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Dimensional Stabilization of African Whitewood by Treatment with Modified Chitosan

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Abstract
Effect of modified chitosan on physical and mechanical properties of *Triplochiton scleroxylon* (African whitewood) wood was investigated. The chitosan was chemically modified by introducing more amino groups to the backbone of chitin using parabenzoquinone (pBQ). Obeche wood blocks were impregnated with modified chitosan and commercial chitosan at six different concentration levels (0.2%, 0.4%, 0.8% of modified chitosan (MC) and 0.2%, 0.4% 0.8% of unmodified Chitosan (C). The derivatives were characterized by Fourier Transformed infrared (FT-IR) spectroscopy. Physical properties – water absorption (WA) and water repellent efficiency (WRE) and mechanical properties – modulus of rupture (MOR) and modulus of elasticity (MOE) were determined. The IR spectra at different major peaks confirmed the modification of chitosan. Water Absorption for all the treated samples after 24 -hour and 168- hour water-soak tests ranged between 43.41-50.37% and 86.82-99.68% which were lower than the untreated with 57.92% and 119.5% respectively. The WRE of modified chitosan-treated wood improved considerably with the treatment of samples. There was no significant reduction in the mechanical properties of the treated samples over the untreated ones. Therefore, treating wood with chitosan or modified chitosan is advised for outdoor uses where the wood would be exposed to moisture.

Keywords: Chitosan, Parabenzoquinone, Water absorption, Water Repellent Efficiency, Triplochiton scleroxylon

Introduction

Wood is a natural material that has been universally used in furniture, buildings, and construction due to its good mechanical properties, less difficulty in processing and appealing appearance (Qui *et al*., 2018). In addition, with the increase of deterioration of human activities on the environment and shortage of resources, the inherent structural properties of wood have been of interest in recent years (Song *et al*., 2018). While wood has been useful in various applications due to its outstanding properties, it has downsides, such as dimensional instability and susceptibility to fungal attack, which has been limiting its applications (Hill, 2006). Different methods have been developed for the treatment of wood to overcome some of the problems restricting maximum use of wood. However, most of these methods involve using harmful chemicals or processes, which would provoke environmental worries during service and after end of life of wood materials (Militz and Lande, 2009). Therefore, it would be of great importance to modify wood using environmentally friendly processes. In recent years, more attention has been paid to the development of eco-friendly method of modifying wood. Methods such as thermal (Esteves and Pereira, 2009) and chemical modification (Roussel *et al*., 2001; Adebawo *et al*., 2020) of wood are also being used but there is a need to develop a treatment that will be energy-efficient and using of renewable agents in wood modification.

Modification of wood material with chitosan has received considerable attention due to its potential to alter the physical, mechanical, and biological durability properties (Torr *et al*., 2005; Larnøy *et al*., 2006; Singh *et al*., 2008) of the chitosan material and can penetrate the wood cell wall.

Chitosan is a natural polysaccharide that is usually obtained from deacetylation of chitin. It is the most abundant natural biopolymer found in nature after cellulose. The major sources of its extraction are from exoskeletons of crustacean's shells, insects, annelids, crabs and shrimps. The structures of chitin and chitosan correspond to those of poly[(1→4)-2-acetamide-2-deoxy-d-glucopyranose] and poly[1→4)-2-amino-2-

deoxy-d-glucopyranose], respectively (Kumar, 2000). The free protonable amino groups in the D-glucosamine units make chitosan to be soluble in acidic conditions while chitin is insoluble in aqueous media (Inmaculada *et al*., 2009). This polymer has numerous applications in various fields such as agriculture fabric and textiles, cosmetics and food processing as it has variety of physical, chemical and biological properties (Linden *et al*. 2000; Kumar, 2000). The chitosan has also been used as modification agent in wood and wood composites. Treu and Larnøy (2007) studied the resistance of Scots Pine (Pinus sylvestris) and Beech (Fagus sylvatica) treated with heated chitosan against soft rot fungi. Influences of the chitosan on some properties of wood such as water absorption, bending modulus of elasticity and rupture and resistance against white rot fungus - *Trametes vesicolor* have been studied (Larnøy *et al*., 2005).

Nowrouzi *et al.* (2014) who worked on the influence of nano-chitosan on properties of treated beech and fir wood revealed that the treated fir wood enhanced dimensional stability of about 40 % after soaking in water for 24 h. However, the mechanical properties of the treated woods were not affected, and they were not resistant against both rotting fungi. This implies that the nano-chitosan only had effect on the physical properties of the wood. Since chitosan is viscous in aqueous solution and its solubility in few dilute acid solutions limits its effectiveness in wood treatments (Coma *et al*., 2006; Lee *et al*., 1993), efforts are being made to modify chitosan chemically to improve its solubility and widen its application. Several methods have been used to increase the ionizable amino groups of the backbone of chitosan but was unsuccessful (Jukka *et al*., 2006). Consequently, a new approach was employed by introducing more amino groups to the backbone of chitin using parabenzoquinone (pBQ) to have animated chitosan (modified chitosan). Nevertheless, there was no documented report on the dimensional stability and mechanical properties of pBQ-chitosan modified wood. Hence, this study was carried out to prepare animated chitosan to investigate their effects on physical and mechanical properties of *Triplochiton scleroxylon* wood.

Materials and Methods

Wood samples preparation

Sapwood of Obeche (*Triplochiton scleroxylon*) was used. The wood samples were cut into blocks with dimension 20 x 20 x 60 mm according to ASTM D 1413 test method for solid wood.

Preparation of modified chitosan

The chitosan was modified following the method of Mohy Eldin *et al.* (2012), using three steps, namely: chitin activation, amination and deacetylation

Chitin activation: Chitin (4g) was dispersed in distilled water (50 ml) at defined pH, parabenzoquinone (pBQ) was dissolved in it and stirred for 6hr. The activated chitin (AC) was separated and washed well with distilled water.

Chitin amination: The AC was dispersed in 50 ml of distilled water and ethylene di amine was dissolved in it and stirred for 6 hr. The aminated modified chitin (AMch) was separated and washed well with distilled water.

Animated chitin deacetylation: Deacetylation of AMch was performed according to Rigby (1936) and Wolfrom *et al.* (1958) methods. The aminated chitin derivative was treated with 40 % aqueous solution of NaOH at 120-150°C for 6hr and aminated chitosan (AMC) was obtained. It was separated and washed well with distilled water.

Preparation of different MW of modified chitosan:

Aminated chitosan was degraded by the method of acetic acid hydrolysis referenced from Chen and Hwa (1996). Aminated chitosan was dissolved in 5% aqueous acetic acid, incubated at 50°C for 48 hr and then centrifuged (5000 rpm) for 20 min. The supernatant was added to 4N aqueous NaOH. The sediment was filtrated and sequentially rinsed in water and ethanol and dried at 50°C.

Impregnation of wood samples

The wood samples were dried to constant weight and the weight (T_1) taken before impregnation. Chitosan and modified chitosan solutions of different concentrations (0.2%, 0.4% and 0.8% chitosan (C) solutions); 0.2%, 0.4% and 0.8% Modified-chitosan (MC) were impregnated into the wood samples by using impregnation chamber at a vacuum of 0.004 MPa and pressure of 0.8 MPa for 1 h. Immediately after the impregnation, all samples impregnated with chitosan and modified-chitosan solution were removed and weighed (T_2). The samples were conditioned reweighed (T_3).

Water Absorption (WA) and Water Repellent Efficiency (WRE)

The WA and WRE for both modified and unmodified samples were measured according to ASTM -1037 (1999). Five oven-dried samples (for samples treated at each concentration level with dimensions (20 X 20 X 10 mm)) were soaked in a water bath at a temperature of 20±1 °C for 168 h; the weight and dimension of specimens were determined before and after soaking. Water absorption was calculated according to equation 1

$$\text{WA } (\%) = \frac{W2-W1}{W1} \text{ X } 100 \text{ ….. } (1)$$

Where;

WA= Water Absorption;

W2 = Weight of specimen after water soaking,

W1= Weight of specimen before water soaking.

Water Repellent Efficiency was calculated according to equation 2.

$$\text{WRE } (\%) = \frac{Wu-Wh}{Wu} \text{ X } 100 \text{ ….. } (2)$$

Where;

Wu = Water absorption of untreated specimens,

Wm= Water absorption of heat-treated specimens.

Fourier Transformed Infrared (FT-IR) Spectroscopy

The IR spectra of the activated chitin, animated chitin, animated chitosan and untreated wood samples were obtained using Perkin Elmer FT-IR spectrometer Frontier by an accumulation of 64 scans at a resolution of 4 cm^{-1} at 600—4000 cm^{-1} following the previous reported methods (Adebawo *et al*., 2016).

Statistical Analysis

Data obtained were analyzed using analysis of variance (ANOVA). Means of untreated and heat-treated specimens were separated using Duncan multiple range test at $\alpha 0.05$.

Results and Discussion

FTIR

The IR spectra of chitin, chitosan, activated chitin, deacetylated chitin and modified chitosan are presented in Figure 1. The major difference between the IR spectra of chitin and chitosan before modification is the peak at 3255cm^{-1} (conforming to the O-H and N-H stretching) and this peak was very sharp for chitin spectrum but not obvious for the commercial chitosan. However, the peak became more intense for modified chitosan because of alteration in the O–H groups with N–H groups. The absorbance intensity for peaks between 2870 and 2853 cm^{-1} corresponding to C-H stretching was sharp for both chitin and chitosan but the peak was reduced for the activated chitin, deacetylated chitin and modified chitosan. The reduction in the peaks may be due to the removal of the acetyl groups after deacetylation of chitin as reported by Mohy Eldin *et al*. (2012). There was also a difference in the absorbance intensity at 1554 cm^{-1} and 1552 cm^{-1} corresponding to the carbonyl groups which increased in activated chitin and modified chitosan compared to chitosan. This could be due to introduction of extra carbonyl groups from PBQ as shown in Figure 1 (B, C, E). The peaks at 1010 and 1000 cm^{-1} correspond to the O-bridge stretching of the glucosamine residue. All the peaks for the deacetylated chitin were reduced due to the removal of the acetyl groups in modified chitosan. This confirmed the modification process to get animated chitosan also referred to as modified chitosan in this study (Figure 1 (e).

Water Absorption (WA)

The results of the water absorption of the *Triplochiton scleroxylon* modified with different concentrations of Chitosan are presented in Figure 1. The water absorption was measured for a period of 168 hours (7 days). After 24h, the water absorption for all the treated samples ranged between 43.41-50.37% lower than WA for the untreated samples (57.92%). Among the treated samples, 0.2% MC samples had the lowest WA (43.41%). After 168h, the WA of the untreated samples increased to 119.5% while the treated samples ranged between 86.82-99.68%. This indicated that the modification influenced the water absorption irrespective of the concentration used. The water absorption of the treated wood was lower than the untreated ones. This is related to the work of Mehmet and Ergun (2009) who worked on the treatment of particleboard with chitosan to improve its physical properties. They reported that there was a reduction in the water absorption of the treated particleboard over the untreated panels after a 24-hour water-soak test. High WA is an indication of porous structures in the cell wall polymers which are affected by the treatment solutions. The reduction in the WA of the treated samples could be because of chitosan treatment which has reduced micro-spaces in the cell walls, thereby preventing penetration of the water molecules, leading to a reduction of water molecules at the sorption sites.

Water Repellent Efficiency (WRE)

The WRE of wood samples treated with different concentrations of modified chitosan is given in Figure 3. The WRE of 0.2%MC, 0.4%MC, and 0.8%MC after 2-hour water soak test was 20.45, 11.54 and 23.45 % respectively. After 24-hour of water soak test, WRE increased to 25.05 and 20.35% for 0.2%MC and 0.4%MC respectively while there was a decrease to 13.04% in WRE for 0.8% MC. Meanwhile after 168-hour of water soak test, WRE was 26.14, 27.36 and 17.59 % for 0.2% MC, 0.4% MC and 0.8%MC respectively. The WRE of wood samples treated with different concentration of chitosan is also given in Figure 3. The WRE of 0.2% C, 0.4% C and 0.8%C after 2-hour of water soak test was 13.34, 8.18 and 15.36 % respectively. After 24-hours of water soak test, WRE decreased to 11.05% for 0.2 % C and it was not consistence till 168 h. However, there was an increase up to 16.60 and 24.62 % in WRE of 0.4%C and 0.8%C after 24-hour of water soak test. Out of all the treated samples, only 0.4%MC had a linear increase that was consistent after 168 h of water soak test. The increased WRE may be attributed to a chitosan film encapsulating the hydroxyls groups of the polymers, thereby blocking some of the hydrophilic hydroxyl groups at the chitosan/ cellulose interface (Basturk, 2012). This modified chitosan acted as a water barrier layer around the hydroxyl groups thereby increasing water repellency. Similar result is reported by Umemura *et al*. (2005), who stated that chitosan and wood have polycationic and polyanionic natures, respectively.

Modulus of Rupture (MOR) and Modulus of Elasticity (MOE)

MOR and MOE are the most studied mechanical property of wood because MOE can be often performed at the same with the MOR. The result of the MOR and MOE of the treated *Triplochiton scleroxylon* wood is presented in Table 1. The MOR ranged between 20.08 – 21.23 N/mm^2 for treated wood and untreated wood had 19.40 N/mm^2. The MOE ranged between 923.96-1001.15 N/mm^2 and 867.15 N/mm^2 for treated and untreated wood respectively. It could be seen that there is no significant difference among all the treated and untreated wood samples both for MOR and MOE. In previously documented reports, it is common to observe the neutral change in bending strength (MOR) after the treatment of wood as reported by Dieste *et al.* (2008). They impregnated veneers with a solution of dimethylol dihydroxy ethylene urea (DMDHEU) and no significant reduction in the bending strength was observed. The same neutral effect on the bending strength after treatment was also reported by Rowell *et al.* (2008) and Esteves *et al.* (2011) who modified wood by acetylation and by fufurylation respectively. However, there are several reports on the improvement of MOR after treatment (Deka and Saikia, 2000; Devi *et al*., 2003) which are contrary to the result of the present study. The modulus of elasticity (MOE) refers to bending stiffness and the value is usually determined at the same time and the same way as the MOR value. The MOE means the temporary maximum force by which deformations return after the load is removed (Kretschmann, 2010). The treatment of the sample wood with modified chitosan and unmodified chitosan did not have a significant effect on the MOE. This corroborates the findings of Nowrouzi *et al.* (2014) who reported that none of the treatments of wood with the chitosan and the nano-chitosan had a significant effect on the bending strength (MOE) of Fir and Beech wood. This suggests that the treatments couldn't increase the wood's strength. However, no reduction occurred in the strength of the woods due to the treatments as well which could also mean good properties of the wood.

Conclusion

This study has investigated the improving properties of *Triplochiton scleroxylon* wood by treating the wood with modified chitosan and chitosan. The results revealed that treatment of the wood with different concentrations of modified chitosan and unmodified chitosan reduced the water absorption and increased WRE, thereby increasing the dimensional stability of the wood. However, any treatment on the wood did not have a significant effect on the bending strength (MOE and MOR) of the wood. Therefore, for outdoor purposes where the wood would be exposed to moisture, treatment with modified chitosan or chitosan is recommended.

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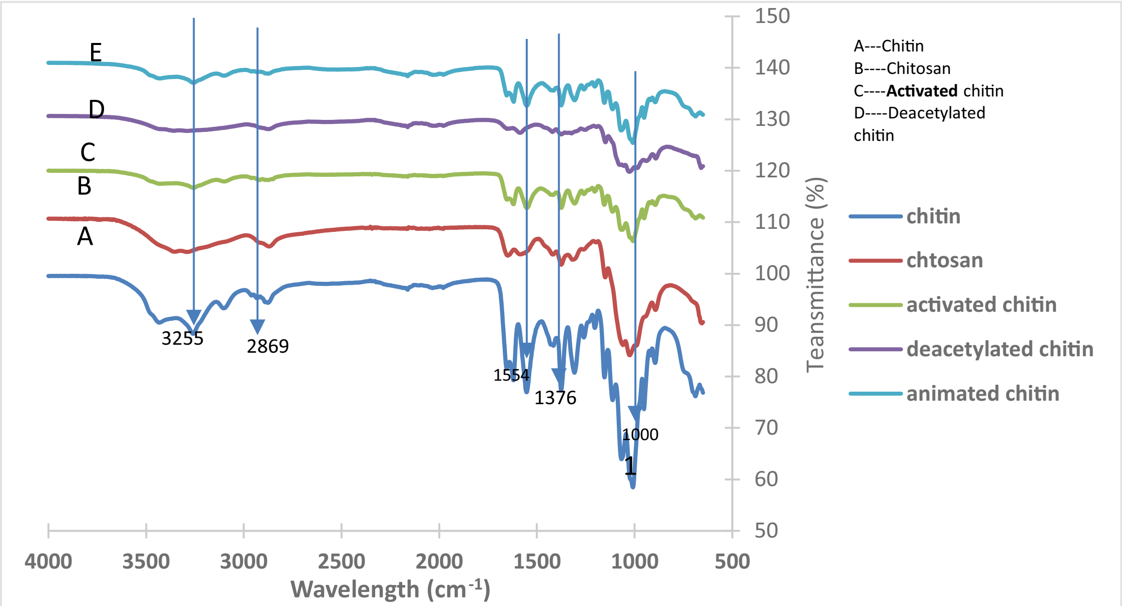

Figure 1: FTIR of Chitin (A), Chitosan (B), Activated chitin (C), Deacetylated chitin (D), Animated/ modified (E)

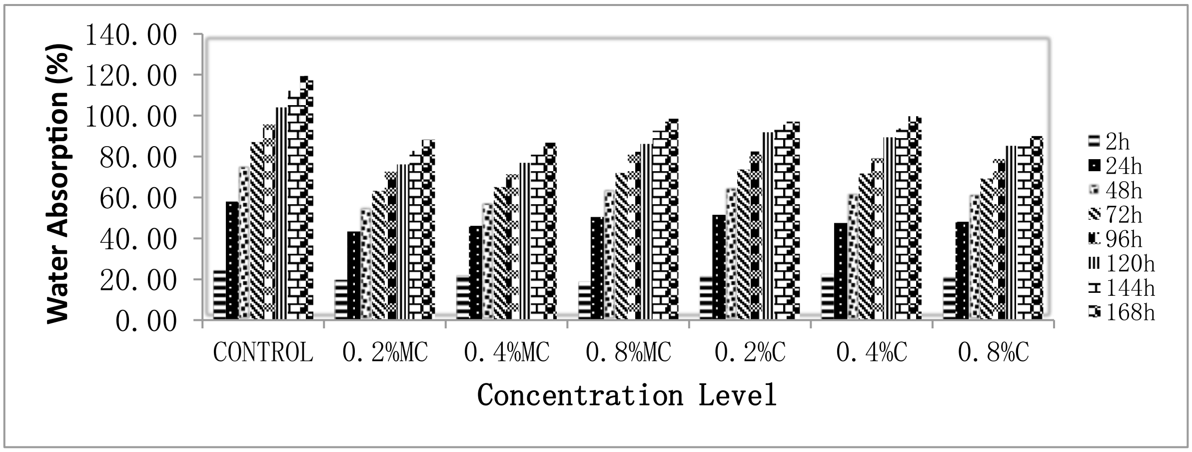

Figure 2: Water Absorption of *Triplochiton scleroxylon* treated with different concentrations of Chitosan and Modified chitosan

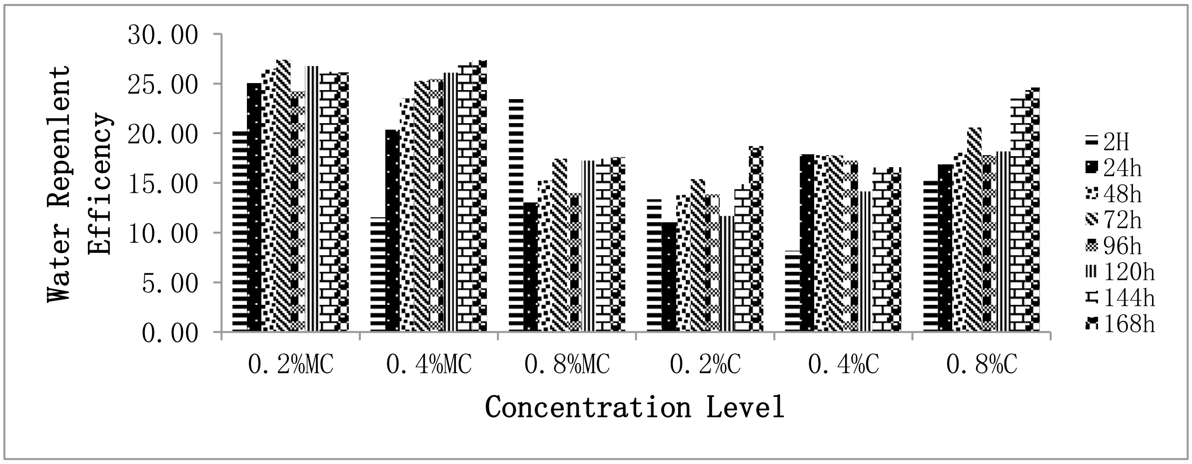

Figure 3: Water Repellent Efficiency of *Triplochiton scleroxylon* treated with different concentrations of Chitosan and Modified chitosan

Table 1: MOR and MOE of Treated *Triplochiton scleroxylon* wood

Conditions	**Concentration**	**Modulus of Rupture (N/mm^2)**	**Modulus of Elasticity (N/mm^2)**
	0.2	20.97(1.68) ^{a}	923.96(268.96) ^{a}
Chitosan	0.4	20.32(1.00) ^{a}	987.51(143.50) ^{a}
	0.8	20.16(0.31) ^{a}	951.06(124.04) ^{a}
	0.2	21.23(0.77) ^{a}	947.48(114.43) ^{a}
Modified Chitosan	0.4	20.08(0.18) ^{a}	1001.15(83.89) ^{a}
	0.8	20.11(0.05) ^{a}	970.92(80.83) ^{a}
Control		19.40(0.73) ^{a}	867.15(36.86) ^{a}

Mean, and Standard Error in Parenthesis; value carrying the same letters are not significantly different from each other (P<0.05)