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Effects of gamma radiation on the structure and thermal properties of ebony wood

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Gamma irradiation is an effective method for disinfestation of wood-made materials, including cultural heritage treatment. Selection of the absorbed dose and dose rate is needed to avoid radiation-induced destruction that would compromise the preservation of the artifacts. Therefore, the side effects of the radiation on different types of wood are worth exploring. This study describes the effects of gamma irradiation with doses up to 25 kGy, absorbed at two dose rates, on ebony wood samples with different radiocarbon age. The investigation aims to identify the side effects of gamma disinfestation on the structure and thermal properties of ebony wood using FTIR/ATR, ESR and TG/DTG analysis. Higher susceptibility to the radiation-induced radical formation both at low (0.037 Gy/s) and standard (1 Gy/s) dose rates was found in the younger ebony wood. Stronger radiation-induced effects were found in the older ebony wood, as revealed by FTIR/ATR analysis. TG analysis showed an increase of the residual weight with 6 % to 17 % after heating up to 700 ^{o}C of the irradiated sample with higher radiocarbon age. This was most strongly expressed in the samples with 15 kGy absorbed doses at standard dose rate. The TG data showed that the gamma irradiation of the younger wood led to 7 % to 10 % increase of the residual weight after heating up to 700 ^{o}C. The DTG analysis did not show significant changes in the temperature of maximum weight loss in both ebony woods before and after gamma irradiation at the two dose rates.

Keywords: ebony wood, gamma irradiation, side effects, electron spin resonance, infrared spectroscopy, thermal gravimetric analysis.

INTRODUCTION

The application of gamma irradiation is a widely used method for effective decontamination of various organic-based materials, such as wood, paper, leather, textile etc. [1-5]. These materials often become a favorable source of food for insects and their larvae, fungi, molds and bacteria, when stored in improper conditions (high temperature and humidity). This may cause their modification and destruction to varying degrees. Thus, microorganisms and fungal strains destroy the chains of biopolymers, which causes deterioration of their mechanical resistance, molecular structure and change in their color. Such problems related to biologically induced damage to materials are particularly risky when they concern artifacts, as the latter may be irretrievably lost for history and society. In this aspect, gamma irradiation is recognized as a particularly effective method for treatment of biodeteriorated cultural heritage objects [1, 6-8], and the specification of appropriate absorbed doses that do not damage the structure and properties of artifacts is a subject of interest for various research laboratories [9-12]. Gamma irradiation is a preferred method of biological pest control and cultural heritage preservation due to its many advantages: high penetrating ability of gamma rays, rapidity, absence of residual toxic or radioactive products, safety for personnel and control of the absorbed dose [1]. While disinfestation can be successfully achieved with absorbed doses of 0.5-3 kGy, fungal and mold contamination usually requires absorption of radiation with doses of 9-13 kGy (sometimes up to 20 kGy), and sterilization dose of 25 kGy is needed to decontaminate artifacts infected with bacteria [1] which appears to be the greatest challenge. Knowledge of the structural changes that can occur in materials as a result of radiation exposure is the basis of successful decontamination of artifacts and their preservation. Investigations have shown that wooden materials can be irradiated with gamma rays at doses up to 20 kGy without causing significant changes in their properties [1]. However, obtaining data on radiation effects found after irradiation at different dose rates on various types of wood is important for planning safe and effective decontamination and conservation of wooden artifacts. Previous research has found that gamma irradiation at a low radiation dose rate causes an acceleration of the aging of materials, which is explained by the formation of radicals [6, 13]. Radiation-induced oxidative degradation was found to increase at low dose rates due to increased oxygen diffusion time [13].

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The present paper describes the results of a study on the side effects on the radical concentrations, molecular structure and thermal properties of ebony wood samples after gamma irradiation with doses from 5 to 25 kGy at low dose rate (0.006 - 0.06 Gy/s) and standard dose rate (0.6 - 6 Gy/s). Ebony samples of different age previously determined by radiocarbon dating, were selected to study not only the side effects of gamma irradiation treatment with different dose rates, but also to identify if the age of the samples influences the radiation-induced changes.

MATERIALS AND METHODS

Materials

Samples from two ebony woods were selected for the experiment. The samples were kindly provided by the Laboratory for low-level radioactivities, Division of experimental physics at the Rudjer Bojkovic Institute in Zagreb, Croatia, where their radiocarbon age was determined. The sample preparation and the application of the radiocarbon method was performed as described in [14, 15].

The dated sample numbers and their ages were as follows:

Z-5906 – Radiocarbon age: 1914 y ± 70 BP;

Z-6106 – Radiocarbon age: 955 y ± 51 BP.

Methods

- *Gamma irradiation.* The irradiation of the ebony wood samples was performed in the gamma irradiation facility BULGAMMA based on JS-850 ^{60}Co type gamma irradiator at Sopharma. JS-850 ^{60}Co gamma irradiator is a wet storage, tote-box irradiator, produced by MDS Nordian, Canada. The absorbed dose distributions were measured with ethanol chlorobenzene routing dosimeters, consisting of dosimetric solution encapsulated in a glass ampoule with diameter of 10.7 mm and volume of 2 ml. The absorbed dose was calculated from a calibration curve connecting it with the electric conductivity of the dosimetric solution measured with oscilotitrator. This dosimeter consisted of an aerated solution of chlorobenzene and water in ethanol to which a small quantity of acetate was added. Irradiator BULGAMMA is certified by the Quality Management System ISO 9001: 2008, applicable to processing, decontamination and sterilization of products by gamma irradiation for industrial, medical and scientific purposes.

The ebony samples were separately packed in plastic bags, closed in paper envelopes and irradiated at low dose rate (0.037 Gy/s) and standard dose rate (1 Gy/s) with absorbed doses of 5 kGy, 10 kGy, 15 kGy and 25 kGy, at temperature of 25 ^{o}C.

- *Electron spin resonance spectroscopy.* The ESR analysis of the samples was performed with the system Bruker EMX premium X. The calculation of the spin concentrations was performed by using ESR Xenon software with application Absolute Number of Spins. The ESR measurements were carried out at room temperature, with 9.4 GHz frequency of radiation of the samples in X band of the instrument. All the measurements were carried out at modulation of the magnetic field 100 kHz.
- *Attenuated total reflectance Fourier transform infrared spectroscopy.* The infrared spectra were recorded on Bruker Tensor 27 FTIR spectrometer in the range of 4000 - 500 cm^{-1} with a resolution of 2 cm^{-1} and 64 scans by means of reflection technique using MIRacle-Diamond/ZnSe Crystal Plate ATR accessory (Pike technology).
- *Thermal gravimetric analysis.* The thermal properties of the samples were studied by thermal gravimetric analysis (TG/DTG) in pure argon, using Perkin-Elmer TGS-2.

RESULTS AND DISCUSSION

Electron spin resonance spectroscopy

The results obtained by ESR analysis of the studied ebony samples Z-5906 and Z-6106 are presented in Figures 1 and 2. In the non-irradiated samples a slightly asymmetric signal with g-factor = 2.0049 and line width $\Delta H \approx 0.8$mT was found. When lowering the measurement temperature from 295K to 120K, the intensity of the signal observed in the non-irradiated samples increased twice. The g-factor in the range of values of the free electron g-factor and the two-fold increase in intensity at low temperatures were evidence of the existence of a radical in the structure of both non-irradiated woods. In the irradiated samples, the asymmetric shape of the line was preserved, with identical ESR parameters as those observed in the non-irradiated samples. The younger non-irradiated ebony sample Z-6106 was found to have higher spin concentration than the older non-irradiated sample Z-5906, as can be seen from the data on Figures 1, 2. The effects on the spin concentration after irradiation with low dose rate can be summarized as follows:

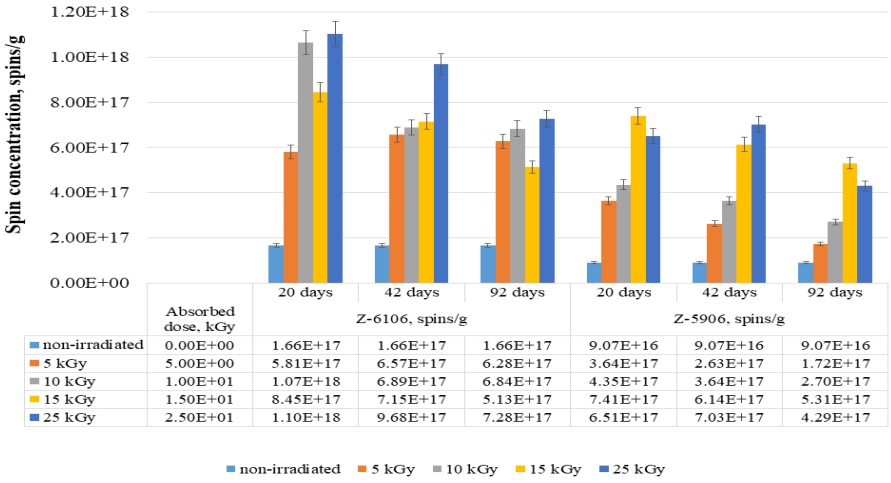
✓ Increase of the spin concentrations with the increase of the absorbed doses was measured in the older ebony sample Z-5906. Decrease of the spin concentrations with time elapsed after the gamma irradiation was also detected in this sample, which was due to radical recombination. On the 92nd day after irradiation the spin concentrations in Z-5906 remained from 2 to 6 times higher as compared to the non-irradiated sample.

✓ Clearly expressed radiation effect on the spin concentration was measured in Z-6106 after 5 kGy absorbed dose, which remained unchanged with time. Higher spin concentrations in the younger ebony wood were detected after 10 kGy and 25 kGy, and lower after 15 kGy. This might be explained by cross-linking of broken chains of biopolymers at 15 kGy, which does not occur at doses of 10 kGy, while 25 kGy caused subsequent breaking of chemical bonds. On the 92nd day all the irradiated samples of Z-6106 reached an equilibrium spin concentration, which was 3 to 4 times higher than that in the initial non-irradiated ones. A decrease of the spin concentrations with time after the gamma irradiation was also noticed.

The effects after irradiation at standard dose rate can be summarized as follows:

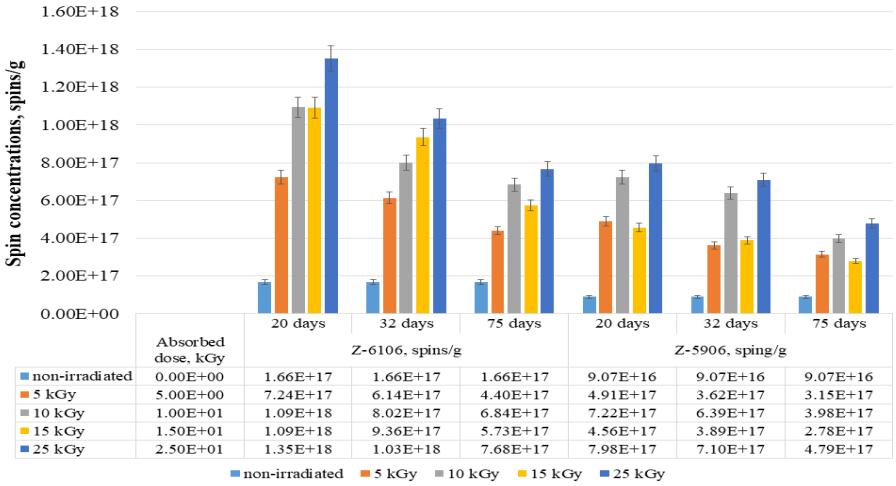
✓ Increase of the radical concentrations in Z-5906 with the absorbed dose, which followed the absorption dose dependence, mentioned above: the radical concentration after 15 kGy was lower than those at 10 kGy and 25 kGy, and could be attributed to cross-linking of broken biopolymer chains. Slight decrease of the radical concentrations with the time was measured. On the 75th day after the irradiation the spin concentrations in the irradiated samples Z-5906 have reached an equilibrium concentration, which was 3 to 5 times higher than that in the non-irradiated sample.

✓ Increase of the spin concentration with the increase of the absorbed dose by sample Z-6106 was noticed; however, the samples with 10 and15 kGy doses had very similar radical concentrations. The tendency to decrease the spin concentrations with time was observed for all the analyzed samples. On the 75th day after irradiation the radical concentrations in the samples remained from 2.6 to 4.6 times higher as compared to the non-irradiated sample.



	Absorbed dose, kGy	Z-6106, spins/g			Z-5906, spins/g		
		20 days	42 days	92 days	20 days	42 days	92 days
non-irradiated	0.00E+00	1.66E+17	1.66E+17	1.66E+17	9.07E+16	9.07E+16	9.07E+16
5 kGy	5.00E+00	5.81E+17	6.57E+17	6.28E+17	3.64E+17	2.63E+17	1.72E+17
10 kGy	1.00E+01	1.07E+18	6.89E+17	6.84E+17	4.35E+17	3.64E+17	2.70E+17
15 kGy	1.50E+01	8.45E+17	7.15E+17	5.13E+17	7.41E+17	6.14E+17	5.31E+17
25 kGy	2.50E+01	1.10E+18	9.68E+17	7.28E+17	6.51E+17	7.03E+17	4.29E+17

Fig. 1. Change of the spin concentrations of the ebony wood samples with time, before and after gamma irradiation with 5, 10, 15 and 25 kGy at low (0.037 Gy/s) dose rate.



	Absorbed dose, kGy	Z-6106, spins/g			Z-5906, sping/g		
		20 days	32 days	75 days	20 days	32 days	75 days
non-irradiated	0.00E+00	1.66E+17	1.66E+17	1.66E+17	9.07E+16	9.07E+16	9.07E+16
5 kGy	5.00E+00	7.24E+17	6.14E+17	4.40E+17	4.91E+17	3.62E+17	3.15E+17
10 kGy	1.00E+01	1.09E+18	8.02E+17	6.84E+17	7.22E+17	6.39E+17	3.98E+17
15 kGy	1.50E+01	1.09E+18	9.36E+17	5.73E+17	4.56E+17	3.89E+17	2.78E+17
25 kGy	2.50E+01	1.35E+18	1.03E+18	7.68E+17	7.98E+17	7.10E+17	4.79E+17

Fig. 2. Change of the spin concentrations of the ebony wood samples with time, before and after gamma irradiation with 5, 10, 15 and 25 kGy at standard (1 Gy/s) dose rate.

Attenuated total reflectance Fourier transform infrared spectroscopy

The FTIR-ATR spectra of the ebony samples irradiated with doses of 5 kGy and 10 kGy did not indicate any change in the molecular structure, compared to the non-irradiated samples.

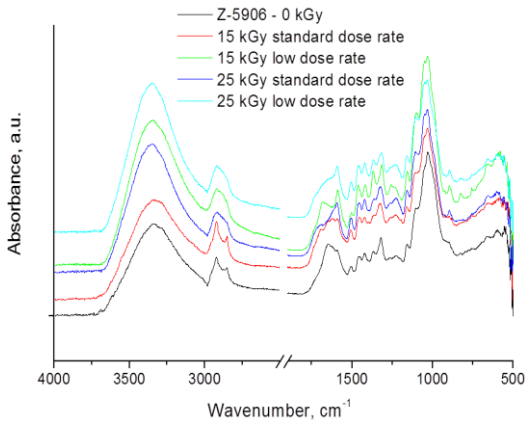


Fig. 3. FTIR/ATR spectra of the ebony wood sample Z-5906 before and after gamma irradiation with 15 kGy and 25 kGy at low and standard dose rate.

The data from the FTIR-ATR analysis of the ebony wood samples before and after gamma irradiation with 15 kGy and 25 kGy at the two dose rates are presented in Figures 3 and 4. The higher degree of the radiation-induced oxidation (leading to hydroxylation) at low dose rate is clearly pronounced in the spectra of the sample Z-5906 (Fig. 3), where higher intensity of the band at 3347 cm^{-1} (-OH groups, H-bonded) and the band between 1105 cm^{-1} and 1030 cm^{-1} (C-O) is observed.

The radiation-induced effects on the ebony sample Z-5906, observed in the FT-IR/ATR spectra (Fig. 3), can be summarized as follows: The two discrete bands at 2920 and 2842 cm^{-1}, attributed to $–CH_2$ and CH_3 groups, are transformed into a wide absorption band centered at about 2897 cm^{-1} in the spectra of the samples irradiated with absorbed doses of 15 kGy at low dose rate and 25 kGy at both dose rates. This might be ascribed to oxidation (hydroxylation) of methyl and methylene groups, as a result of the radiation-induced formation of OH radicals. Expectedly, the oxidation effects are higher expressed at low dose rate (at 15 kGy absorbed dose) and increase with increase of the absorbed doses (25 kGy).

The deviations of the frequencies at 1158 cm^{-1} (-C-O-C- vibration of cellulose and hemicellulose), 1320 cm^{-1} (CH- vibration in cellulose, CO vibration in syringyl derivative) and 1592 cm^{-1} (aromatic C-C) to lower frequencies with the increase of the absorbed doses, as observed in sample Z-5906, could be explained by weakening of the corresponding bonds (probably by oxidation of the near-by carbon atoms).

The above-mentioned changes in the FTIR/ATR spectra of Z-5906 sample were not observed in the spectra of the ebony sample Z-6106. No significant changes in the molecular structure were observed in the irradiated ebony sample Z-6106, as revealed by the FTIR/ATR spectra in Figure 4. According to the obtained results, one can conclude that the ebony wood sample with higher radiocarbon age Z-5906 undergoes stronger radiation-induced side effects including oxidation (hydroxylation) of the methyl and methylene groups and weakening of –C-O-C-, CH-, CO and aromatic C-C bonds, compared to the younger ebony sample Z-6106.

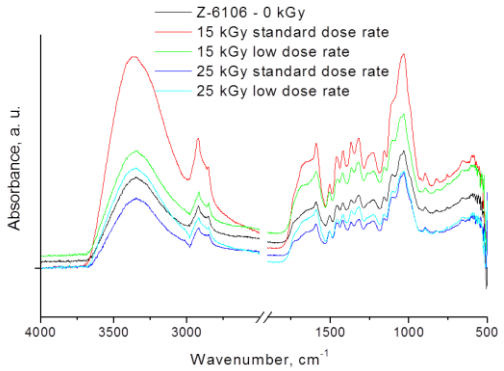


Fig. 4. FTIR/ATR spectra of the ebony wood sample Z-6106 before and after gamma irradiation with 15 kGy and 25 kGy at low and standard dose rate.

Thermal gravimetric analysis

The results from the thermal gravimetric analysis of the ebony wood samples before and after gamma irradiation with 15 kGy and 25 kGy at low and standard dose rates are presented in Figures 5 and 6. Increase of the weight with 6 % to 17 %, remained after heating up to 700 °C was noticed in all the irradiated samples of ebony wood Z-5906. The relative increase of the weight is highest in the samples with 15 kGy absorbed doses at standard dose rate.

The TGA data showed that the gamma irradiation of the ebony sample Z-6106 led to 7 % to 10 % increase of the residual weight after heating up to 700 °C, which could be explained with changes in the molecular structure as a result of the interaction of the wood with the radiation-induced radicals. The DTG analysis did not show significant changes in the temperature of maximum weight loss in both ebony wood samples before and after gamma irradiation at low and standard dose range. Fig. 7 presents the weight loss rates of sample Z-5906

before and after 25 kGy absorbed dose at standard dose rate. Three areas are observed: water loss (at about 60 ºC), destruction (at about 330 ºC) and carbonization of the wood (625 ºC). The results obtained show that the changes in the maximum weight loss temperatures vary by less than 1% after the applied gamma irradiation.

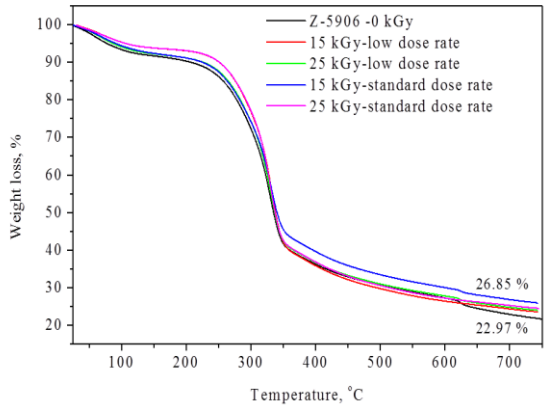


Fig. 5. TGA curve of the ebony wood sample Z-5906 before and after gamma irradiation with 15 and 25 kGy at low and standard dose rates.

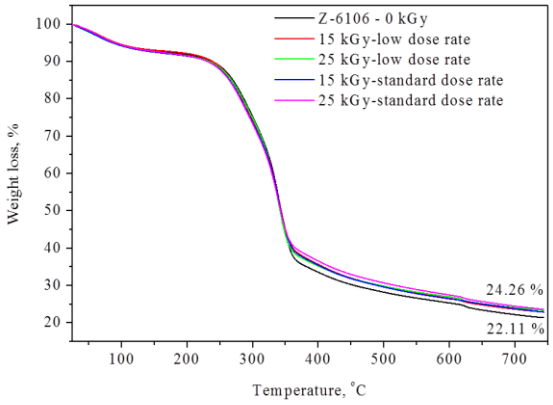


Fig. 6. TGA curve of the ebony wood sample Z-6106 before and after gamma irradiation with 15 and 25 kGy at low and standard dose rates.

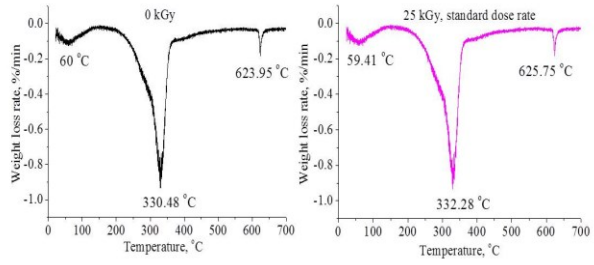


Fig. 7. DTG diagrams of ebony sample Z-5906 before and after gamma irradiation with 25 kGy at standard dose rate.

CONCLUSIONS

The results obtained within the study can be summarized as follows:

The younger non-irradiated ebony sample Z-6106 was found to have higher spin concentration than the older non-irradiated sample Z-5906. Decrease of the radical concentrations with time due to recombination processes was observed in all the ebony samples. An exception is the younger ebony sample, irradiated with 5 kGy at low dose rate, where the spin concentration remained constant for the period 20th – 92nd day after the irradiation. For the studied period of 92 days after the irradiation the spin concentration of the irradiated samples did not reach the initial level of the non-irradiated samples, which showed radiation-induced stable radical formation. Higher susceptibility to the radiation-induced radical formation both at low and standard dose rate was found in the younger ebony wood sample Z-6106.

The ebony wood sample with higher radiocarbon age Z-5906 was found to undergo stronger radiation-induced side-effects, including oxidation (hydroxylation) of the methyl and methylene groups and weakening of –C-O-C-, CH-, CO and aromatic C-C bonds, compared to the younger ebony sample Z-6106, as revealed by the FTIR/ATR analysis. The TG analysis showed an increase of the weight with 6 % to 17 %, remained after heating up to 700 ºC in all the irradiated samples of ebony wood Z-5906 and 7 % to 10 % increase of the weight of Z-6106, which could be explained with changes in the molecular structure as a result of the interaction of the wood with the radiation-induced radicals. The DTG analysis did not show significant changes in the temperature of maximum weight loss in both ebony wood samples before and after gamma irradiation at low and standard dose range.

The obtained results showed that doses of 15 kGy and 20 kGy may provoke changes in the structure of the ebony woods that could have impact on their mechanical properties and they are worth to be further studied.

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