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HYDROLYTIC STABILIZATION OF CHEMICALLY - MODIFIED BAMBOO (*BAMBUSA VULGARIS*)

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Abstract:
One of the main drawbacks which limit the utilisation of bamboos is its high moisture intake. To prevent excessive dimensional changes and improve moisture properties of bamboo, Bambusa vulgaris was chemically treated with acetic-anhydride without co-solvent. Weight gain (WPG), Bulking coefficient (BC), Rate of reaction (RR), Volumetric Swelling (VS) and Anti-swelling Efficiency (ASE) as well as changes in VS and ASE upon long term water soaking and weight loss to leaching (WL) were determined to evaluate the influence of acetylation on the moisture properties. The results indicated no significant effect of reaction temperature and time on the WPG, BC, VS and ASE of the acetylated bamboo while reaction time had significant influence on RR and WL. None of the acetylated bamboo samples had more than 3.67% WPG and 54.69% ASE. The maximum values of ASE of acetylated bamboo was 54.69% at 2.79 WPG, 100°C and 90 minutes while the lowest 13.08% was recorded at 2.89% WPG, 140°C and 30 mins reaction times. Reaction temperature had no influence on the initial and final volumetric swelling and final anti-swelling efficiency of the modified bamboo samples but reaction time had significant effect on initial ASE. Volumetric swelling of modified and unmodified samples increased from 8.47 to 18.58% and from 9.42% to 43.22% respectively within 7 days water soak period. Acetic anhydride form chemical bonds that were stable to solvent extraction in B. vulgaris. Acetylating at 120°C for 30 and 60 minutes is suitable for B. vulgaris to positively influence its sorption properties.

Key words: *anti-swelling efficiency; B. vulgaris; cell bulking; dimensional changes; WPG.*

INTRODUCTION

Bamboo like wood changes dimension when it loses moisture. However, unlike wood, its dimension starts to change as soon as it starts to lose moisture (Wahab et al. 2006). Similarly, the dimensional changes of bamboo vary in different orthotropic directions as found in wood. According to Sadiku (2016), the mean volumetric shrinkage of *B. vulgaris* varies from 10.48% - 25.83% while the volumetric swelling varies from 9.52% - 43.22%. These are extremely higher to what is reported for most economic tropical timbers (Sadiku 2016) if bamboo is to supplement wood. Bamboo has a different anatomical structure compared to timber. It lacks radially-oriented cells like wood. Thus, the dimensional movement is expected to be different from that of wood.

The main drawback of using bamboos is their high moisture intake, biodegradation, and physical properties changes with environmental variations, this greatly limit their use. As with wood, the dimensional changes of bamboo can be minimized either by reducing water absorption and swelling, bulking the fibres to reduce water holding capacity or by cross linking the cellulose chains of the component fibres (Stamm 1964). These can be achieved by appropriate chemical treatments (Rowell 1983, Deka and Saikia 1999). Chemical modification of cell wall polymer is one of the effective methods to induce dimensional stability among others in bamboo as with wood (Rowell 2005, Rowell 2006, Hill 2006). Among chemical modification methods, acetylation with acetic anhydride has received the most attention (Yang et al. 2014) due to its effectiveness in improving anti-swelling efficiency and its easiness to perform (Hill 2006, Rowell 2006) and it exhibits very good dimensional stability compared to other chemicals (Rowell 2005). Acetylation helps to reduce wood permeability due to the bulking chemical restricting pore space and this has helped to reduce the moisture absorption of wood (Rugevitsa et al. 1977).

Modifying bamboo will help largely in improving the dimensional stability especially when it is to be used for outdoor application. Bulking the cell wall with bonding chemicals would reduce the tendency of bamboo to swell or shrink excessively with changes in moisture, because the bamboo would already be in a partially, if not completely, swollen state (Rowell 1983). However, few reports exist in scientific literatures on the acetylation of bamboo. The use of modified bamboo in construction could reduce the demand for tropical heavy hardwood. In order to prevent excessive dimensional changes and improve moisture properties, in this work, *Bambusa vulgaris* was treated with acetic-anhydride without co-solvent. As with wood, it is expected that modifying bamboo with acetic anhydride will improve its dimensional stability among others and at the same time give little effect on its strength properties (Hill 2006, Rowell 2006).

EXPERIMENTAL METHODS

Collection of samples

Bambusa vulgaris culm (2-4 years old) were extracted from naturally growing bamboo grooves in Agba Forest Reserve in Ilorin Kwara State. Agba Forest Reserve lies on Longitude 50°E and Latitude 83°N. The area has an altitude of 2652 feet and elevation of 1054 feet (Solomon 2015). The bamboo culms were sampled at 10% and 50% sampling height which represented the base and the middle portion of the culm, because bamboo is thickest at these portions compared to the top. This made these portions suitable as samples to be used for this research. The sampled culms were dried to constant weight, have the outer skin removed, sanded and then cut to 10x20x20mm (longitudinal x tangential x radial) following EN 113 (1996).

Acetylation Treatments

All the samples were reacted with acetone for 6 hours to remove the acetic acid naturally present in the bamboo samples, they were then wipe dried and oven dried till constant weights were achieved. These weights were used as the starting weight of the bamboo samples. The oven dried samples were sorted into four groups prior acetylation.

The strips were acetylated without the use of co-solvent or catalyst in a reactor under an atmospheric pressure of 756mmHg. The reactor was filled with enough acetic anhydride not only to cover the strips at the initial filling, but also to cover them after absorption of chemical. The samples were then acetylated based on the stipulated time and temperature. After reaction, the samples were soaked in distilled water for 10 minutes to stop further reaction. Thereafter, they were wiped dried and oven dry to constant weight and volume. The experiments were replicated five times. The outline of the acetylation treatment is shown below:

Acetylation at 100ºC for 30 minutes, 60 minutes and 90 minutes.
Acetylation at 120°C for 30 minutes, 60 minutes and 90 minutes.
Acetylation at 140°C for 30 minutes, 60 minutes and 90 minutes.
No acetylation serve as the Control

Property Determination of Acetylated Bamboo

Weight percentage gain (WPG), bulking coefficient (BC), rate of reaction (RR)

The weight percent gain (WPG) which determine the extent of reaction was determined as:

$$WPG = \left[\frac{W_t - W_o}{W_o}\right] \times 100 \quad (1)$$

where: *WPG* is the weight percent gain; W_o is the weight of oven-dried sample before acetylation; W_t is the weight of oven-dried sample after acetylation.

The bulking coefficient (B) was determined as:

$$BC = \left[\frac{V_t - V_o}{V_o}\right] \times 100 \quad (2)$$

where: *BC* is the bulking coefficient; V_u is the volume of oven-dried wood before acetylation; and V_o is the volume of oven-dried wood after being acetylated.

The rate of reaction was calculated as:

$$RR = \left[\frac{WPG}{t}\right] \quad (3)$$

where: RR is the rate of reaction (% h^{-1}); WPG is the weight percent gain (%); and t is the reaction time (h).

Estimation of Dimensional Stability of Acetylated Bamboo

The degree of Dimensional stability was determined by estimating the volumetric swelling (VS) and anti-swell efficiency (ASE), using the repeated water-soaking method described by Rowell and Ellis (1979). The samples were soaked in water for a period of seven days until samples attained constant volume. Excess water was drained and the weights and volume of the specimens were determined. Thereafter, they were oven-dried at 70°C till constant weights were attained. Their final weights were taken to determine their weight losses due to leaching.
Water absorption (i.e, weight gain) of the acetylated bamboo was determined as:

$$WA = \left[\frac{W_a - W_b}{W_b}\right] \times 100 \tag{4}$$

where: WA is water absorption, W_b is the initial weight of an oven-dried sample before water soaking, and W_a is the weight after water soaking for 7 days.

The volumetric swelling coefficients were calculated as:

$$VS = \left[\frac{V_{wet} - V_{dry}}{V_{dry}}\right] \times 100 \tag{5}$$

where: VS is volumetric swelling, V_{wet} is the volume of wood after soaking and V_{dry} is the volume of wood before soaking.

Anti-swelling efficiency was calculated as:

$$ASE = \left[\frac{S_{unmod} - S_{mod}}{S_{mod}}\right] \times 100 \tag{6}$$

where: ASE = Anti-swelling efficiency, S_{unmod} is the volumetric swelling coefficient of the untreated samples, and S_{mod} is the volumetric swelling coefficient of the treated samples.

While weight loss to leaching was determined as:

$$WL = \left[\frac{W_o - W_t}{W_o}\right] \times 100 \tag{7}$$

where: WL= weight loss to leaching;
W_t = oven dry weight after immersion in water;
W_o = oven dry weight before water treatment.

STATISTICAL ANALYSIS

Significant differences between treated and untreated bamboo samples were evaluated by means of Analysis of Variance (ANOVA). Duncan Multiple Range Test at 95% confidence level was used for mean separation. Relationship of the weight gain and other properties of modified bamboo were also examined.

RESULTS AND DISCUSSION

WPG, BC and RR of Acetylated *B. vulgaris*

The weight gain of the modified samples ranged from 1.6% to 3.67% (Table 1). Acetylating at 140°C for 60 minutes had the highest weight gain of 3.67% followed by acetylating at 120°C for 90 minutes while the lowest weight gain (1.6%) was recorded at 140°C for 90 minutes reaction time. Generally, reaction time and temperature have no significant influence on the WPG of the modified samples. However, their were increase in WPG from 100°C to 140°C during 30 minutes reaction time. This showed that the higher the temperature of reaction, within short period, the higher the WPG which was in line with findings of (Rowell 2005). However, in this work, the longer the reaction was run, the lower the WPG which goes contrary to the findings of Rowell (2005) that the longer the reaction is run the higher the WPG. However, he stressed that no matter how it is done, once acetylation reaches a maximum WPG of about 22% further reaction time does not increase this value. This observation may be due to the anatomical properties of bamboo which is quite different from that of wood.

However, acetylating at 140°C for 60 minutes gave the best weight gain while 90 minutes reaction time and 140°C reaction temperature gave the lowest WPG (Fig. 1). This indicated that, the higher the temperature within a short time, the higher the WPG. However, in the case of 90 minutes reaction time, WPG was maximum at 120°C. But lowest at 140°C reaction temperature. This clearly showed that the longer the reaction time at higher temperature, the lower the WPG.

The result of the Bulking Coefficient followed similar pattern with the WPG. Bulking Coefficient of the modified samples ranged from 1.58% to 3.54%. However, there were no significant variations in the BC among all the samples. Acetylating at 140°C for 1 hour gave the largest cell bulking to the modified samples while acetylating at 140°C for 90 min gave the lowest similarly with WPG. There was an increase in BC from 100°C through 140°C for 30 mins reaction time. BC decreased at 120°C but highest at 140°C during 60 min reaction time but with a sharp decline at 140°C during 90 mins reaction time (Fig. 2). Generally, all the samples gained increase in volume after reaction. This indicated that reaction has taken place in the cell wall and not in the void spaces of the bamboo (Rowell 1983). At the same time, since the results of the BC were similar to that of WPG, it shows that there is a linear relationship between the WPC and the BC of the modified bamboo samples.

Although there were similarities in the Rate of reaction (RR) when acetylating at different temperatures. However, significant variations occurred in RR at different reaction times. This indicated that only duration of reaction had influence on the reaction rate. The rate of reaction was fastest during 30 mins period and lowest at 90 mins reaction time. Precisely, the rates of reaction were fastest at 120°C and 140°C during 30 mins reaction period (Fig. 3). These findings showed that the reaction rate was fastest when the temperature was highest and the time of reaction shortest. This finding is in line with earlier report by Stamm (1964) that if the reaction time is long, the temperature required for complete reaction must be low enough. Fast rate of reaction is gotten if the reactions proceed at a high temperature (up to 170 °C) for a very short reaction time (Stamm 1964). However, the fastest reaction did not lead to highest weight gain and bulk of the modified samples.

Table 1

Influence of Reaction Temperature and Time on WPG, BC and RR of Modified B. vulgaris

Source of Variation	F-values and level of significance		
	WPG (%)	BC (%)	RR (%ˉh)
Temp	0.079 ns	0.087 ns	0.279 ns
Time	0.461 ns	0.468 ns	8.174 **
Temp*Time	1.205 ns	1.217 ns	0.654 ns

** = Significant at (p≤0.05); ns = Not significant at (p≤0.05).

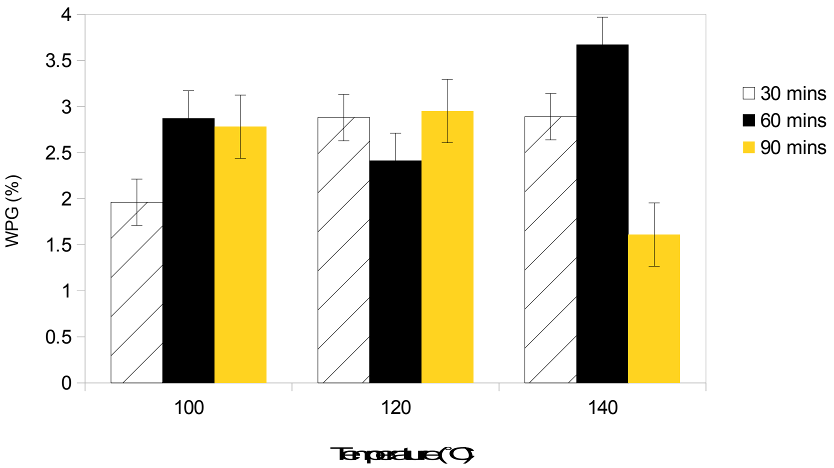

Fig. 1.
Influence of Reaction time and temperature on weight gain of B. vulgaris.

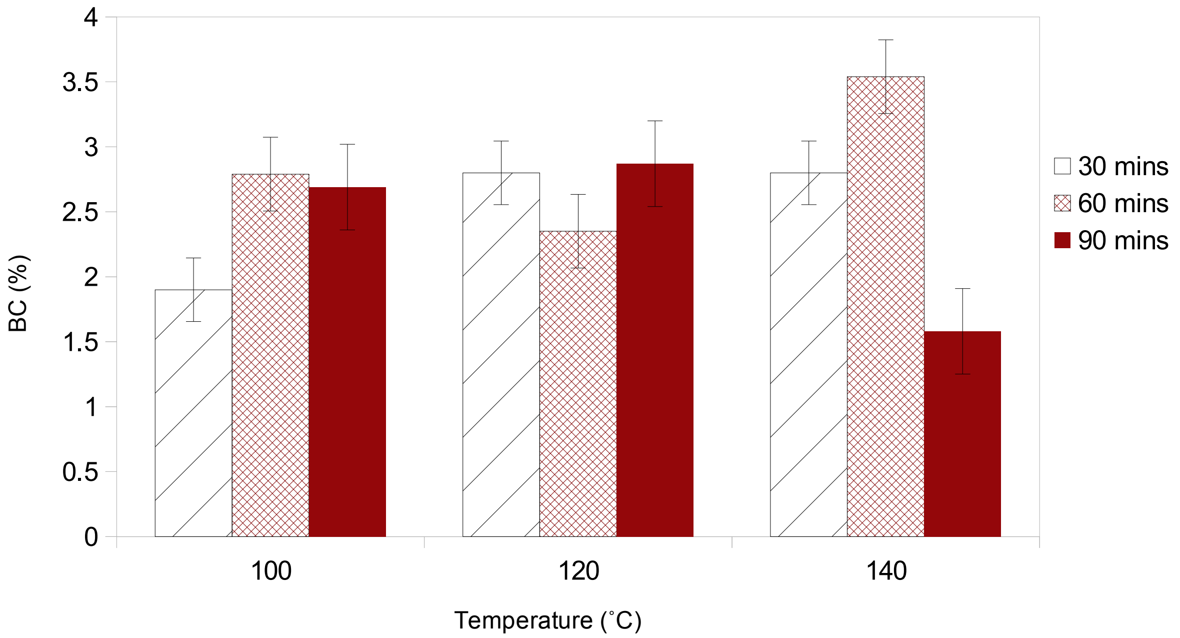

Fig. 2.
Influence of Reaction time and temperature on bulking coefficient of B. vulgaris.

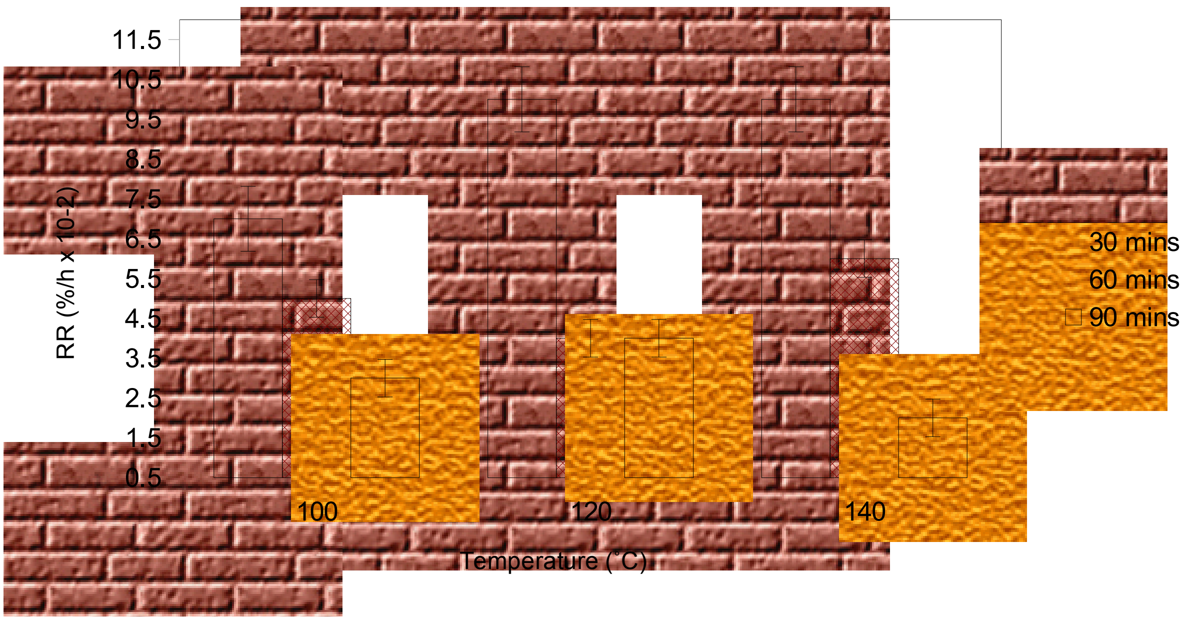

Fig. 3.
Influence of Reaction time and temperature on Reaction Rate of Acetic anhydride with B. vulgaris.

Moisture Response of the Modified Samples

Acetylation at 100°C and for 60 mins gave the lowest and best percentage volumetric swelling while at 120°C and 30 mins reaction time, highest volumetric swelling of 20.61% was recorded. There were decline in the volumetric swelling from 100°C to 140°C during 90 mins duration. However, acetylating for 60 mins, the volumetric swelling increased from 100°C all through 140°C. The pattern of changes in the anti-swelling efficiency (ASE) was quite different from that of volumetric swelling. Generally, ASE varied from 13.08 % to 54.69%, the lowest being recorded at 140°C, 30 mins reaction time while the highest dimensional stability (54.69%) was recorded at 100 °C during a period of 90 mins (Fig. 5). There were no statistical difference in the initial and final volumetric swelling and final anti-swelling efficiency of the modified bamboo samples but there were significant differences in the initial ASE considering the duration of treatments (Table 2). Running the reaction at 100 ^{o}C for 60 mins gave the lowest (11.21%) volumetric swelling while at 100^{o}C for 90 mins, the highest ASE was recorded. According to Rowel (2005), the extent of dimensional stability (ASE) increases with increasing weight percent gain (WPG) and attains an optimum value around 20-30% WPG and then decreases with further modification. None of the bamboo samples had more than 3.67% WPG and 54.69% ASE which may be linked to the anatomical structures of the bamboo cells which are not similar to that of wood. Acetylating wood up to 20% WPG, the swelling and shrinkage is reduced by up to 80% (Rowel 2005). Also, ASE of over 60% is achieved by acetylation of up to 20-25% Kumar and Agarwal (1983) and Tarkov et al. (1950). Therefore, if the WPG obtained in this study is increased, it is believed there will be an improvement in the ASE.

The maximum values of ASE of acetylated bamboo was 54.69% at 2.785 WPG while the lowest ASE (13.08%) was recorded at 2.89% WPG. Whereas at the lowest WPG of 1.61%, ASE of 35.88% was recorded while at the highest WPG of 3.67% ASE of 32.84% was recorded. These results are consistent with earlier findings of Deka and Saikia (2000) where ASE of 70.59% was recorded at 33.7% WPG for Phenol Formaldehyde, 68.23% at 34.1 WPG for Melamine Formaldehyde and 48.5% at 33.8 WPG for Urea Formaldehyde.

Table 2

ANOVA for Influence of Reaction Temperature and Time on Volumetric Swelling, Anti-swelling Efficiency and Weight Loss to Leaching of Modified B. vulgaris

Source of variation	F-values and level of significance				
	Properties				
	VS_i (%)	VS_f (%)	ASE_i (%)	ASE_f (%)	Weight loss to leaching (%)
Temp	0.737 ns	0.285 ns	1.461 ns	2.687 ns	2.453 ns
Time	0.046 ns	0.834 ns	16.073 **	1.953 ns	7.222**
Temp*Time	0.946 ns	0.258 ns	5.154 ns	5.138 ns	0.899 ns

ASE_i = Initial Anti swelling efficiency; ASE_f = Final Anti swelling efficiency;
VS_i = Initial Volumetric swelling; VS_f = Final Volumetric swelling;
** = Significant at ($p \leq 0.05$); ns = Not significant at ($p \leq 0.05$).

Generally, reaction time and temperature as well as the interaction of the two variables had no significant influence on the initial and final volumetric swelling as well as the final anti swelling efficiency (ASE) of the samples. However, acetylation time was able to influence the initial ASE (Table 2).

The WPG of the modified samples increased from 100^{o}C to 140^{o}C during 30 minutes reaction time. This showed that the higher the temperature of reaction, within short period, the higher the WPG which was in line with findings of (Rowell 2005). However, in this work, the longer the reaction was run, the lower the WPG which goes contrary to the findings of Rowell (2005) that the longer the reaction is run the higher the WPG. However, he stressed that no matter how it is done, once acetylation reaches a maximum WPG of about 22% further reaction time does not increase this value. This observation may be due to the anatomical properties of bamboo which is quite different from that of wood.

Changes in VS and ASE after long term water sorption.

Changes in the Volumetric Swelling and Anti-swelling Efficiency upon 7 days water soak are illustrated in Fig. 4 & 5. Volumetric swelling of modified samples increased gradually from 8.47% to 18.58% compared to the unmodified samples which swelled from 9.42% to 43.22% within the 7 days water soaking - drying period. From the figure, there were no changes in volumetric swelling during the 96 hours of soaking. The difference in the volumetric swelling of both treated and untreated samples showed that acetylation resulted in reduced volumetric swelling of treated compared to the untreated samples. Reduction in swelling of the acetylated samples showed that samples modified at a temperature of 120^{o}C as well as 30 mins reaction time showed highest reduction in their ability to swell on exposure to water while those modified at 140^{o}C for 60 minutes had the least reduction (Fig. 4 & 5). Generally, acetylation of the bamboo samples really brought about reduced tendency to swell of *B. vulgaris* as against the unacetylated samples.

The ASE on the other hand reduced gradually from 54.69% to 7.86% for all the samples. However, there were variations in the reduction. Samples modified at of 100^{o}C and 60 minutes had the lowest reduction while those modified at 120^{o}C and 90 minutes had the highest (Fig. 6 & 7).

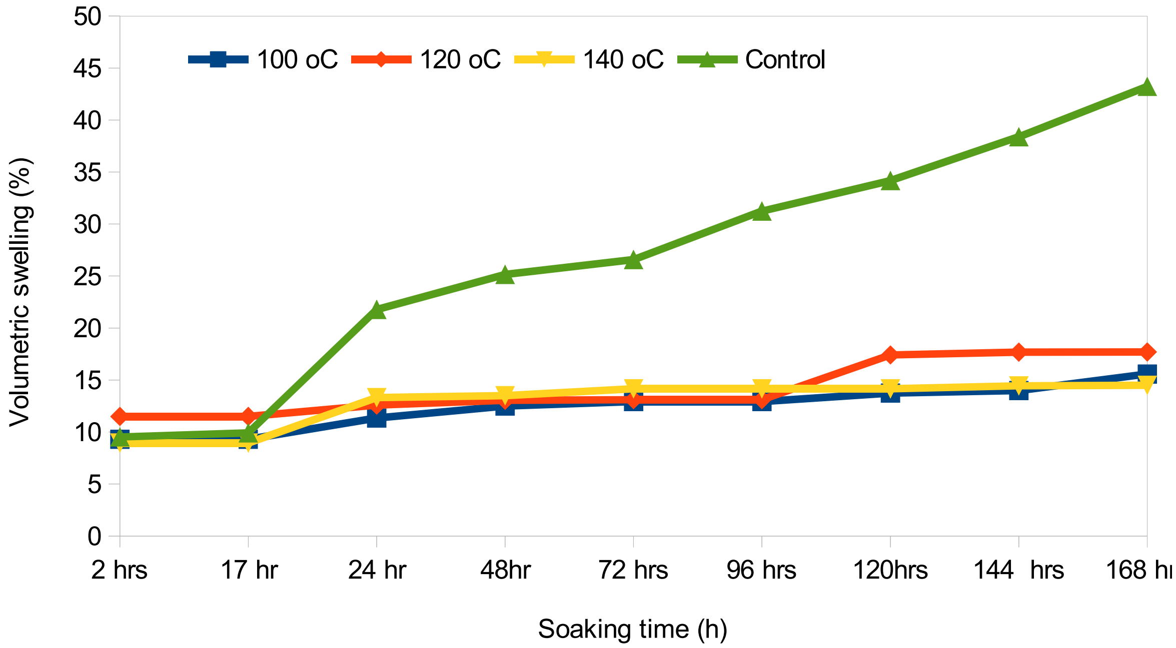

Fig. 4.
Influence of Reaction Temperature on the change in volumetric swelling due to Repeated water soaking.

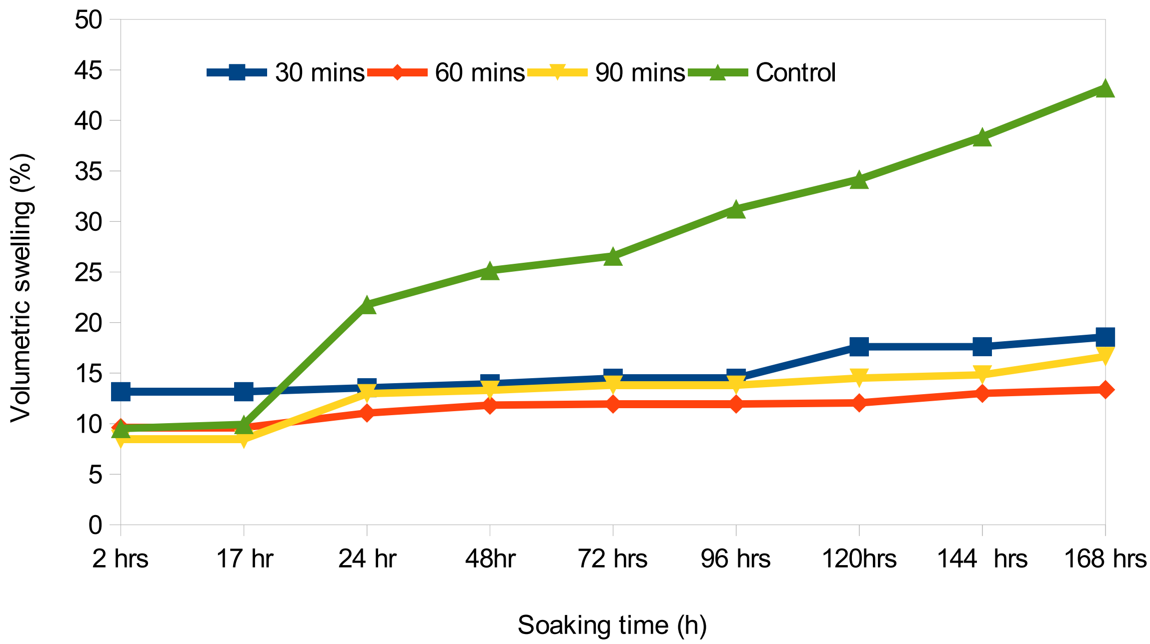

Fig. 5.
Influence of Reaction Time on the change in volumetric swelling due to Repeated water soaking.

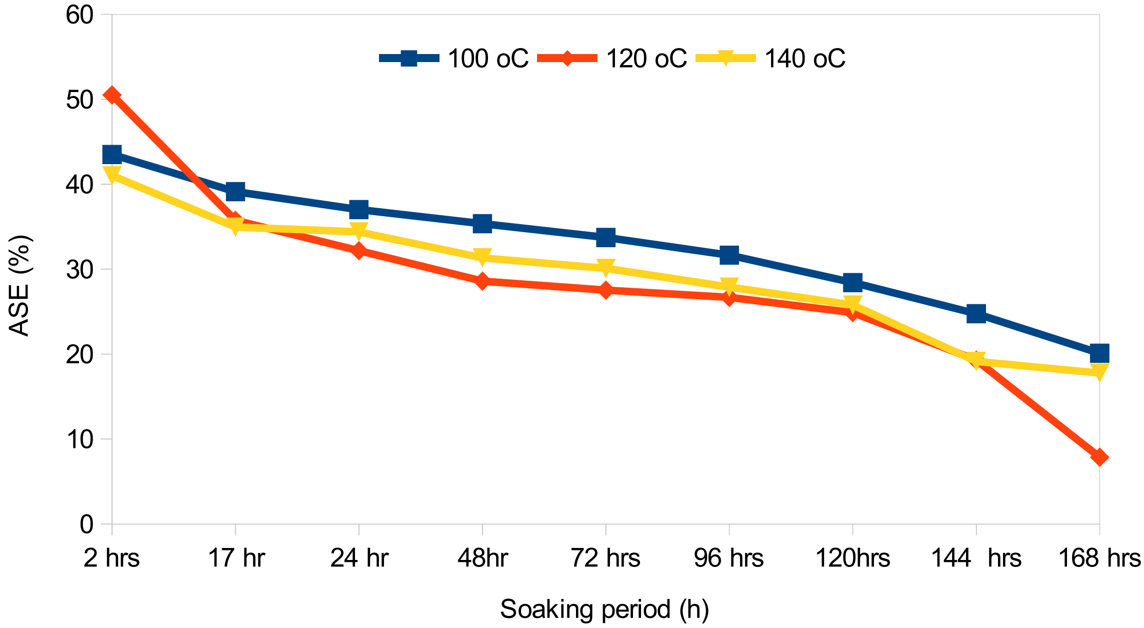

Fig. 6.
Influence of Acetylation Temperature on Reduction in ASE.

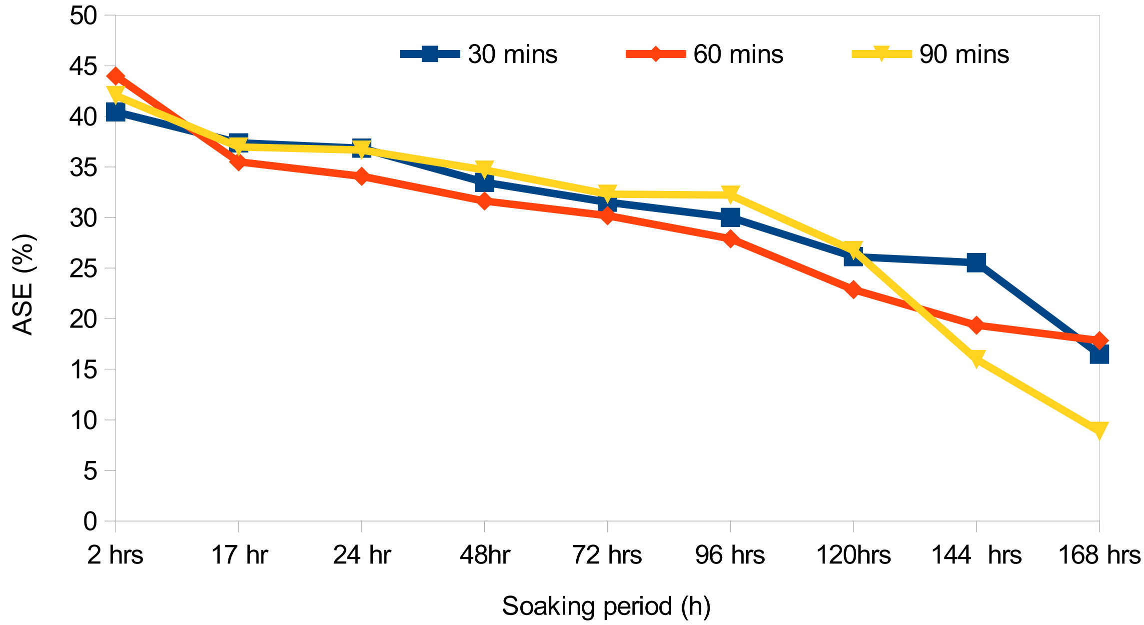

Fig. 7.
Influence of Acetylation Time on Reduction in ASE.

Weight Loss to Leaching

Increase in wood volume and resistance to leaching of added chemical are two proofs that chemical reaction has taken place in the cell wall and that bonding has occurred with the cell wall polymers (Rowell 2005). If the chemical that caused the cell wall to swell to accommodate it is bonded to the cell wall polymers, then solvent extraction would not be able to leach it out. Non-bonded chemicals would be leached out resulting in high weight loss (Rowell 2005). At 100°C and 30 mins reaction time, the extent of modification tends to be high owing to the lowest (6.56%) weight loss to water leaching. However, weight loss was high (11.63%) when samples were modified at 140°C for 90 mins (Fig. 6). Statistically the weight loss to leaching were similar for all the samples when acetylating at any of the reaction temperatures. However, there were statistical differences in the weight loss based on the reaction time (Table 2). This shows that only reaction time had influence on the weight loss of the samples to leaching similarly to the result of Rate of reaction. Generally, the weight losses were low compared to the findings of Rowell (2005) who got similar result for wood reacted with acetic-anhydride, he got between 1.2% – 12.2% weight loss to water leaching. The result of the work indicated that reactions of bamboo with acetic anhydride form chemical bonds that are stable to solvent extraction although some of the chemicals were lost. *A*cetylation was able to maintain between 29.91 - 39.59% ASE value even after 7 days water leaching (Table 2). This further indicated that the bulking chemical is staying in the cell wall of the bamboo samples.

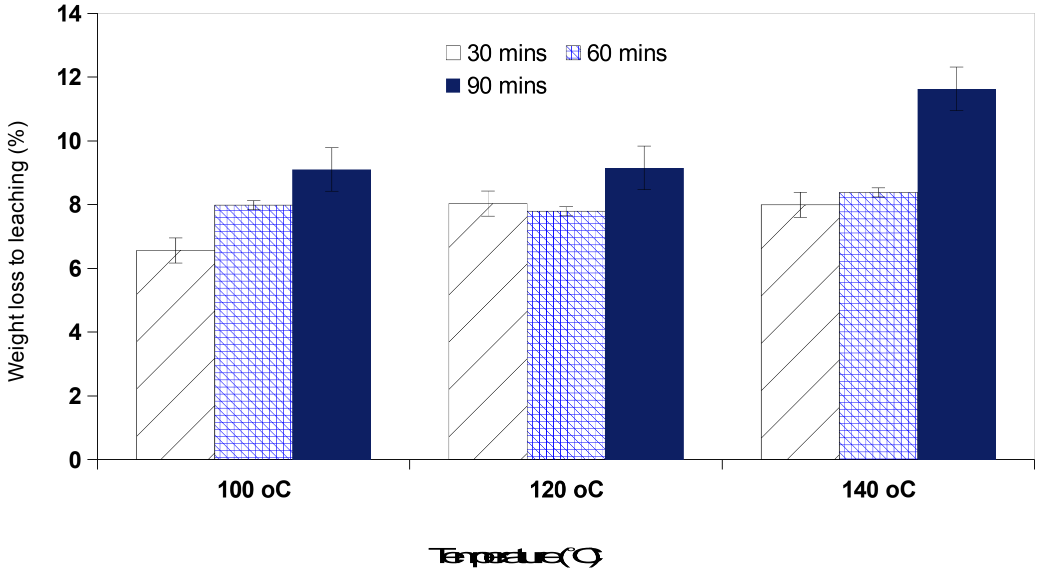

Fig. 8.
Influence of reaction time and temperature on weight loss to leaching of B. vulgaris.

Relationships of Weight Percentage Gain (WPG) with Bulking Coefficient (BC), Volumetric Swelling (VS), Anti-swelling Efficiency (ASE) and Weight loss (WL)

The regression equations of correlation analysis between WPG and BC, VS, ASE and WL are plotted in Fig 7 & 8. It was difficult to find correlation between WPG and BC, VS, ASE and WL. The relationships were weak. However, the relationship of WPG with VS was strongest (R^2 = 0.34) while WPG and ASE was weakest (R^2 = 0.17). This implied that WPG is not suitable enough to describe the extent of dimensional stability conferred on the bamboo as a result of acetylation. Therefore, more than one mechanism contributing to dimensional stability of *B. vulgaris* in this study existed in the modification process.

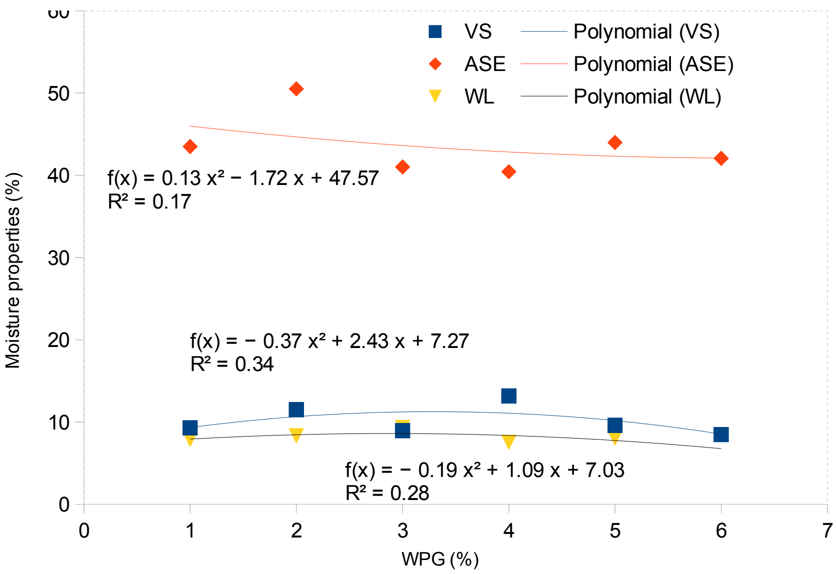

Fig. 9.
Relationship of WPG with VS, ASE and WL.

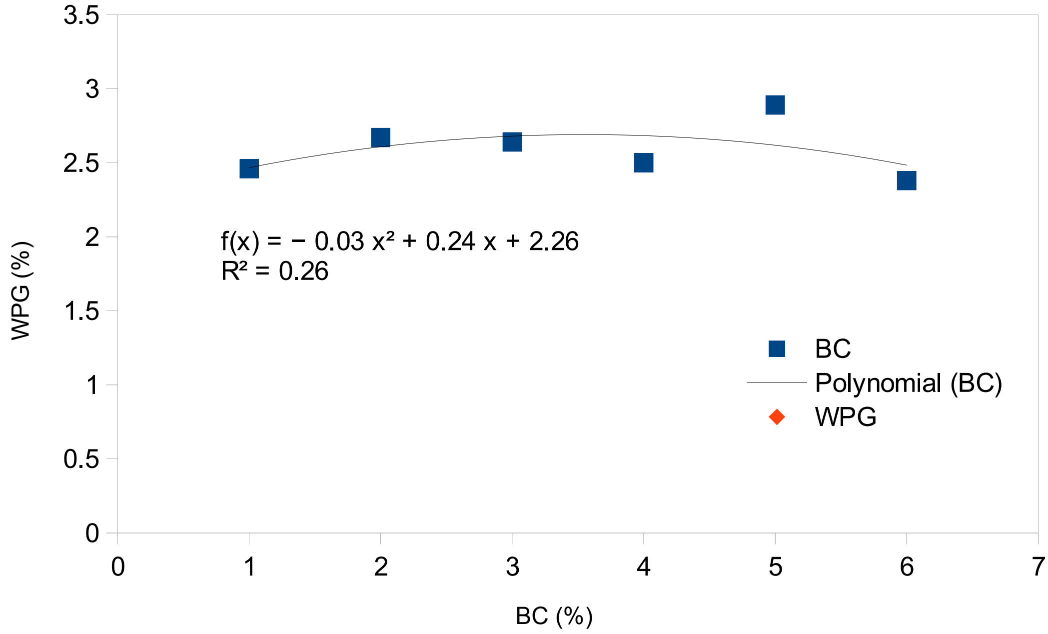

Fig. 10.
Relationship of WPG with BC.

CONCLUSIONS

The finding from this study revealed that there were no significant effect of reaction temperature and time on the WPG, BC, VS and ASE of the acetylated bamboo. The extent of cell bulking depended on the weight gained by individual bamboo samples. Only reaction time had significant influence on RR and weight loss to leaching. Acetylating at 120°C for 30 and 60 minutes is most suitable for *B. vulgaris* to positively influence its sorption properties. There was no strong relationship between WPG and BC, VS, ASE and WL.

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