SPECTROSCOPY AND ROCKWELL HARDNESS TO CHARACTERIZE THE DETERIORATION OF WOOD TREATED WITH NATURAL PRODUCT

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Resumo

Espectroscopia e dureza Rockwell para caracterizar a deterioração da madeira tratada com produto natural. O presente estudo teve como objetivo utilizar a dureza Rockwell e espectroscopia para caracterizar a deterioração da madeira com tratamento convencional e natural. Para tal, cinco árvores de acácia foram utilizadas para a confecção de 70 amostras, sendo 20 para tratamentos com tanino, 10 para tratamento com mistura de Borato de Cobre Cromatado (CCB), 10 para posterior avaliação da resistência natural da madeira ao fungo e 30 controles não expostos. Os corpos de prova destinados aos tratamentos preservativos foram impregnados com as soluções utilizando o método de pressão de célula cheia em autoclave. Em seguida, as amostras foram expostas ao fungo *Pycnoporus sanguineus* por 16 semanas, por meio de ensaio de apodrecimento acelerado. Passado o período do ensaio, a deterioração foi avaliada pela espectroscopia e dureza Rockwell. A mistura CCB foi a mais adequada para preservar a dureza da madeira, seguida dos tratamentos com 10 e 5% de tanino, todos os tratamentos apresentaram valores similares indicando que produziram efeitos semelhantes. A análise por espectroscopia no infravermelho médio indicou que o material tratado com 5 e 10% de tanino apresentou a maior similaridade com os espectros das amostras controle.
Palavras-chave: biodeterioração, espectroscopia FTIR, qualidade da madeira, fungo podridão branca.

Abstract

The objective of study was to characterize wood deterioration in samples with conventional and natural treatments using Rockwell hardness and spectroscopy. Five acacia trees were used to make 70 samples, of which 20 were treated with tannin and 10 with a Copper Chrome Borate mixture (CCB), while 10 samples exposed to fungus received no treatment and 30 were used as unexposed controls. The specimens for preservative treatments were saturated with the solutions, using full cell pressure in autoclave. Shortly after the treatment, the samples were exposed to *Pycnoporus sanguineus* for 16 weeks, using the accelerated rot test. Then, deterioration was evaluated by spectroscopy and Rockwell hardness. CCB was the most suitable to preserve wood hardness, followed by treatments with 10 and 5% of tannin, and all treatments presented similar values indicating they produced similar effects. Medium infrared spectroscopy analysis indicated that the material treated with 5 and 10% tannin showed the greatest similarity to the spectra from control samples.
Key words: biodeterioration, FTIR spectroscopy, wood quality, white rot fungi.

INTRODUCTION

Wood is a valued material for its mechanic and aesthetic characteristics, which are suitable for several purposes. Because it is an organic material, it is prone to attacks of wood-deteriorating organisms and this characteristic, as a downside, makes it a disposable material. Due to environmental concern arising from the extraction of wood from native forests for raw material, planted forests stand out for their quality products and because they help to avoid depletion of natural forests (VIDAL; HORA, 2011).

Vidaurre *et al*. (2011) point out that even though they are renewable, planted forests are a limited resource that require a rational strategy based on sustainable yield. For this to happen, it is essential to preserve the raw wood in order to extend its shelf life. According to Poubel *et al*. (2013), one of the greatest challenges for research in wood technology has been to find solutions for natural wood durability. In this context, wood preservatives that cause less damage to the environment and other living beings have attracted the attention of researchers, including the use of botanical extracts as an alternative to traditional preservatives.

Some tree species have natural resistance to several decomposer organisms, related to the presence of extractives in their wood (SMEDS *et al*., 2011). Among them, tannin, a polymeric phenolic compound of plant secondary metabolism, naturally serves as a defense against microorganisms. Because of this, it is understood that compounds such as tannin can extend the useful life of wood (YAO *et al.*, 2010; MAKINO *et al*., 2011).

It is known that wood under attack by fungi shows alterations in the chemical composition and natural color, in addition to decreased mechanical resistance, mass, calorific yield and acoustic capability and increased permeability, flammability and proneness to insect attacks, which lowers its quality and makes it less suitable for technological purposes (GOSH *et al*., 2012).

Two parameters used to evaluate wood deterioration and its consequent alterations are Rockwell hardness and Fourier-Transform Infrared Spectroscopy (FTIR). Rockwell hardness is a direct measurement of hardness and is considered an advantageous method because of its high accuracy (STANGERLIN *et al*., 2013), while FTIR is based on molecular bond vibrations induced by infrared radiation (TRAORÉ *et al*., 2016). Both are important tools to examine the loss of mechanical resistance and the alterations in the chemical structure of organic materials after deterioration by decomposing fungi (XU *et al*., 2013). In this context, under the hypothesis that tannic extract preserves the natural characteristics of wood when compared to treatment with commonly used substances, in addition to presenting similar protective properties, the present study aimed to use Rockwell hardness and spectroscopy to characterize wood deterioration in conventionally and naturally treated wood.

MATERIAL AND METHODS

The wood and the natural extract of black wattle used for this study were obtained from the company Sociedade Extrativa Tanino de Acácia (SETA S.A.) and the selection of trees was based on the standard of the American Society for Testing and Materials, ASTM - D5536-94 (2010). The colony of white-rot fungi, *Pycnoporus sanguineus*, was obtained from the Sector of Wood Biodegradation and Preservation- LPF/ IBAMA.

The two first wood logs of five *Acacia mearnsii* trees produced 30 discs, which were removed lengthwise and used to make the samples in accordance with the American Society for Testing and Materials - standard ASTM 2017 (2005).

A total of 70 samples were produced, 20 of which were used for preservative treatment with tannin (at concentrations of 5 and 10%), 10 for treatment with Copper Chrome Borate (CCB) and 10 for posterior evaluation of the natural resistance of wood (without treatment). From the remainder, 30 samples were not exposed to the fungus (higher witness).

After being sanded, selected and conditioned, the samples were submitted to the following treatments: T1 (5% concentrated tannin solution); T2 (10% concentrated tannin); and T3 (2.5% CCB mixture), utilizing the method of pressuring the full cell in autoclave, with an initial vacuum of 15 minutes, followed by a 60-minute period of pressure. No preservative treatment was used for T0 (lower witness) and for the control samples, to evaluate the natural resistance and properties of the wood not exposed to rot.

After treatment, the samples were exposed to the *Pycnoporus sanguineus* fungus for 16 weeks, by means of accelerated rot according to the recommendations of the American Society for Testing and Materials - ASTM 2017 (2005). After the test, deterioration of the samples was evaluated using mechanical and chemical parameters.

Rockwell hardness

The mechanical characteristics of the deteriorated samples were evaluated using equipment with a 1/4-inch spherical penetrator to measure hardness. The testing load was applied to the transversal sector (2.5 x 2.5 cm) at two different stages. First, a preload of 10 kgf was applied, followed by the final test load of 60 kgf. At three separate points, Rockwell hardness was read directly from the analogical display.

A randomized experimental design was used, with five treatments and 10 repetitions. The results were compared by orthogonal contrasts at a 5% level of significance.

Analysis of alterations in chemical parameters

Chemical alterations were determined using FTIR spectroscopy. The infrared absorption spectra were obtained with an IR Prestige 21 Shimadzu spectrophotometer, using the KBr pellet method. For each sample, 45 scans were performed with a resolution of 4 cm^{-1} at a range between 700 and 2000 cm^{-1}, where the mean of theses scans corresponded to a spectrum. The original spectra were manipulated with noise reduction and baseline adjustment.

RESULTS

Because the treatments presented significant variation for Rockwell Hardness, the means were compared by orthogonal contrasts. Table 1 shows that all contrasts were significant by the t test at 5% significance.

Table 1. Orthogonal contrasts from the Rockwell hardness test.
Tabela 1. Contrastes ortogonais para o teste de dureza de Rockwell.

Contrast	Hardness (H_{RM})	
	Mean x Mean	**Variation**
Lower Witness x T1*	84.47 x 90.67	-6.2
Lower Witness x T2*	84.47 x 91.61	-7.14
Lower Witness x T3*	84.47 x 92.04	-7.57
L. Witness x H. Witness*	84.47 x 94.43	-9.96
Higher Witness x T1*	94.43 x 90.67	3.76
Higher Witness x T2*	94.43 x 91.61	2.82
Higher Witness x T3*	94.43 x 92.04	2.39

T1 – treatment with 5% tannin; T2 – treatment with 10% tannin; T3 – treatment with CCB mixture; Lower Witness – wood without preservative; Higher Witness – control sample, without treatment or exposure; * Significant by the t test at 5%.

In the comparison between higher and lower witnesses, the degree of hardness decreased by around 10% after exposure to the fungus, showing the effect of decomposition on hardness.

In the analysis of preservative treatment performance, the CCB mixture (T3) was the most suitable to preserve hardness, followed by treatments T2 and T1. It is important to highlight that this chemical mixture is already marketed for wood preservation and the similar values found in the treatments utilizing tannin indicate its similar efficiency and the consequent potential for introducing this natural product.

The FTIR absorption spectra (Figure 1), in addition to a quantitative analysis, also provides a qualitative evaluation of the chemical alterations of wood attacked by the xylophagous fungus, as it identifies the altered constituents. The bands characteristic of wood, as reported in the literature, were used to interpret these constituents.

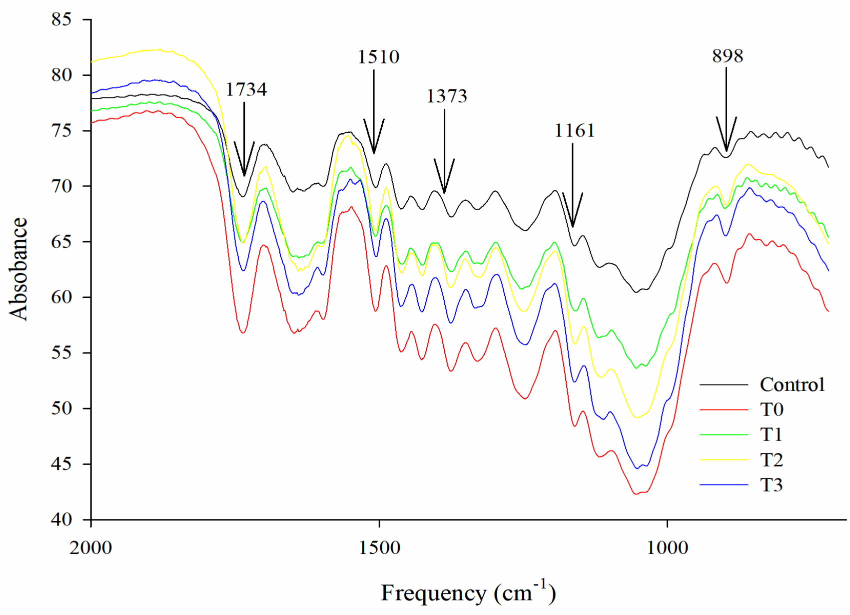

Figure 1. Absorption spectra by spectroscopy in the infrared region (FTIR). Each prominent spectral band represents a main constituent of wood affected by the deterioration caused by *Pycnoporus sanguineus* fungi.
Figura 1. Espectro de absorção por espectroscopia na região do infravermelho (FTIR). Cada banda espectral proeminente representa um constituinte da madeira afetado pela deterioração causada pelo fungo *Pycnoporus sanguineus*.

DISCUSSION

In line with the results of this study, reduced wood hardness was also shown by Bari *et al*. (2015), who tested the species *Fagus sylvatica* and reported that an extended period of exposure to white rot fungi resulted in the loss of 32% to 95% of this property. Rockwell hardness was found to be an important parameter to evaluate attacks by xylophagous fungi, because it is sensitive to changes from the early stages (STANGERLIN *et al*., 2013). The same author noted that this sensitivity may make it more efficient in the determination of wood deterioration than in the determination of mass loss, for which it is commonly used.

The toxicity of the tannic extract to *Pycnoporus sanguineus* fungi was reported by Silveira *et al*. (2017), who showed that the addition of the extract reduced mycelial growth of the fungi in tests in culture medium. This corroborates with the present study, as samples treated with tannin presented increased preservation. The close values between T2 and T3 demonstrate the similar performance between treatment with the natural product and the chemical mixture. From an environmental and social point of view, use of the natural product tannin would be beneficial as it is less toxic to the environment and easy to handle.

The distribution of bands of structural components of wood has been shown by previous studies (PANDEY; PITMAN, 2003; ZHANG *et al*., 2007): 1734 cm $^{-1}$ for uncoupled -C-O- in hemicellulose; 1510 cm^{-1} for the aromatic skeleton in lignin; 1373 cm^{-1} for C-H deformation in cellulose and hemicellulose; 1161 cm^{-1} for C-O-C vibration in cellulose and hemicellulose; and 898 cm $^{-1}$ for C-H deformation in cellulose. The results of this study show differences between the treatments, indicating decreased absorption in the bands of interest after the material is exposed, in addition to presenting a positive effect on absorption for the natural treatments.

Samples of biodegraded wood present decreases in the bands linked to a strong absorption of -C-O- present in polysaccharides (FERRAZ *et al*., 2000), a situation that occurs because of the consumption of the xylophagous fungi. Another effect of the process of biodeterioration by rot fungi is the reduction of crystallinity of the cellulose (POPESCU *et al*., 2016), lowering the chemical quality of the wood. According to Darwish *et al.* (2013), the formation of aldehyde groups resulting from the hydrolysis of the bonds in two glucopyranose rings causes a variation in intensity in the band of hemicellulose. Pandey and Pitman (2003) reported that the variation in the intensities of lignin-related bands is associated with the metabolism of carbohydrates, and not with the content of this chemical composite. In this sense, Darwish *et al*. (2013) reported that reduced absorption in the lignin band indicates that a depolymerization process has occurred, indicating degradation of lignin and cellulose. Alterations in wood components were also observed from variations of intensity of the bands of carbonyl and carboxyl groups formed from cellulose, associated with the aliphatic chain of lignin. This may be related to the fact that wood loses mass during degradation of its main components (POZO *et al*., 2016), which also leads to the reduction of chemical constituents in the wood.

Due to the food preference of the xylophagous fungi, it is possible to verify changes in the band attributed to lignin (1510 cm^{-1}) (PANDEY; PITMAN, 2003; POPESCU *et al*., 2010a; POPESCU *et al*., 2010b; POPESCU *et al*., 2013). In this band, a drop in absorption intensity was observed after the exposure period. There were variations in the intensity of the bands attributed to the carbonyl and carbohydrate / lignin components, also confirmed by Popescu *et al*., 2016. The FTIR analysis showed that the reduction in the absorption of the lignin bands was lower than in those of carbohydrates (NAZARPOUR *et al*., 2013), as a result of deterioration.

The spectra showed the influence of the treatments on the chemical components of the wood. The intensity of bands of interest generally decreased after exposure and the witness presented the greatest decrease. The material treated with 5 and 10% tannin presented spectra closest to those of control samples, followed by the CCB treatment.

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CONCLUSION

- The Rockwell hardness evaluation showed that the performance of tannic extract was similar to that of CCB mixture in the protection of wood from the *Pycnoporus sanguineus* white rot fungi.
- The FTIR spectroscopy analysis showed decreases in the absorption spectra, indicating alterations in the main components of wood after exposure. The treatments that presented results closest to those of undeteriorated wood were T1 (5% tannin solution), T2 (10% tannin solution) and T3 (2.5% CCB mixture), respectively, highlighting the positive effect of the natural tannin treatment.

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