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Influence of gamma radiation on properties of common Brazilian wood species used in artwork

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ABSTRACT

Woods, as other materials, are susceptible to alterations in their internal structure because of physical, chemical or biological agents. Wood can be considered a natural composite with high strength capacity provided by cellulose and hemicellulose agglutinated by lignin, substances with very distinct structures. In several applications, the use of radiation can be interesting, once it turns wood more resistant to biological demand. The application of gamma radiation in work of arts and archeological artifacts preservation began in 1970, in France. By other side, no changes in wood properties were desirable. Gamma radiation from a cobalt-60 source usually is applied as a tool to the decontamination of insects and microorganisms, as well as to provide resins cure in impregnated wood. In this way, the aim of this paper is to evaluate gamma radiation effects on some physical, thermal and mechanical properties of Brazilian wood species used in carving, as Cedro-Rosa (*Cedrella fissilis*) and *Imbuia* (*Ocotea porosa*). Gamma radiation influences were detected in the studied wood properties in the dose range applied This is a relevant conclusion that will improve safety on arts conservation around the world.

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1. Introduction

Wood species have had major roles in many ancient and modern cultures due to the possibility of manufacturing furniture, sculptures and pieces of art, which can be found especially in churches, such as paintings, altar decorations, frames and others (Mendes and Baptista, 2005).

Essentially, the wood fibers are composed of cellulose and lignin. As cited by Zickler et al. (2007), the crystalline cellulose microfibrils represent the fiber reinforcement and the amorphous hemicelluloses and lignin represent the composite matrix.

The elementary cellulose microfibrils are aligned parallel to each other and wind around the wood cell in a helical manner at a characteristic microfibril angle with respect to the cell axis. Two polymorphs of cellulose I exist, triclinic cellulose I α and monoclinic cellulose I β . Cellulose produced by primitive organisms were said to have the I α component dominant, while those produced by the higher plants have the I β form dominant (Zickler et al., 2007).

Native lignin is an amorphous, three-dimensional copolymer of phenylpropanoid units linked through ether and carbon–carbon

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bonds (Mao et al., 2006; Alves et al., 2006). It provides mechanical support for plants, as well as facilitating transport of nutrients and providing defense against attack from microorganisms due to, as discussed by Lawako et al. (2006), covalent linkages between lignin and carbohydrates in native lignin in spruce (*Picea abies L.*) wood.

Besides the content of lignin, the degree of resistance is greatly dependent on the quality and quantity of extractives in wood (Kollmann and Cõté, 1986). As described by van Beek et al. (2007), these constituents are basically resin acids, free fatty acids, sterols, triglycerides and sterol esters, which are present in small concentrations (1-3% wt.).

Besides the extractives, there are other factors that contribute to increase the natural resistance of wood, such as shape, size and arrangement of the cells (anisotropy) (Green et al., 1999; Fengel and Wegner, 1989). There are also some important differences between the cell wall structures of hardwoods and softwoods. Native softwood tracheid tend to be longer (3–4 mm) than hardwood tracheids (0.5–1.5 mm), as well as somewhat wider (35 μ m vs 20 μ m, respectively) (Beck-Candanedo et al., 2005).

Xu et al. (2006) investigated, by means of dual-axis electron tomography, the cell walls of radiata pine early wood, and noticed that individual cellulose microfibrils measure 3.2 nm in diameter, and appear to consist of a 2.2 nm unstained core and a 0.5 nm thick surface layer that is lightly stained. Both individual and clustered



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cellulose microfibrils are seen surrounded by more heavily stained and irregularly shaped residual lignin and hemicellulose.

In Brazil, the specie *Cedrella fissilis* (locally denominated as *cedro-rosa*) has great economical importance because of its huge application in furniture, naval and aerospatiale industries. It can be generally found at southeast Brazil in Atlantic-pluvial forest regions (Xavier et al., 2003; Munhoz and Amaral, 2007). Another wood greatly used for luxury furniture and civil construction is *Ocotea porosa* (regionally known as *Imbuia*), which is a plant largely found at southern Brazil and it can reach 30 m height (Tonin and Perez, 2006; Rego et al., 2008).

Wood, as well as all other materials, are able to undergo modifications that occur over time with varying pace (Panshin and de Zeeuw, 1980). These changes are produced by physical, chemical or biological agents (Fengel and Wegner, 1989). The climate of some tropical countries which present both high temperature and air relative humidity, like Brazil, encourages the development of insects, termites, fungi and microorganisms that attack and deteriorate trees and wood made artifacts, as well as derivative materials such as paper. Silva et al. (2006) said that fungi are able to hydrolyse a wide variety of polymers, including cellulose, as a result of their efficient degradative enzymes.

In this context, some studies have been performed to evaluate the use of ionizing radiation in the recovery and preservation of wood-made art works. This process has been highlighted since 1970's when the gamma rays were applied to the destruction of living organisms present in woods without radioactive waste production. Moreover, gamma radiation from ⁶⁰Co can be used to cure resins that are impregnated into wood pieces to keep its form (Rizzo et al., 2002; Severiano et al., 2008).

Gamma radiation as sterilizing treatment direct damages DNA cells through ionization, inducing mutation, single and double strand DNA breakages, and even the death of the cell. This effect is a result of radiolysis of cellular water which generates active oxygen species, free radicals and peroxides (Silva et al., 2006).

Gamma rays, electromagnetic waves with high penetrating power, pass through materials without leaving any residue (Haji-Saedi et al., 2007). Fungi have been successfully inactivated from different materials, such as paper, wood and soil with radiation doses ranging from 6 to 15 kGy. However, in a Brazilian study some fungi from books could not be completely eliminated after irradiation with doses of 20 kGy (Tomazello and Wiendl, 1995).

The insect infestation control can be performed by submitting wooden objects to lower radiation doses, e.g. 0.2–0.5 kGy whereas the fungi and microorganisms infestation can be prevented by doses of 3–8 kGy and 15–20 kGy, respectively (Magaudda, 2004). It is asserted to mention that irradiation technique for disinfestation of cultural heritages, frames and wooden-made artifacts has shown to be very efficient but this process does not protect the material to a re-infestation (Cutrubinis et al., 2008).

By this way, this work aims to investigate the effects of gamma radiation on disinfestation and decontamination processes of *C. fissilis (cedro-rosa)* and *O. porosa (imbuia)* by accompanying their thermal and mechanical properties.

2. Materials and methods

2.1. Sample preparation

Samples of *C. fissilis* and *O. porosa* were prepared according to standard NBR ABNT 7190, Annex B Associação Brasileira de Normas Técnicas, 1997 for the compression parallel to the grain. For thermal analysis, each wood was cut in several pieces in order to obtain homogeneous samples.

2.2. Irradiation

The samples were irradiated in a multipurpose irradiator by gamma rays from Co-60 source at a dose rate of 10 kGy h^{-1} , and absorbed doses of 25 kGy, 50 kGy and 100 kGy. These doses were considered because gamma radiation is a very effective treatment for recovering biodeteriorated artifacts (Association for Advancement of Medical Instrumentation, 1994) for the first time or after a re-infestation (doses are cumulative in materials). This irradiator is located at Centro de Tecnologia das Radiações (CTR/IPEN/CNEN-SP).

2.3. Thermogravimetry (TG) and derivative thermogravimetry (DTG)

The thermogravimetry was performed using a TGA50, Shimadzu Co. TG results were obtained applying mass samples of around 5 mg, heating rate of 10 °C min⁻¹ from room temperature up to 700 °C, in dynamic atmosphere of compressed dry air with flow rate of 50 mL min⁻¹.

2.4. Mechanical tests

The compression tests of the parallel fibers were performed in equipment for universal testing machine, AMSLER. The samples were subjected to different loads to verify the limits of resistance for different wood species. The strength is calculated by:

$$f_{c0} = \frac{F_{c0}, \max}{A}$$

where F_{c0} , Máx is the applied force for rupture and A is the cross section area.

3. Results and discussion

Table 1 presents the average values for tensile strength at break for compression parallel to the fibers of samples of *imbuia* (*O. porosa*) and *cedro-rosa* (*C. fissilis*) with different radiation doses: 0 kGy, 25 kGy, 50 kGy and 100 kGy.

By Table 1, it can be seen a similar mechanical behavior when different irradiation doses were applied to the samples of *imbuia* and *cedro-rosa*, although the latter can be considered softer than the former. As described by Rocco Lahr (1990), the variability on properties of different wood species is due to the growing and physiology of the trees, their biological classification and to some micro and macro aspects.

Twenty-five kGy-irradiated samples showed an increasing of 2% on the tensile strength at break average values when compared to the non-irradiated *imbuia* samples (Table 1). Moreover, the same results were observed to *cedro*-rosa irradiated samples. By this way, neither higher dose (100 kGy) nor lower dose (25 kGy) in the studied dose range has meaningfully modified the mechanical properties of the studied wood species.

Table 1

Average values of tensile strength at break for irradiated and non-irradiated *Imbuia* and *Cedro-rosa* samples.

| Radiation dose (kGy) | Strength (MPa) | Strength (MPa) | |
|----------------------|----------------------------------|----------------------------------|--|
| | Imbuia | Cedro-rosa | |
| 0 | 51.5 ± 1.0 | 31.2 ± 0.4 | |
| 25 | $52,4\pm1.6$ | $\textbf{32.6} \pm \textbf{0.3}$ | |
| 50 | 50.6 ± 4.4 | $\textbf{31.9} \pm \textbf{0.6}$ | |
| 100 | $\textbf{50.7} \pm \textbf{1.1}$ | 31.2 ± 0.9 | |



Fig. 1. TG/DTG curve for non-irradiated Imbuia.

These results are corroborated by Magaudda (2004) because the longer are irradiation time and irradiation doses, the greater is the possibility for oxygen in air interacts with radicals originated from material irradiation processes. Although the moisture, weather and other factors had interfered on the mechanical properties of woods, it is possible to observe no meaningful alterations on the reproducibility of the performed tests for the different irradiation doses.

The TG data allow the quantitative determination of main components of the two wood species studied. Figs. 1–6 and Table 2 and Table 3 show TG/DTG curves of samples of *imbuia* (*O. porosa*) and *cedro-rosa* (*C. fissilis*) non-irradiated and submitted to different irradiation doses of 25 kGy, 50 kGy and 100 kGy.

In all TG curves, the first weight loss step refers to volatile components of the samples. The second one (around $150 \degree C-430 \degree C$) corresponds to cellulose weight loss and the third step (starting around 430 $\degree C$) is attributed to lignin thermal decomposition (Campanella et al., 1991).

The data from Table 2 and Table 3 allow to observe that ratio between cellulose: lignin is higher for *cedro-rosa* than for *imbuia*, which agree with the evaluated mechanical properties and suggest that *cedro-rosa* is a softwood meanwhile *imbuia* is a hardwood, comparatively.

According to Campanella et al. (1991) the cellulose thermal degradation occurs in many steps, starting by its depolymerization, generating glucose and oligosaccharides. Later on, during the



Fig. 3. TG curves for non-irradiated, 25 kGy-, 50 kGy-, 100 kGy-irradiated Imbuia.

pyrolysis, water and acids are also produced from cellulose derivatives. Additionally, the thermal degradation of lignin is attributed to α - and β -aryl-alkyl-ether bonds breakage, followed by aromatic ring bonds breakage and finally a rupture of carbon-carbon bonds between the structural units of lignin (Schniewind, 1995).

By this way, after irradiation of samples, as presented in Table 2 and Table 3, cellulose and lignin components of both wood studied species slightly undergo to chain breakage when absorbed radiation dose reaches 50 kGy or higher. Some samples have also presented traces of non-volatile inorganic residual components, which are derived from wood extractives.

Weight loss curves in function of temperature allow quantifying the main structural components in wood samples, as well as some phenomena observed during their thermal decomposition (Costa et al., 2004):

- Water evaporation, around 140 °C;
- Gases formation due to pyrolysis reactions, in the range of 200 °C–450 °C, with maximum liberation at around 375 °C;
- Tar formation up to 350 °C, with maximum liberation around 290 °C.

This behavior, as described by Costa et al. (2004), is attributed to kinetic mechanisms of carbonization, where time and temperature



Fig. 2. TG/DTG curve for 100 kGy-irradiated Imbuia.



Fig. 4. TG/DTG curve for non-irradiated cedro-rosa.



Fig. 5. TG/DTG curve for 25 kGy-irradiated cedro-rosa.

could affect the heat transfer through the charcoal layer already formed, by conduction of heat from the outside surface of the sawdust, initiating the process of pyrolysis followed by the movement of gases by convection in the opposite direction to heat transfer, initiating the formation of coal, without the volatile components in the structure.

Confirming the statement quoted by Campanella et al. (1991), the first stage of mass loss of about 9-12% occurs up to 150 °C and corresponds to the elimination of all moisture from the sample. The second and third stages correspond to the thermal oxidative degradation of cellulose and lignin from the wood samples and occur between 160 °C and 400 °C. The hemicellulose undergoes thermal degradation at temperatures from 200 °C to 260 °C. The thermal degradation of lignin starts around 200 °C with the reactions of dehydration. Up to 300 °C, there is the breaking of bonds α - β -aryl-alkyl-ether. Around this temperature, the aliphatic side chains begin to separate from the aromatic rings. Finally, between 370 °C and 400 °C, approximately, there is the breaking of carboncarbon bond between the structural units of lignin. The temperature range in which these events occur depends on the atmosphere that involves the sample during the pyrolysis process (air or nitrogen). The residual mass measured at temperatures higher than those discussed above corresponds to the residue of ash.



Fig. 6. TG curves for non-irradiated, 25 kGy-, 50 kGy-, 100 kGy-irradiated cedro-rosa.

Table 2

TG weight loss data for non-irradiated, 25 kGy-, 50 kGy-, 100 kGy-irradiated Imbuia.

| Radiation dose (kGy) | Volatile components (%) | Cellulose + lignin (%) | Weight loss (%) |
|-------------------------|----------------------------|---------------------------|--------------------|
| 0 | 11 | 89 | 98 |
| 25 | 10 | 87 | 100 |
| 50 | 9 | 86 | 96 |
| 100 | 8 | 86 | 97 |

Table 3

TG weight loss data for non-irradiated, 25 kGy-, 50 kGy-, 100 kGy-irradiated *cedro-rosa*.

| Radiation dose (kGy) | Volatile components (%) | Cellulose + lignin (%) | Weight Loss (%) |
|-------------------------|----------------------------|---------------------------|--------------------|
| 0 | 9 | 85 | 95 |
| 25 | 10 | 87 | 99 |
| 50 | 12 | 85 | 100 |
| 100 | 11 | 86 | 100 |

4. Conclusions

The applied gamma radiation range dose does not promote significant alterations on mechanical and thermal behavior of the studied wood samples.

In other words, gamma rays can be used for decontamination and disinfestation purposes without damaging the art work artifacts even if the treated material is once more exposed to radiation source, i.e. due to a re-infestation by biodeteriorating agents.

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