J Therm Anal Calorim (2011) 106:783–786
DOI 10.1007/s10973-011-1840-y

Evaluation of the effects of gamma radiation on thermal properties of wood species used in Brazilian artistic and cultural heritage

Lucio Cesar Severiano · Francisco Antonio Rocco Lahr · Marcelo Augusto Gonçalves Bardi · Luci Diva Brocardo Machado

CBRATEC7 Conference Special Issue

Abstract The wood is considered a natural composite of extreme complexity, mainly composed of cellulose, lignin, hemicellulose (polyposis), and extractives. Its composition encourages biological attacks from different species. In this context, several techniques have been studied and applied for disinfecting and decontaminating wood-made works of art and cultural heritage objects, which have been damaged by fungi, bacteria, and insects. Gamma radiation has been studied as an alternative to chemical methodologies for this purpose. By this way, the aim of this article is to illustrate the effect of gamma radiation on some physicochemical properties of *Pinnus patula*, *Pinnus cunninghamia*, *Cedrella fissillis*, and *Ocotea porosa* wood species. The irradiation has shown itself to be a fast and efficient process to eliminate infestations by both insects and microorganisms and no quarantine is required because of the no generation of toxic residues. On the other hand, this process does not protect the irradiated material from re-infestations or re-contamination. In this study, relatively high gamma radiation doses were applied up to 100 kGy so that radiation effects, which are cumulative, could be retrieved by means of thermal properties. The results have shown that gamma radiation, in the studied dose range, does not promote meaningful alterations on the evaluated properties, which allows that artifacts be irradiated multiple times, even if a re-infestation occurs.

Keywords Gamma radiation · Wood · Thermal properties · Cultural heritage

L. C. Severiano · M. A. G. Bardi · L. D. B. Machado (✉)
Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear (IPEN/CNEN-SP), Centro de Tecnologia das Radiações, Av. Prof. Lineu Prestes, n. 2242, Cidade Universitária, São Paulo, SP 05508-000, Brazil
e-mail: lmachado@ipen.br

F. A. R. Lahr
Laboratório de Madeiras e Estruturas de Madeiras, Universidade de São Paulo (USP), Av. Trabalhador São-Carlense, n. 400, São Carlos, SP 13566-590, Brazil

Introduction

Wood has strongly influenced cultures throughout the centuries because of its easy manufacturing of furniture, sculptures, and pieces of art and artifacts found in ancient churches, such as paintings, frames, decorations, sculptures, furniture, and so on. In Brazil, due to the variety of wood species, the preliminary study about mechanical characteristics of wood has started at the beginning of the century. The results obtained at the time were used to study the properties of some species. By means of the collected materials, it was possible to establish peculiar strength limits of species as well as evaluate relative values of their properties based on the required application [1].

According to Mano [2], wood is considered a natural composite of extreme complexity, where the structural elements are represented by cellulose and lignin fibers. Its ultra-structure and chemical composition as well as its physical and mechanical properties significantly differ among species, among trees of the same species, and even among different parts of the same tree [3].

As described by Lara [3], a large number of Brazilian wooden cultural heritages is undergoing a deterioration process and so requires methodologies to its protection against weathering and biological attacks. With regard to Cappitelli [4], in the last decades growing concerns on the use of chemical compounds has resulted in an in-depth evaluation of the effects of pesticides on the human health and safety. Any process should be safe for the operator and the environment and no chemical residues should remain in the treated materials. In this context, some researchers [5–9] have suggested the use of gamma radiation as an alternative for disinfection and decontamination of such artifacts attacked by fungi, termites, and others.

When gamma radiation is absorbed by a biological material, two effects can occur on living cells. As a direct effect of radiation, where the dominant process occurs by irradiating dry spores of microorganisms, molecules of DNA are ionized or excited inducing succeeding events that culminate in the cells death [10]. By the indirect process, radiation may interact with other atoms or molecules in the cell, particularly water, to produce free radicals and thus damaging DNA molecules. This indirect effect of radiation is important in vegetative cells where the cytoplasm contains about 80% of water.

As described by Wellheiser [11], gamma radiation is effective in killing biodeteriorating organisms (insects, bacterial spores, fungal spore or conidia), but the doses required for kill cause physical changes in adhesives, cotton, leather, paper, parchment, pigments, plastics, and wood. If the damage by the organisms is greater than that of the treatment, it maybe a last resort treatment.

The doses are relatively high for decontamination and disinfection of materials attacked by bacteria and fungi. However, as the radiation treatment does not prevent recontamination, doses were chosen to reveal the effects of radiation on the wood even if it is necessary to repeat the process of irradiation due to reinfestation of the object, always taking into account that the absorbed dose is cumulative.

Borysiak [12] investigated the effect of radiation dose on pine wood (*Pinnus sylvestris* L.) by analyzing the content of cellulose in the samples after irradiation. The content of cellulose in wood is similar during the initial stage of gamma radiation at the dose range 20–300 kGy. However, when the doses of irradiation increase above the level of 500 kGy then the cellulose content decreased rapidly. The authors observed that only trace amount of cellulose in wood was obtained for the irradiation dose of 4.5 MGy. Additionally, the highest irradiation dose studied (9 MGy) leads to the total destruction of wood, i.e., the content of cellulose in this sample is 0%. When analyzing the properties of *Cryptomeria japonica* after gamma irradiation, Katsumata et al. [8] verified a reduction on the degree of polymerization of cellulose by increasing the dose up to 100 kGy. It was also observed that termite wood consumption rates for some species have increased by the increasing of the dose, suggesting that higher doses can make this wood specie more susceptible to biological damages.

So, the aim of this study is to evaluate the effects of gamma radiation on thermal properties of *Pinus* (*Pinnus patula* and *Pinnus cunninghamia*), *Cedro-rosa* (*Cedrella fissillis*), and *Imbuia* (*Ocotea porosa*) wood species largely used in artistic and cultural heritage of Brazil.

Experimental

Sample preparation

For thermal analysis, *Pinus* (*P. patula* and *P. cunninghamia*), *Cedro-rosa* (*C. fissillis*), and *Imbuia* (*O. porosa*) wood species samples were cut in several pieces to obtain homogeneous samples of dimensions 2 × 2 × 45 cm (following the growth axis of the tree), avoiding nodes and other irregularities commonly observed on some natural wood species.

Irradiation

The wood 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, 50, and 100 kGy. These doses were performed after considering that the gamma irradiation is a very effective treatment for recovery biodeteriorated artifacts. This irradiator is located at CTR/IPEN/CNEN-SP.

Thermogravimetry (TG)

Tests of thermal analysis for wood samples were performed using TG50 Shimadzu Co. (Tokyo, Japan) apparatus, in air with flow rate of 50 mL min^{-1}. Around 5 mg pieces from different parts of the samples far from the cutting surface were placed into platinum crucible and heated at a constant rate of 10 °C min^{-1} up to 700 °C.

Results and discussion

Figures 1, 2, 3, and 4 present the results of TG for, respectively, *P. patula*, *P. cunninghamia*, *C. fissillis,* and *O. porosa*, non-irradiated and irradiated at 25, 50, and 100 kGy. The curves of mass variation as a function of temperature allow the quantitative determination of the main components present in the samples.

By the analysis of Figs. 1, 2, 3, and 4, it can be seen that the TG curves for both wood species basically consisted of two steps, wherein the first one is probably due to depolymerization and later combustion of cellulose.

More specifically, it can also be highlighted that, up to 130 °C, the mass loss due to moisture and highly volatile

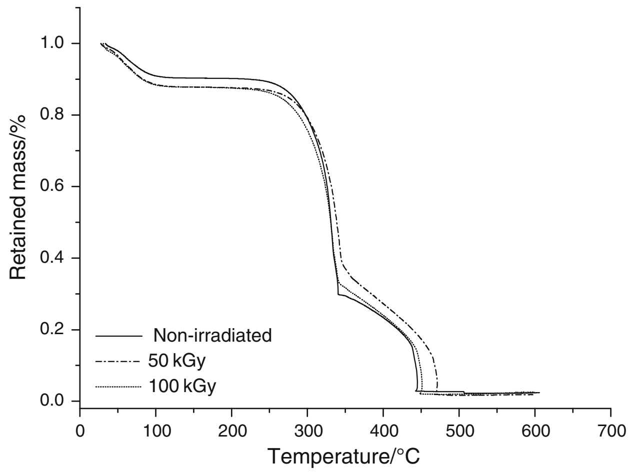

Fig. 1 TG curves for non-irradiated and irradiated *P. patula* samples

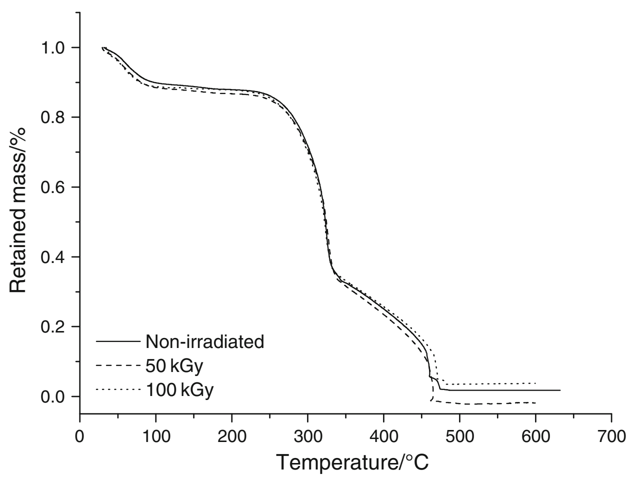

Fig. 2 TG curves for non-irradiated and irradiated *P. cunninghamia* samples

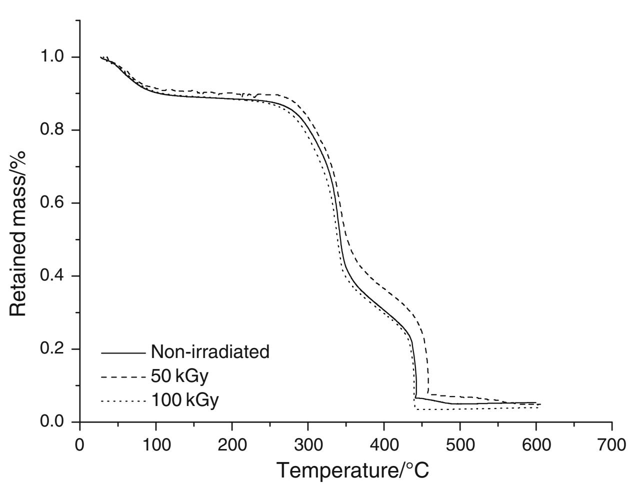

Fig. 3 TG curves for non-irradiated and irradiated *C. fissillis* samples

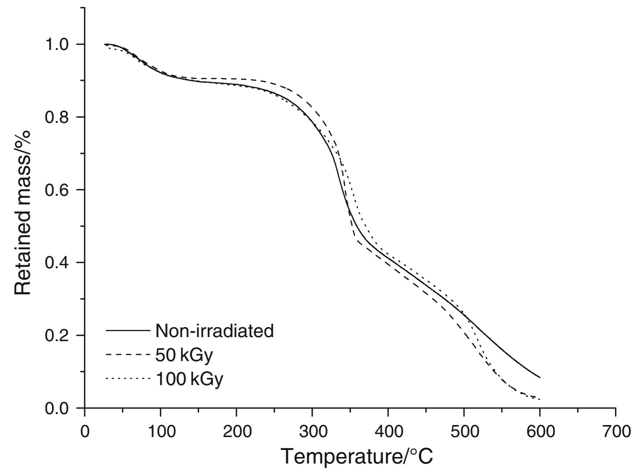

Fig. 4 TG curves for non-irradiated and irradiated *O. porosa* samples

matters in the samples is around 9% [13]. Around 250 °C, thermal oxidation of crystalline and amorphous components of cellulose takes place. At 330 °C, the wood had a mass loss around 64% suggesting the presence of a low molecular weight fragment, cleavage of glucosidal groups, and breakdown of anhydroglucose units in cellulose [14, 15]. At the temperature range from 330 to 440 °C, the oxidation of lignin has occurred presenting a mass loss of 20% [16]. The results above are similar and corroborated by Campanella et al. [17], Korosěc et al. [18], and Franceschi et al. [19], when analyzed other wood species.

It can also be observed that TG curves from non-irradiated and irradiated wood samples do not differ very much from each other, reflecting that gamma radiation does not promote meaningful changes on thermal stability of the samples. Therefore, gamma radiation can be considered an alternative to traditional wood preservation methods, such as exposition to ethylene oxide, methyl bromide carbon dioxide, inert gases, or freezing processing, which let toxic substances impregnated onto material or do not eliminate mold, just letting them in a dormant state [20, 21].

Conclusions

Based on the thermal analysis, it is possible to conclude that there were no meaningful alterations on the wood samples submitted to irradiation at the studied dose range. Therefore, the use of gamma rays from a 60-cobalt source was shown to be efficient when subsequent treatments for disinfection and decontamination of wood-made cultural heritage are required, once it does not damage the wood structure nor generate sub-products that could harm people in physical contact to the artifacts.

Acknowledgements The authors thank Mrs. Marcia Mathias Rizzo and Mr. Danilo Bras dos Santos by suggesting the wood species; Mr. Alex Correia dos Santos by helping during TG tests; Ms. Yasko Kodama and Mr. Paulo de Souza Santos by the 60-cobalt irradiation procedure; and Brazilian National Commission for Nuclear Energy (CNEN) by funding this research (Grant no. 01341.001411/2008-80).

References

1. Lelis AT, Brazolin S, Fernandes JLG, Lopez GAC, Monteiro MBB, Zenid G. Biodeterioração de madeiras em edificações. São Paulo: IPT; 2001.
2. Mano EB. Polímeros como materiais de engenharia. 3rd ed. São Paulo: Edgard Bluncher; 2003.
3. Lara FM. Princípios de entomologia. 3rd ed. São Paulo: Ícone; 1992.
4. Cappitelli F, Sorlini C. From papyrus to compact disc: the microbial deterioration of documentary heritage. Crit Rev Microbiol. 2005;31:1–10.
5. Katušin-Ražem B, Ražem D, Braun M. Irradiation treatment for the protection and conservation of cultural heritage artefacts in Croatia. Radiat Phys chem. 2009;7–8:729–31.
6. Despot R, Hasan M, Brischke C, Welzbacher CR, Rapp AO. Changes in physical, mechanical and chemical properties of wood during sterilisation by gamma radiation. Holzforschung. 2007;3:261–6.
7. Betiku E, Adetunji OA, Ojumu TV, Solomon BO. A comparative study of the hydrolysis of gamma irradiated lignocelluloses. Braz J Chem Eng. 2009;2:251–5.
8. Katsumata N, Yoshimura T, Tsunoda K, Imamura Y. Resistance of gamma-irradiated sapwood of *Cryptomeria japonica* to biological attacks. J Wood Sci. 2007;4:320–3.
9. Katsumata N, Tsunoda K, Toyoumi A, Yoshimura T, Imamura Y. Comparative termite (Isoptera: Rhinotermitidae) feeding preference among gamma-irradiated and unirradiated wood. Sociobiology. 2007;1:155–62.
10. Panshin AJ, de Zeeuw C. Textbook of wood technology. New York: Mc-Graw-Hill; 1990.
11. Wellheiser JG. Nonchemical treatment processes for disinfestation of insects and fungi in library collections. Munich: K. G. Saur; 1992.
12. Borysiak S. A study of transcrystallinity in polypropylene in the presence of wood irradiated with gamma rays. J Therm Anal Calorim. 2010;101:439–45.
13. Yorulmaz SY, Atimtay AT. Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis. Fuel Process Technol. 2009;90:939–46.
14. Khan F, Ahmad SR, Kronfli E. γ-Radiation induced changes in the physical and chemical properties of lignocellulose. Biomacromolecules. 2006;7:2303–9.
15. Corradini E, Teixeira EM, Paladin PD, Agnelli JA, Silva ORRF, Mattoso LHC. Thermal stability and degradation kinetic study of white and colored cotton fibers by thermogravimetric analysis. J Therm Anal Calorim. 2009;97:415–9.
16. Popescu C-M, Lisa G, Manoliu A, Grandinariu P, Vasile C. Thermogravimetric analysis of fungus-degraded lime wood. Carbohydr Polym. 2010;80:78–83.
17. Campanella L, Tomassetti M, Tomellini R. Thermoanalysis of ancient, fresh and waterlogged woods. J Therm Anal Calorim. 1991;8:1923–32.
18. Korosěc RC, Lavrič B, Rep G, Pohleven F, Bukovec P. Thermogravimetry as a possible tool for determining modification degree of thermally treated Norway spruce wood. J Therm Anal Calorim. 2009;98:189–95.
19. Franceschi E, Cascone I, Nole D. Thermal, XRD and spectrophotometric study on artificially degraded woods. J Therm Anal Calorim. 2008;91:119–25.
20. Zervos S, Moropoulou A. Methodology and criteria for the evaluation of paper conservation interventions: a literature review. Restaurator. 2006;27:219–74.
21. Selwitz C, Maekawa S. Inert gases in the control of museum insect pests. Los Angeles: The Getty Conservation Institute; 1998.