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Evaluation of Modified-Chitosan as Wood-Preservatives Against Termites Attack

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Abstract

Over the past decades, several studies have confirmed that chitosan exhibits antimicrobial and antifungal properties, which have been used as wood- protecting agent. The chitosan was chemically modified by introducing more amino groups to the backbone of chitin using parabenzoquinone (pBQ). However, the antitermitic potential of the modified chitosan has not been reported. Thus, this study examined the termite's resistance of wood treated with modified chitosan and commercial chitosan at different concentration levels (0.2%, 0.4%, 0.8% of modified chitosan (MC) and 0.2%, 0.4% 0.8% of unmodified Chitosan (C)). Obeche (*Triplochiton scleroxylon*) wood samples were impregnated with six different concentrations of chitosan. The absorption and retention rate of the chitosan solution by the wood were determined while the treated and untreated wood samples were exposed to termites at the graveyard and their weight loss was determined after twelve weeks. Absorption and retention of chitosan solution at different concentrations significantly showed differences. The result revealed that 0.4% MC had the highest resistance to termites by reducing 57.6% weight loss of the untreated to 2.19%. It is worth mentioning that the modified chitosan could protect wood against termite attacks.

Keywords: Chitosan, parabenzoquinone, *Triplochiton scleroxylon*, termites, weight loss

Introduction

Wood is one of the natural renewable resources that play an important role in the building and construction industries. Due to its biological makeup, wood has some weaknesses such as biodegradation and dimensional instability which have been restricting its applications. For eras, researchers have been working to develop methods of improving the properties of wood that limit its application (Goldensten *et al.* 1961; Peterson and Thomas, 1978; Takahashi *et al.* 1989; Beckers*et al.* 1994). Traditional wood protection methods are based on inorganic and synthetic chemicals containing copper, chromium and arsenic, zinc etc. Though these wood preservatives are effective in protecting wood from biodeterioration, but have detrimental effects on human health and cause environmental toxicity (Hill, 2005). Many other methods such as thermal (Esteves and Pereira, 2009) and chemical modification (Roussel *et al*., 2001; Rowel and Dickerson, 2014; Adebawo *et al*., 2020; Adebawo *et al*. 2021) of wood have also been used but there is a need to develop a treatment that will be energy efficient, not having a negative effect on the wood and the environment. Hence, the focus is on protecting wood using eco-friendly sustainable treatments against wood-destroying organisms.

Chitin is a natural polysaccharide that is found in the exoskeleton of shellfish and arthropods, and in the cell walls of fungi and yeast. The insolubility of chitin in water and other common organic solvents has made its conversion to chitosan by deacetylation under alkaline a regular practice. Chitosan, a linear polysaccharide, is made up of glucosamine and N- acetyl glucosamine units linked by (1–4) glycoside bonds. The degree of deacetylation (DD) of chitin is determined by the content of glucosamine. Chitin is converted to chitosan when the DD of chitin is higher than 50%, making it soluble in an aqueous acidic medium (Tomihata and Ikada, 1997).

Chitosan is a non-toxic and biodegradable natural polymer that has proven to be effective as an antimicrobial agent. It occurs naturally as a polysaccharide in various array of natural sources found in crustaceans, insects, mollusks, coelenterate etc. (Muzzarelli et al, 1990). Chitosan is normally produced from crustaceans (shrimp, crab, krill, and crayfish), primarily because the exoskeleton of a crustacean is available in large quantities as a by-product of the food processing industries. Chitosan consists of β-1→4-linked D-glucosamine residues with a variable number of randomly located N-acetyl-glucosamine groups.

Recently, chitosan has attracted considerable attention for its potential applications in food, agriculture, medicine, pharmaceuticals, cosmetics and wood preservation, due to its interesting physicochemical, and biological properties (Eikenes *et al*., 2005, Torr, K. *et al*., 2005) and antimicrobial properties (Jeon, *et al*., 2001). As a result, there has been a growing investigation on the potential of chitosan and its derivatives as organic biocides for wood protection (Eikenes *et al*., 2005), and against decay resistance (Vesentini *et al*., 2007; Hussain *et al*., 2012). Although, the effect of chitosan on different insects such as Lepidoptera and aphids has been documented (Zhang *et al.* 2003; Badawy and El-Aswal, 2012), only a few reports of termiticidal activity of chitosan against subterranean termites, *Reticulitermes flavipes* and *Reticulitermes virginicus* has been reported (Raji *et al.*2018). However, chitosan is viscous in aqueous solution and its solubility in a few dilute acid solutions limits its use as a wood preservative (Coma *et al*., 2006; Lee *et al*., 1993). Hence, 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 were 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, no documented report on the resistance of pBQ-chitosan-modified wood against termite exposure. Hence, this study was carried out to investigate the resistance-modified chitosan-treated wood against termites using exposure to the graveyard.

Materials and Methods

Wood sample preparation

The sapwood of Obeche (*Triplochiton scleroxylon*) were 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 MohyEldin*et al.* (2008) using three steps namely, chitin activation, amination and finally 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^{o}C for 6hr and aminated chitosan (AMC) was obtained. It was separated and washed well with distilled water.

Preparation of different Molecular weights (MW) of modified chitosan: Aminated chitosan was degraded by the method of acetic acid hydrolyzes referenced by Chen and Hwa (1996). Aminated chitosan was dissolved in 5 % aqueous acetic acid incubated at 50 ^{o}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 ^{o}C.

Impregnation of wood samples

The wood samples were dried to constant weight and the weight (T_1) was taken before impregnation. Chitosan and modified-chitosan solutions of different concentrations (0.2% , 0.4% and 0.8% chitosan (C) solution; 0.2%, 0.4% and 0.8% Modified-chitosan (MC) were impregnated into the wood samples by using impregnation chamber at the 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 and reweighed (T_3).

Percentage absorption and Retention of chitosan solution

After the impregnation of the sample with different concentrations of chitosan, the absorption and retention of the chitosan solution were determined according to ANSI/ASTM D281 (1979) using equations 1 and 2.

Absorption rate (%) =

$$\frac{T2 - T1}{T1} \times 100 \qquad (1)$$

Retention level (g/cm^3) = $\frac{G \times C \times 10}{V}$ (2)

Where,

G = (T_2 – T_1) = amount of treated solution absorbed by the wood specimen (g)

T_1 = initial weight of the conditioned wood specimen before impregnation (g)

T_2 = weight of the wood specimen after impregnation (g)

C = grams of chitosan in 100ml of solution,

V = volume of wood specimens (cm^3).

Graveyard test

The method for the graveyard test was adopted from ANSI/AWP A (1988) D1413-76. The treated and untreated wood samples were exposed to termite attack at Graveyard Plot of the department of Wood and Paper Technology, Federal College of Forestry, Ibadan Nigeria. They were laid on the surface of the ground at 0.5m apart for twelve weeks. The visual rating was employed weekly to check the termite degradation resistance of the wood samples.

Visual observation and evaluation

The visual rating of wood samples was done according to the standard American Society of Testing Materials ASTM D 3345-74 (1974).

The visual rating was determined as follows:

10 = Sound surface bites permitted

9 = Light attack

7 = Moderate attack penetration

4 = Heavy attack, 40% of the wood cross-section eaten up by termites

0 = Failure, over 50% of the wood cross-section eaten up by termites

After 12 weeks of exposure, the wood samples were removed and weighed (T4).

Determination of Weight Loss

Weight loss after exposure to termite's attack was calculated using equation 3

Weight Loss (%) =

$$\frac{T3 - T4}{T3} \times 100 \qquad (3)$$

Where,

T3 = conditioned weight after treatment (g),

T4 = weight of conditioned wood samples after exposure to termites' attack (g).

Results and Discussion

Percentage Absorption rate of *Triplochiton scleroxylon*

The result of the absorption rate is presented in Table 1. The wood samples treated with different concentrations of chitosan showed an increase in the initial weight of the wood after impregnation. The effect of different concentrations of chitosan on the absorption by the wood samples varied significantly as shown in Table 1. The percentage absorption of unmodified chitosan (C) treated wood ranged between 66.78%and 88.79% while modified chitosan (MC) ranged between 61.21% and 114.68%. The absorption rates of modified chitosan were significantly higher than the unmodified chitosan. The difference in absorption rate could be attributed to the viscosity of the solution. Viscosity is a function of the absorption by the wood. The more viscous the preservative, the slower the absorption rate.

Table 1: Absorption and retention of Chitosan Treated *Triplochiton scleroxylon* wood

Concentration level	Absorption(%)	Retention(%)
Control(untreated samples)	0	0
0.2%MC	90.84±21.51d^{d}	62.39±15.35^{ab}
0.4%MC	114.68±23.60^{e}	145.56±35.04^{cd}
0.8%MC	61.21±8.71^{a}	159.63±17.08^{d}
0.2%C	88.79±8.71^{c}	58.94±7.19^{ab}
0.4%C	66.78±26.08^{a}	82.95±34.88^{bc}
0.8%C	70.58±3.31^{b}	184.75±67.30^{e}

Values with the same superscript are not significantly different at $p \leq 0.05$

Chitosan Solution Retention by *Triplochiton scleroxylon*

The retention of the chitosan solution by the wood is presented in Table 1. The quantity of chitosan retained in the wood is known as retention. For the modified chitosan (MC) at different concentrations, retention ranged from 62.39-159.63% while for unmodified chitosan (C) ranged from 58.94-184.75%. It could be observed that 0.8% C had the highest retention rate of 184.75% followed by 0.8% MC with a retention of 159.63%. The lowest retention is found in 0.2%C with 58.94%. However, it is noted that an increase in concentration levels of both the modified and unmodified chitosan solution did have an effect on the increased retention rate. This is obviously seen in 0.8% MC having a retention that is higher than what is found in 0.2% MC. This is in line with the work of Eikenes *et al.* (2005) who reported that retention of chitosan increases as the concentration of chitosan solution increases.

Visual observation After Termite Attack

The results of visual observation of *Triplochiton scleroxylon* after 12 weeks of exposure to termite is presented in Figure 1. It could be observed from the figure that in the first two weeks, there was no visible attack on all the wood samples treated with chitosan except the untreated samples. At 4 weeks of exposure, all the chitosan-treated wood samples had light attacks compared with the untreated wood samples. At 10 weeks of exposure, the untreated wood samples had been eaten up by termites while the wood samples treated with modified chitosan had moderate attacks by the termites. However, there was a significant level of resistance in all the wood samples treated with different concentrations of chitosan. At the end of 12 weeks, more than 50% of the untreated wood samples had been eaten up by termites.

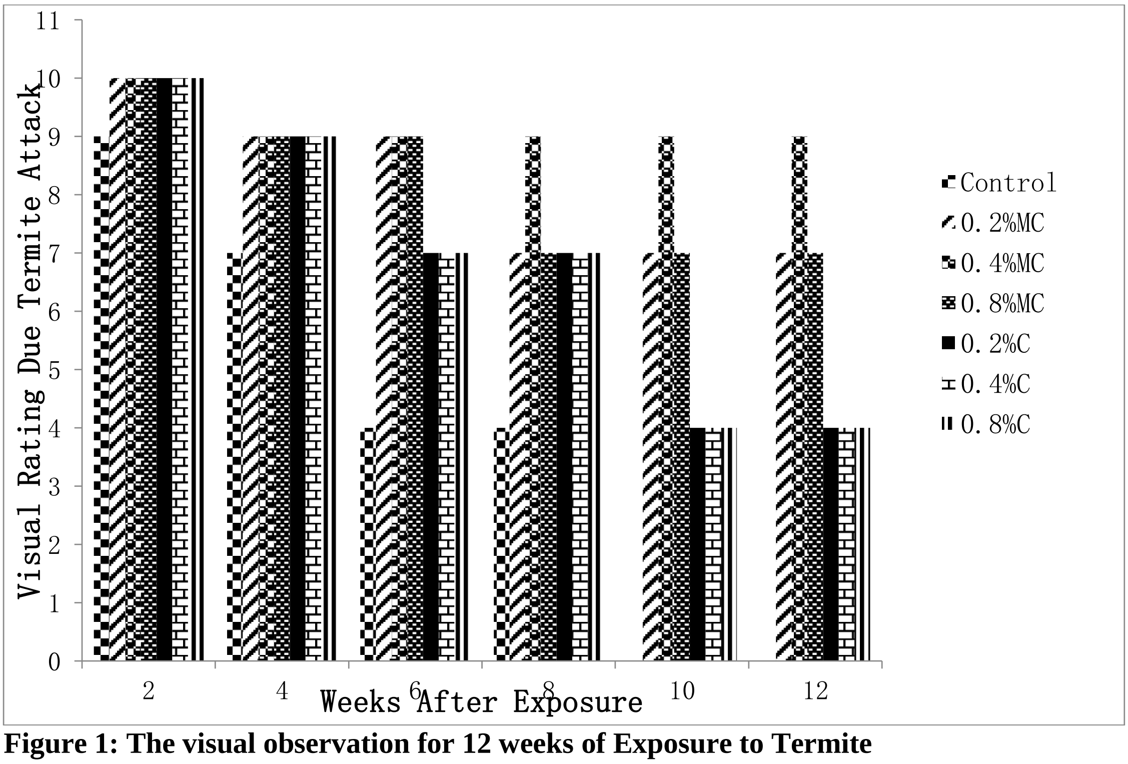

Figure 1: The visual observation for 12 weeks of Exposure to Termite

Percentage Weight Loss as a Result of Termite Infestation

The result for the percentage weight loss of *Triplochiton scleroxylon* wood treated with different concentrations of modified and unmodified chitosan after 12 weeks of exposure to termite attack is presented in Figure 1. The weight loss ranges between 2.19% and 57.6%. The lowest weight loss (2.19%) is observed in 0.4%MC followed by 0.2%MC and 0.8%MC while the highest weight loss (57.6%) was observed in untreated samples. There is a significant difference among different concentrations of chitosan used to modify the wood species as presented in Table 2. This means 0.4%MC treated wood had the highest resistance to termite attack (0.4%MC±2.19). The weight loss of wood treated with unmodified ranged chitosan was between 31.48-37.18% indicating that their resistance to termite attack is lower than the wood treated with modified chitosan. Although 0.8% C had the highest rate of absorption in comparison to other substances, it did not provide the greatest protection against termite assault.

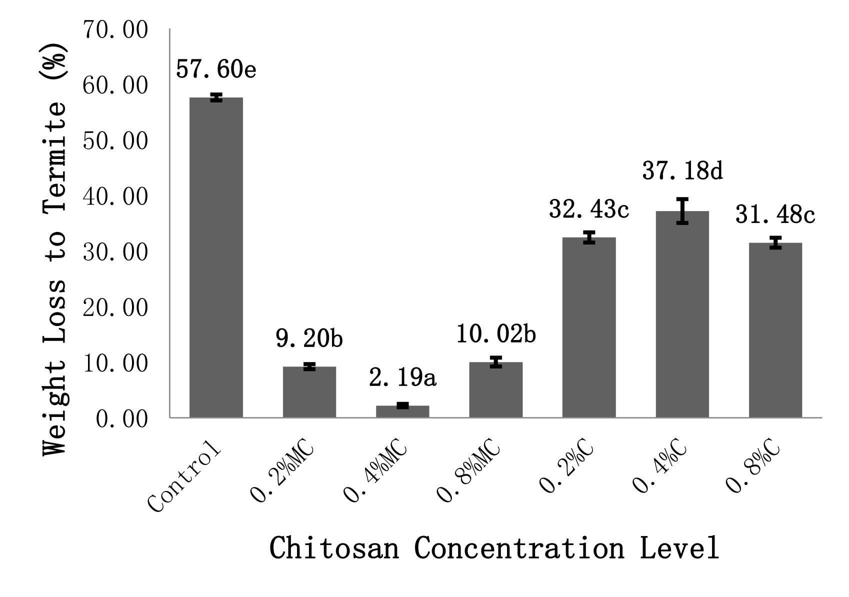

Figure 2: Weight loss of *T. scleroxylon* wood treated with different concentrations of chitosan

Table 2: Analysis of variance of weight loss of *T. scleroxylon* wood to termite attack

Source of variation	df	Sum of Squares	Mean Square	F	Sig.
Chitosan concentration level	6	4598.17	766.36	361.33	0.00*
Error	7	14.85	2.12		
Total	**13**	**4613.02**			

**Significant* ($P \leq 0.05$)

Thus, it does not follow that the higher the retention the higher the resistance to termite attack. This observation is similar to the work of Adeduntan (2015) who reported that higher absorption and retention of preservatives did not correspond to higher resistance to termite attack. He added that what determines the resistance to termite attack could be the active ingredient in the preservative chemical. It could also be observed that the percentage weight loss of wood samples treated with 0.2%MC and 0.8%MC were not significantly different from each other.

It is well documented that decreasing the pH increases the antimicrobial activity of chitosan because the amino groups of chitosan ionize and carries a positive charge at a pH below 6 (Yang *et al.* 2005). However, unmodified chitosan does not dissolve in water since it does not have any positive charge on the amino group and thereby, is not antimicrobial active at pH 7, Increasing the degree of deacetylation increases the number of ionizable amino groups, thereby increasing its solubility and antimicrobial activity (Chung *et al.* 2005). The high resistance of wood treated with modified chitosan to termite attacks could be due to an increase in the number of ionizable amino groups on chitosan. Comparing the termiticidal effectiveness of modified chitosan with disodium octaborate tetrahydrate (TIM-BOR) which is one the most effective termiticidal wood preservatives, modified chitosan seems to perform better than TIM-BOR-treated wood in terms of weight loss of wood after termite exposure. TIM-BOR-treated wood exposed to *C. formosanus* for three weeks gave 100% mortality and wood weight loss of 8.4% (Grace *et al*. 1992) whereas 0.2% modified chitosan-treated wood gave a weight loss of 2.9% after 12 weeks exposure.

Conclusion

In this study, modification of chitosan to increase the number of ionizable amino groups on the backbone of chitosan was achieved. The rate of absorption and retention of modified and unmodified chitosan varied significantly. However, high absorption and retention do not correspond to higher resistance to termite attack. Compared with unmodified chitosan, modified chitosan showed higher resistance to termite attacks. More than 50% of the untreated wood samples were eaten up by termites while wood samples treated with 0.4%MC gave the lowest weight loss of 2.19% after 12 weeks of the graveyard test. The results showed that modified chitosan has a potential of increasing termite resistance of wood.

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