface energy (polar and dispersive components) for the control and acetylated samples as shown in Table 3. The total free surface energy ranged dropped from 61.84 for the control to 33.57 mJ/m^2 for the longest treated acetylated sample; thus, the surface free energy decreased as acetylation time increased. It was found that the polar component of the total surface energy dropped more drastically than the dispersive coupon. The dispersive component, in fact, dropped about 30% relative to the control for the longest acetylation treatment. These differences are due to the fact that the polar character of the acetylated wood surface is no longer pronounced thereby increasing the hydrophobicity of the wood surface. The replacement of OH groups by acetyl ones during acetylation should be responsible for the decrease in the polar component relative to the dispersive component. [45, 46, 46 18.] Using Zisman as a basis, [39, 40] only when the surface tension of the liquid is less than the critical surface tension of the solid, can the liquid spread on the solid surface. In case of water, there is a tendency for water droplets to form a thin layer on the wood surface because the water surface tension has been overcome by the surface energy of the wood because of the hydroxyl groups (-OH) on the wood surface. On the other hand, the high contact angles observed from the acetylated samples result from a relatively intact water surface tension because most of the hydroxyl groups (-OH) in wood have been replaced with acetyl groups leaving a wood surface with a reduced energy; thus, the water surface tension prevents wetting, because the wood has become hydrophobic. In the case of untreated samples, hydroxyl groups (-OH) in the wood are intact; thus, the surface tension of the water is overcome and a water droplet spreads and wets the wood.

Table 3: Surface free energy for control and acetylated *Triplochiton scleroxylon* wood coupons.

	Surface energy components, mJ/m^2		
Specimens	γ_S	γ_S^{d}	γ_S^{p}
Control	61.84(5.1) ^{a}	47.15(0.6)^{a}	14.68(5.4)^{a}
60 min	49.26(2.5)^{b}	44.13(0.3)^{b}	5.14(2.3)^{b}
120 min	43.96 (1.0)^{c}	41.22(1.2)^{c}	2.74(0.2)^{b}
180 min	42.68(0.5)^{c}	39.60(0.1)^{cd}	3.08(0.5)^{b}
240 min	39.97(1.0)^{c}	38.35(0.7)^{cd}	1.62(0.4)^{b}
300 min	33.57(2.2)^{d}	32.24(2.6)^{e}	1.32(0.5)^{b}

Standard deviations are in parentheses. Means with the same superscript letters in the same column are not significantly different at α = 0.05 using Duncan Multiple Range Test.

Conclusions

Acetylation of tropical hardwood by increasing reaction times resulted in increasing WPGs with the highest occurring at 300 min of acetylation time. Water absorption and volumetric swelling of wood diminish as the reaction time increases, whereas ASE and WRE increase as the reaction time increases. The contact angle between the reference liquids and the wood samples also increases as reaction time increases, thereby reducing the surface free energy of the acetylated wood. Therefore, dimensional stability and hydrophobicity of tropical hard wood samples can be significantly improved by acetylation.

Acknowledgements

We acknowledge partial support obtained from the Faculty Research & Professional Development Program (Grant No. 257807-04214) at NCSU that made parts of this work possible. We are also indebted to Prof. M.A. Hubbe for his discussions and generous use of his equipment.

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