PHYSICOCHEMICALLY MODIFYING WOOD BY LOW ENERGY HYDROGEN ION SHOWER: AN ALTERNATIVE PLASMA-BASED ANTITERMITE METHOD

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Abstract. Blantocas et al (2007) reported that low-energy hydrogen ion shower (LEHIS) irradiation of wood produced inhibited flammability and surface inactivation of wood. In this study, pest control performance of LEHIS compared with conventional pesticide (pyrethroid toxin) was assessed. Subsequent statistical analyses indicated that LEHIS was equally as effective as pyrethroid toxin in arresting *microcerotermes losbañosensis* subterranean termite infestations. LEHIS functions not as a toxicant, but rather as a treatment that made wood unpalatable to infesters. LEHIS treatment smoothened wood exterior and decreased surface pore sizes restricting moisture penetration. The change rate constant k in the wetting model equation ($d\theta/dt = -k\theta$) fell two orders of magnitude from 0.25/s (initial $\theta = 25°$) for the control to 0.0019/s (initial $\theta = 60°$) for the treated sample. Hydrophobization was attributed to molecular reorientation resulting in loss of bonding sites for polar molecules. Fourier transform IR spectra showed that LEHIS treatment decreased absorption intensities of hydroxyls (O–H at 3360 cm^{-1}) and carbonyls (C=O at 1730 and 1647 cm^{-1}) suggesting the breakdown of hydrophilic components, in particular that of hemicellulose. With less moisture absorptive capacity, wood became less palatable to termites, thus inhibiting further decimations.

Keywords: Plasma, termites, FTIR, SEM, wetting model.

INTRODUCTION

In earlier studies (Blantocas et al 2006b, 2007; Ramos et al 2006), a plasma-based method was developed to modify wood surfaces making them more moisture-resistant and flame-retarding. It was demonstrated that after being exposed to low-energy hydrogen ion showers (LEHIS), irradiated surfaces exhibited inhibited combustibility and increased resistance to wetness, issues that are important in wood technology. There are, however, other concerns requiring similar special attention. For instance, wood products are subject to attacks from termites. If preventive measures are not taken, service life may be significantly decreased resulting in severe economic losses. The traditional approach in battling pests relied heavily on chemical substances. In some cases, their use involved long-term toxicity (Blaylock et al 1995; Al-Rahji 1990; Linnett 2008). However, during the last several years, more stringent regulatory measures have decreased the use of chemically based wood preservatives for antipest strategies. Nowadays, alternative methods are constantly being developed to provide wood preservatives that are environmentally benign and less toxic to humans yet effective against pests. LEHIS is believed to be one such method. Plasmas, from which LEHIS is extracted, are neither hazardous to humans nor destructive to the ecosystem. Hence, in this respect, it is superior to chemical treatment. The objective of this

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study is to ascertain if the LEHIS method can protect wood against termite decimations. Albizia (*Albizia lebbeck* [L.] benth.) wood was chosen as the test material for the study. Commonly known as "Woman's Tongue," this species is in the Fabaceae family. Its timber, which has a specific gravity of 0.55-0.66, is suited for construction, furniture, and veneer (Morton 1983; Brown 1997). Subterranean termites are soil inhabitants attacking wood in contact with the ground. Although these insects are important in the recycling of dead and decaying plant material, which serves to protect topsoil from erosion, they become biohazards when their appetite extends to human homes and building structures.

MATERIALS AND METHODS

Physical Experiment

Albizia wood samples were cut into equal blocks measuring $2 \times 2 \times 4$ cm^3 for the irradiation process. Samples underwent conditioning to obtain their constant weight. Conditioning involved sequential heating of samples until a specific minimum weight change was obtained. The processing facility consisted primarily of a reaction chamber about 2400 cm^3 in volume onto which a compact gas discharge ion source (GDIS) was attached. The GDIS had a negative focal strength capable of producing divergent ion showers. The generated beams were round, diffused, and homogenous, appropriate for surface modification of wood polymers. A 3-D illustration of the GDIS is shown in Fig 1. A detailed description of the GDIS is reported elsewhere (Blantocas et al 2006a; Salapare et al 2008, 2009). The facility was evacuated by a 16-m^3/h rotary pump up to a medium-level vacuum background. A schematic of the overall set-up is shown in Fig 2. Hydrogen feed was set at 3 mtorr gas-filling pressure. A potential difference of about 1 kV applied across the anode and cathode terminals of the GDIS ionized H_2 gas, ejecting a positively charged hydrogen ion shower out of the discharge region. Prior to the wood treatment process, beam diagnostics were done using a cast steel mass spectrometer (CSMS). The ejected beam was intercepted by the CSMS placed 80 mm downstream measured from the reaction chamber's entrance port. Automatic data acquisition routines stored and processed the detected signals. The design and operational characteristics of the CSMS were reported in an earlier article (Blantocas et al 2004).

During LEHIS irradiation, wooden blocks were held by a sample holder inside the reaction chamber positioned approximately in the same spot as the CSMS. Each side of the sample holder could accommodate one sample. The holder was rotatable and could run lengthwise allowing the exposed surface of each block to be directly irradiated for 15 min. Hence, only one surface of each sample was irradiated, and the rest of the surfaces were marked off as untreated. This way, two samples could be processed before breaking vacuum.

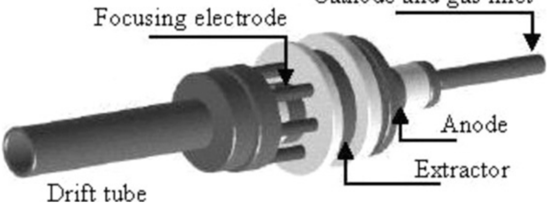


Figure 1. 3-D illustration of gas discharge ion source (GDIS).

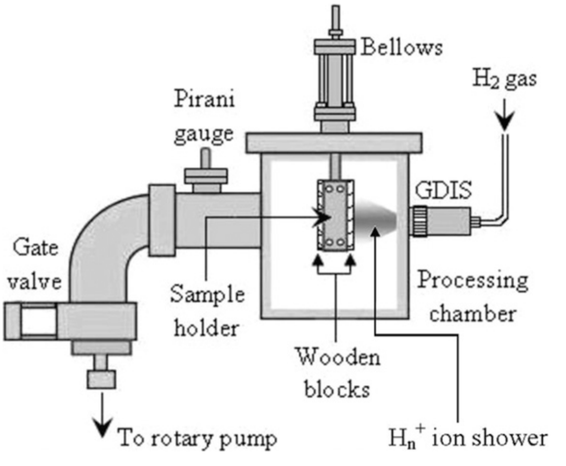


Figure 2. Schematic diagram of the overall facility.

The antitermite chemical used was a generic pyrethroid toxin with 37% active ingredient at ≈19 mL/L of water. Synthetic pyrethroid is highly lethal because it affects the nervous system of insects causing paralysis and death. All samples in the chemical treatment had only one surface coated to match the one-faced irradiation of LEHIS. The unadulterated surfaces were coated with paraffin to prevent entry of infesters through these sides.

A subterranean termite (*Microcerotermes losbañosensis*) nest was built using a vertically half-sawn drum placed on top of a steel stand. Then, a secondary termite nest extracted from a graveyard was implanted into the drum shown in Fig 3. The drum was filled almost to the brim with soil dug from the same spot where the secondary nest was taken. A U-shaped concrete foundation was provided around the nest. Six $5 \times 5 \times 15\text{-cm}^3$ *Anthocephalus chinensis* wood pieces were stuck into the soil between the secondary nest and the concrete to act as wood interceptors. As soon as termite tunnels occurred in the interceptors, wood samples were introduced randomly into the set-up arranged on top of the concrete structure. To satisfy the balanced fixed-effects model (Montgomery 2001), only one side of each wood sample was exposed to the infesters. The remaining five sides were coated heavily with paraffin to prevent infestation. Tunnel formation was observed weekly. The test was terminated at the end of 6 wks and quantified by means of observing percentage volume, surface damage, and overall appearance, representing the three response variables for subsequent statistical tests. Volume was measured using the volume–mass–density relationship. Surface damage was measured using a routine image processing program whereby five measurements were taken for each sample expressed as percentage average of the whole surface. Overall appearance was assessed by ocular inspection and quantified via an ordinal scale ranked according to the degree of damage as follows: 1) zero tunnel formation; 2) tunnel formation without damage; 3) tunnel formation with damage; and 4) heavily damaged.

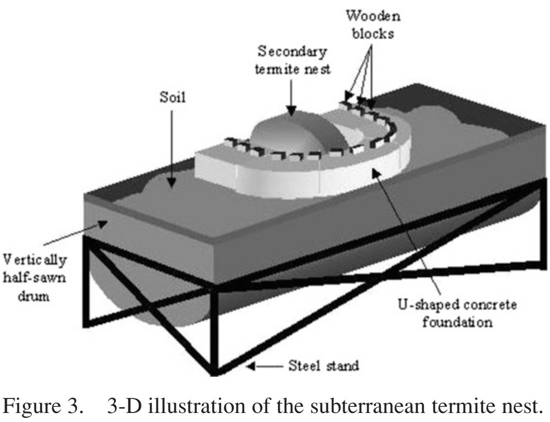


Figure 3. 3-D illustration of the subterranean termite nest.

In this study, the termite test did not fully conform to ASTM standards. ASTM and other established protocols were used only as models on which the parameters of interest such as sample dimensions and termite exposure time were based. Because of limited size of the plasma processing chamber, sample dimensions were scaled down in proportion with ASTM criteria. For this reason, the test had to be accelerated instead of lasting the usual half-year duration. It is believed that these slight deviations from standard methods did not lead to serious problems in the results.

Three characterization tests were performed on the wood samples: 1) wettability test or the sessile drop contact angle measurement using an Intel (Santa Clara, CA) Play QX3 Computer Microscope to investigate the wood's water sorption attributes; 2) scanning electron microscopy using Dual Beam Versa 3D SEM-FIB (FEI Corporation, Hillsboro, OR) to extract surface topographical information; and 3) Fourier transform IR (FTIR) spectroscopy using a Shimadzu (Columbia, MD) Prestige 21 FTIR spectrophotometer and Pike Technologies (Madison, WI) Miracle Single Reflectance ATR to identify chemical constituents of the wood pre- and post-LEHIS treatment. In the wettability test, absorption of a water droplet by a particular sample is recorded at a rate of one frame every 5 s. For each sample, time evolution of the contact angle is recorded at three different sites. Hence, the contact angle for a single timeframe is actually a mean value averaged across three different points on the sample. Because of the danger of contaminating the characterization equipment, wood substrates treated with pyrethroid toxin were not characterized.

Statistical Experiment

The experiment was conducted to evaluate effectiveness of LEHIS against termite attack. This was done using three treatment levels or methods; first LEHIS (L), second chemical (C), and last no treatment (U), which served as the control in which samples were left untreated. Statistical comparison of responses to termite infestations for each of these three treatment levels was made. Thus, a completely randomized, balanced fixed-effects model was considered in which, for each treatment level, there were five LEHIS-treated replicates, five chemically treated replicates, and five untreated replicates (control) for a total of 15 samples. A standard statistical package was used to perform all statistical runs. To ensure objectivity and precision in the statistical interpretation, conclusions of ANOVA were crosschecked through a blanket application of its nonparametric counterpart, the Kruskal-Wallis test (KWT). KWT is advantageous in that it is insensitive to distributional assumptions and is appropriate for ordinal data (the response variable labeled overall appearance). This particular data set was incompatible with ANOVA. Conclusions regarding the efficacy of LEHIS were reached through joint examination of post hoc results and average values of response variables.

RESULTS AND DISCUSSION

Statistical Results

Figure 4 shows photographs of actual physical degradations caused by termites. Table 1 summarizes raw data indicating average values of response variables across all treatment groups (ie percentage surface damage, percentage volume damage, and overall appearance). Table 2 summarizes outcomes of ANOVA and KWT, respectively. Interestingly, results for both tests were similar except for surface damage, which was significant at the 6% level for KWT (not at 5% as in ANOVA). *p* value was slightly greater than default. Nonetheless,

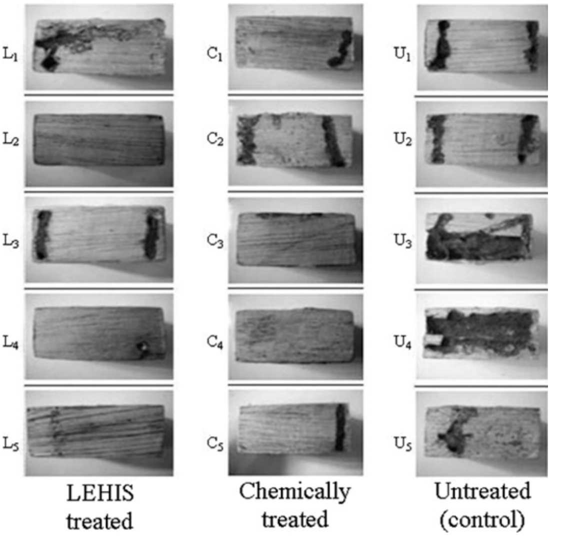


Figure 4. Actual decimations from termites on wood samples. Left column is low-energy hydrogen ion shower-treated, middle column is chemically (pyrethroid toxin) treated, and right column is untreated (control).

Table 1. Raw data and their equivalent codes.

Group[a]	Replicate (sample)	Surface damage (%)	Volume damage (%)	Overall appearance[b]
L	L1	30	15	3
L	L2	0	0	1
L	L3	10	2	3
L	L4	2	0	2
L	L5	0	0	2
C	C1	0	0	2
C	C2	25	2	3
C	C3	0	0	2
C	C4	0	0	1
C	C5	5	0	2
U	U1	20	10	3
U	U2	20	5	3
U	U3	70	30	4
U	U4	90	85	4
U	U5	20	5	3

[a] L, Low-energy hydrogen ion shower (LEHIS) treated; C, chemically treated (using generic pyrethroid toxin); U, untreated or control.

[b] Overall appearance was assessed by ocular inspection and quantified via an ordinal scale ranked according to degree of damage as follows: 1, zero tunnel formation; 2, tunnel formation without damage; 3, tunnel formation with damage; 4, heavily damaged.

the significance level provided 94% likelihood that samples were in fact affected by the treatment processes.

All p values were below or about equal to 0.05 ($p = 0.055$ for surface damage based on KWT). Hence, there was at least one treatment group that was significantly different from the other two. Table 3 shows the summary results of the post hoc analyses. Duncan's multiple range test and KWT pairwise comparison procedures corroborated each other's findings. LEHIS is found to be equally as effective as pyrethroid toxin in minimizing termite attacks, ie responses to both the chemical and LEHIS were statistically similar. As insecticides, both were superior to no treatment. This finding was true for all three measurements: percentage surface damage, percentage volume damage, and overall appearance. However, LEHIS is better than chemical treatment in that the former provides protection without the use of any toxicant. Dead termites were present on the chemically coated wood samples but were absent on the LEHIS-treated ones. This indicated that LEHIS did not act by killing but rather the process possibly made the test blocks unpalatable. This is attributed to the physicochemical modifications brought about by the irradiation process.

Physical Results

The mass spectrum of LEHIS is shown in Fig 5 indicating the presence of charged particles H^+ and H_2^+. Apparently, irradiation of H_n^+ ions triggered morphological and chemical changes in the treated wood. Physical changes can be seen in the electron micrographs of Fig 6 in which treated samples had much less surface voids than the control. Changes in chemical composition can be seen in the FTIR spectra of Fig 7. Interaction between H_n^+ ions and wood surface resulted in formation of intramolecular hydrogen bonds between polysaccharides and cellulose (Blantocas et al 2006b). The bonding in turn enhanced wood surface binding manifested 1) physically in microhole closure

Table 2. Summary results of the one-way ANOVA and the Kruskal-Wallis test.

One-way ANOVA			
Measurement	Response variable	Probability value (p value)	Statistical result
Percent surface damage	Logarithmically transformed data	< 0.05	Significant
Percent volume damage	Square root transformed data	< 0.05	Significant
Kruskal-Wallis Test			
Measurement	Response variable	Probability value (p value)	Statistical result
Percent surface damage	Untransformed data	0.0554	Significant at 6% level
Percent volume damage	Untransformed data	< 0.05	Significant
Overall appearance	Untransformed data (categorical data)	< 0.05	Significant

Table 3. Post hoc comparisons of statistical tests.[a]

Measurement	Response variable	DMRT: comparison procedure for ANOVA	Kruskal Wallis pairwise test: comparison procedure for KWT
Percent surface damage	Untransformed data (subjected to KWT)		$L = C \neq U$
	Logarithmically transformed data (subjected to ANOVA)	$L = C \neq U$	
Percent volume damage	Untransformed data (subjected to KWT)		$L = C \neq U$
	Square root transformed data (subjected to ANOVA)	$L = C \neq U$	
Overall appearance	Untransformed data (categorical data, (subjected to KWT)		$L = C \neq U$

[a] LEHIS was found to be equally as effective as pyrethroid toxin in minimizing termite attacks (L = C).
DMRT = Duncan's multiple range test; KWT = Kruskal-Wallis test.

and smoothing of specimen exterior; and 2) chemically in strengthening of C–O bonds of cellulose at 1160 and 1051 cm^{-1}.

Treated samples also became hydrophobic. Contact angle measurements as a function of time for the control and LEHIS-treated samples are shown in Fig 8. Wettability is quantified via a wetting model wherein the contact angle's time rate equation was numerically solved and fitted onto experimental data (Blantocas et al 2006b; Salapare et al 2008). The model is expressed mathematically as:

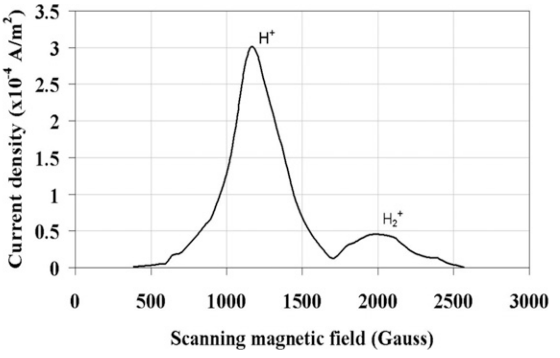
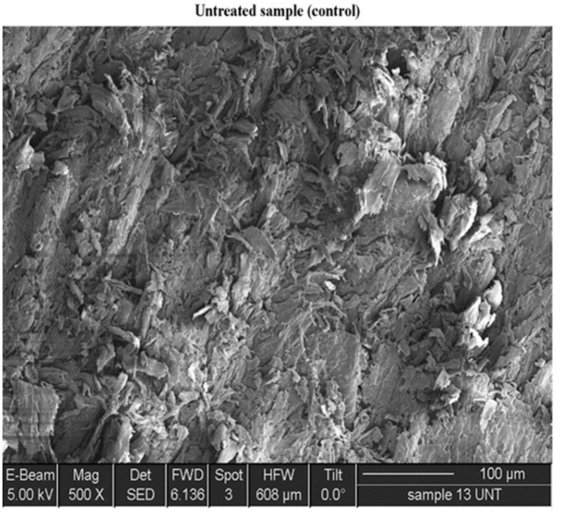


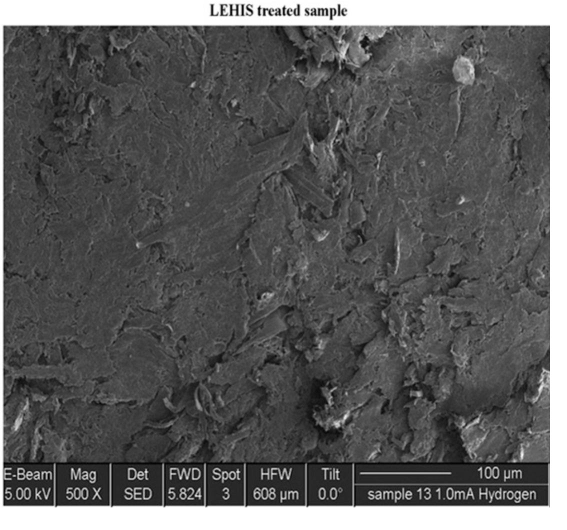
Figure 5. Typical mass spectrum of low-energy hydrogen ion shower. The ion shower consists of H^+ and $H_2{}^+$ ions.

$$d\theta/dt = -k\theta \tag{1}$$

where θ is the contact angle between the supporting solid surface and the tangent to the drop shape of the liquid, and k is the change rate constant or the amount that describes the angle's temporal recession in units of per second. Falling values of k signify decreasing surface wettability. The value of k decreased from 0.25/s to 0.0019/s, which is proof of hydrophobization and decreased hygroscopicity. The effect can be attributed to chemical changes. There was distinct weakening in absorption intensities of polar groups, namely hydroxyls (O–H at 3360 cm^{-1}) and carbonyls (C=O at 1730 and 1647 cm^{-1}) and the C–H stretching mode at 2947 cm^{-1}. Possibly, the irradiation gave rise to molecular substitutions, weakening polar and hydrogen-bonded groups. This in turn decreased moisture affinity, which explains the hydrophobic behavior. Thus, the two concurrent responses of wood to LEHIS application, which were hydrophobization and surface smoothing (decreased surface pores), made the treated wood less inclined to absorb ambient moisture. Loss of water sorption capacity rendered the treated wood unappetizing to termites



(a)



(b)

Figure 6. Typical scanning electron micrographs (5 kV, 500× magnification) of the (a) untreated and (b) low-energy hydrogen ion shower (LEHIS)-treated samples. LEHIS irradiation caused the pores and voids on the surfaces to close.

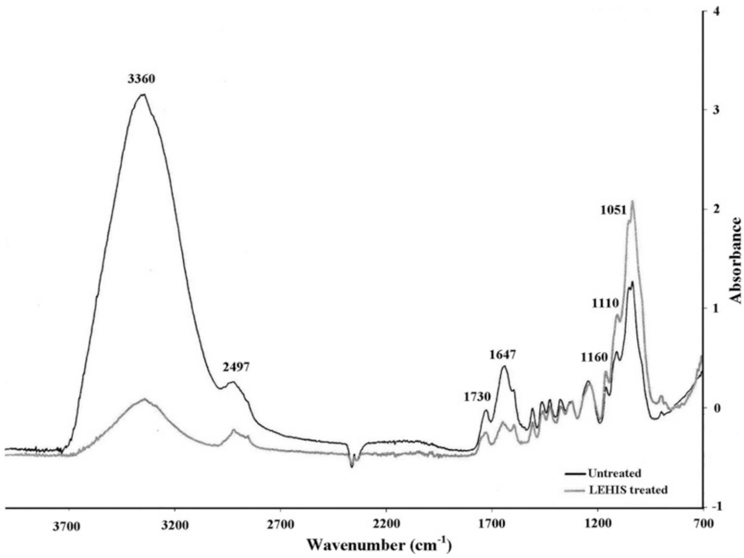


Figure 7. Fourier transform spectra of both control and treated specimens. Treated specimen shows weakening of the polar groups, thus exhibiting enhanced hydrophobic property.

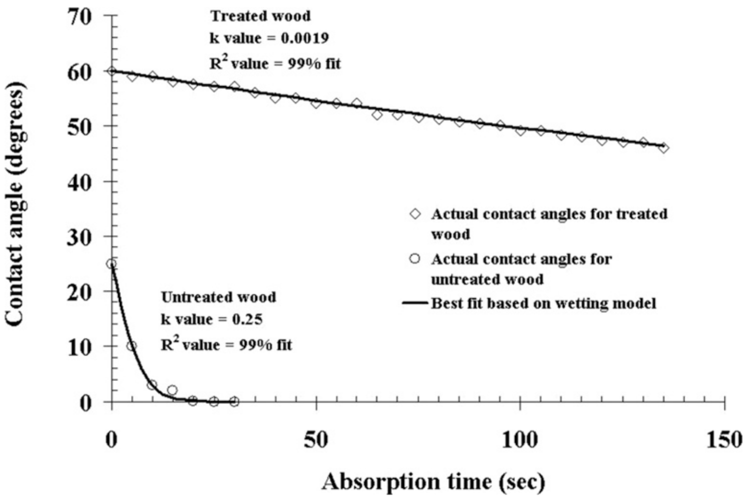


Figure 8. Numerical constructs of $d\theta/dt = -k\theta$ (wetting model) fitted against empirical data. The time rate equation of the wetting model is made to fit actual contact angle data of treated and untreated wood samples. Low-energy hydrogen ion shower-treated sample shows lower k value compared with control. Lower k values denote longer moisture absorption time.

because these infesters demand moisture for survival.

CONCLUSIONS

ANOVA backed up by KWT was used to assess the possibility of LEHIS as a pest control method. The investigation showed it to be efficacious against subterranean termites. Their survival on the irradiated wooden blocks showed that LEHIS did not function as a toxicant but rather possibly made the test blocks unpalatable to the infesters. These results are attributable to physicochemical modifications brought about by the irradiation process. The smoothing of the wood surface seen in the electron micrographs may have retarded the termites' tunneling activity. FTIR spectra showed that LEHIS treatment decreased the absorption intensities in the high-energy stretching region (polar groups) but increased C–O bonds near the low-energy fingerprint region. This is interpreted as decreased moisture sorption capacity caused by loss of bonding sites for polar molecules (Sernek 2002; Guruvenket et al 2003). Increased water repellency suggests breakdown of hydrophilic components, particularly hemicellulose. Having lower affinity for water, LEHIS-treated wood became less palatable to termites, which inhibited further decimations.

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