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Study of free radicals in gamma irradiated cellulose of cultural heritage materials using Electron Paramagnetic Resonance

Yasko Kodama*, Orlando Rodrigues Jr, Rafael Henrique Lazzari Garcia, Paulo de Souza Santos, Pablo A.S. Vasquez

Instituto de Pesquisas Energéticas e Nucleares – IPEN–CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000 São Paulo, Brazil

HIGHLIGHTS

- Gamma irradiation is a safe option to stop fungi and insect attack of books.
- Proposed model fits statistically well.
- Model is useful to calculate order of reaction through EPR signal decay.
- Life of cellulose free radical can be predicted.
- $CaCO_3$ presence did not affect EPR spectra of cellulose, neither the proposed model.
- Further studies of cultural heritage paper should consider low absorbed doses.

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ABSTRACT

Main subject of this article was to study room temperature stable radicals in Co-60 gamma irradiated contemporary paper using Electron Paramagnetic Resonance spectrometer (EPR). XRD was used to study the effect of ionizing radiation on the morphology of book paper. SEM images presented regions with cellulose fibers and regions with particles agglomeration on the cellulose fibers. Those agglomerations were rich in calcium, observed by EDS. XRD analysis confirmed presence of calcium carbonate diffraction peaks. The main objective of this study was to propose a method using conventional kinetics chemical reactions for the observed radical formed by ionizing radiation. Therefore, further analyses were made to study the half-life and the kinetics of the free radical created. This method can be suitably applied to study radicals on cultural heritage objects.

1. Introduction

Considerable work has been done on the application of ionizing radiation (gamma rays) in cultural heritage materials but still, it is necessary to increase knowledge on the advantages and limitations for this kind of processing. The attacks by living organisms, known as “biodeteriorating agents” (BA) is the more severe adverse factors affecting the quality of the paper and in some cases leading to the complete destruction of the product itself. The removal of biodeteriorating agents of materials is essential not only for preservation, but also, to prevent severe health problems for restorers, archivist or librarian.

Radiation processing is well established method for sterilization, with absorbed doses usually in the range of 20–25 kGy. In case of cultural objects, to achieve the more uniform possible bulk irradiation of a single object, gamma irradiation is the most suitable to be used (Adamo et al., 2004).

Contradictory results were published on the effect of ionizing radiation on the properties of cultural heritage materials. Magaudda (2004) and Adamo et al. (2004) studied the effect of absorbed doses on mechanical and physical properties of pure cellulose, paper, and printing inks. No significant harmful effect was detected on the materials, when using the dose necessary for an efficient treatment (roughly 0.2–0.5 kGy for insects; 3–8 kGy for micro-fungi). Area et al. (2014) reported that absorbed dose and dose rate interferes on several properties of a paper in a different way depending on the paper composition or crystallinity. They mentioned that minimum loss of tear resistance and brightness were obtained with doses in the range of 4–6 kGy at any dose rate for all three kinds of paper studied by the authors. For doses of 10 kGy and dose rate of 11 kGy h^{-1}, the authors found 4% of tear resistance and 0.4% brightness variations. Even though Magaudda

* Corresponding author.
E-mail addresses: ykodama@ipen.br, yasko.kodama@gmail.com (Y. Kodama).

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(2004) and Adamo et al. (2004) had discussed that gamma radiation plants of commercial type (for which the time necessary to impart a dose of effective radiation against insects and microscopic fungi takes minutes and not hours) act at a sufficiently high-dose-rate to minimize undesirable effects of free radicals in cellulose, still it is necessary to study paper radicals behavior after radiation processing. During irradiation, free radicals form in the cellulose and they quickly react with oxygen to break cellulose molecules and degrade the paper (Sinco, 2000). The radiation chemical reactions induced by absorption of radiation energy can occur at any carbon atom by hydrogen and hydroxyl abstraction or C–C and C–O bond scission in the cellulose chains, leading to radical formation (Khan et al., 2006). The radicals produced are trapped in the crystalline and semicrystalline region of the cellulose structure. Stable radicals would decay through recombination reactions which may lead to cross-linking. On the other hand, if the chain scission is predominant over cross-linking, the degradation on the properties is expected, and both may induce some modification on irradiated paper (Khan et al., 2006). Assessment of irreversible physical–chemical modification induced by ionizing radiation on preserved materials represents an important aim to guarantee the protection of the radiation processed artifacts (Adamo et al., 2015).

In this study, paper samples were irradiated by sterilization doses and the concentration of the radicals formed and their decay were followed at room temperature using Electron Paramagnetic Resonance spectrometer (EPR). The final goal of this preliminary study is to demystify some beliefs about cultural heritage irradiation.

2. Experimental

2.1. Sample preparation and irradiation

For this study it a contemporary paper was used (made in 2010), manufactured with bleached chemical pulp, mineral load above 10%, pH 4.6 and 100% short fibers. Paper samples were cut into 2 mm × 25 mm pieces. The sample was irradiated in a EPR quartz tube, at room temperature (~25 °C) at IPENs Multipurpose Gamma Facility, with a dose of 22 kGy (June 2015), 24 kGy (October 2015) with 16 kGy h^{-1} dose rate.

2.2. Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy Energy Dispersive Spectrometry (SEM–EDS)

SEM images were obtained using a Hitachi TM3000 equipped with a Bruker Quantax 70 EDS system module. Samples were carbon coated to reduce electron charging effect. Images magnifications were obtained from 1000 × up to 30,000 × using accelerating voltage of 15,000 V. SEM–EDS analyses were performed using Analy mode and Quantax software for images treatment. For quantification of elements, it was chosen calcium, iron, silicon, magnesium and aluminum. It was not considered carbon, hydrogen, oxygen, and nitrogen.

2.3. X-ray diffraction, XRD

Diffratograms were obtained using a Bruker Advance D8 difractometer. Parameters used were 20 s per step of 0.025°; Cu-K α radiation tube operating at 40 kV and 30 mA; scintillation detector and graphite monochromator; antiscatter and divergence slits of 0.6 mm; reception slit of 0.4 mm; goniometer radius of 250 mm and glass sample holder. Samples sizes were about 5 mm × 5 mm. X-ray beam was collimated to minimize sample holder diffraction.

According to Segal et al. (1959), crystallinity index (CI) is calculated from the ratio of the height of the 002 peak and the height of the minimum between 002 and 101 peaks, in accordance with the Eq. 1.

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the intensity of the crystalline peak at the maximum at 2θ between 22.8 and 23.8 for cellulose I (between 18.8 and 22.8 for cellulose II) and I_{am} is the intensity of the amorphous reflection at the minimum at 2θ between 18.8 and 19.8 for cellulose I (between 13.8 and 15.8 for cellulose II).

Due to relative small differences and considerable noise, diffractograms were previously smoothed to present more representatives high and low values, using DIFFRAC.EVA software, version 3.1.

2.4. EPR measurements

Electron Paramagnetic Resonance, EPR, spectra were obtained at room temperature using Bruker EMX plus model, X band, interval from 337.6 to 367.5 mT, field modulation amplitude 0.2 mT, field modulation frequency 100 kHz, microwave power 2 mW.

De-noising treatment of the original signals obtained by EPR were performed using the method suggested by Antoniadis and Oppenheim (1995). By integrating the EPR curves it is possible to obtain area values that can be correlated to concentration, in our case, it is equivalent to spin concentration. Further analyses were made to study the half-life and the kinetics of the free radicals. Comparison of spectra was done through normalization of calculated area (A) corresponding to cellulose spin concentration (Weil and Bolton, 2007), considering the first measurement just after irradiation as 100% (unity).

In this study, decay of radicals through time after irradiation was estimated comparing to the first measurement. EPR spectra were obtained up to 40 days after irradiation.

3. Results and discussion

No effect of the irradiation on the structure of the samples can be observed on the SEM images of non-irradiated and gamma irradiated paper as shown in Fig. 1.

Scanning electron microscopy energy dispersive spectrometry (SEM–EDS) was used to study the homogeneity of the samples. The results are shown in Fig. 2. (SEM image and regions analyzed by EDS). Regions with particles agglomeration within cellulose fibers can be observed. Those particle regions are rich in calcium. Some authors attributed the presence of calcium due to chemical treatment of cellulose source to produce paper and filler for reinforcement (Manso et al., 2011; Hajji et al., 2015).

X-ray diffraction (XRD) was carried out to identify crystalline phases and the effect of ionizing radiation on the crystalline structure of cellulose in paper. Fig. 3 shows XRD pattern of non-irradiated book paper, irradiated in June (22 kGy) and irradiated in October (24 kGy). All measurements were performed in October.

Diffraction peaks of cellulose were identified at 2θ 10–18° and 20–25°. Calcium carbonate was identified at 2θ 29.5, 35.0, 39.4 and 43.1. It can be seen that γ-radiation had practically no effect on the cellulose peak intensities. Crystalline Index was calculated for non-irradiated, irradiated in June and irradiated in October book paper. The non-irradiated sample presented the highest CI, 79.9%, followed by the sample irradiated in October with 24 kGy, 78.8% and the sample irradiated in June with 22 kGy, 78.5% (measured in October). This means that practically no difference in Crystalline Index was detected.

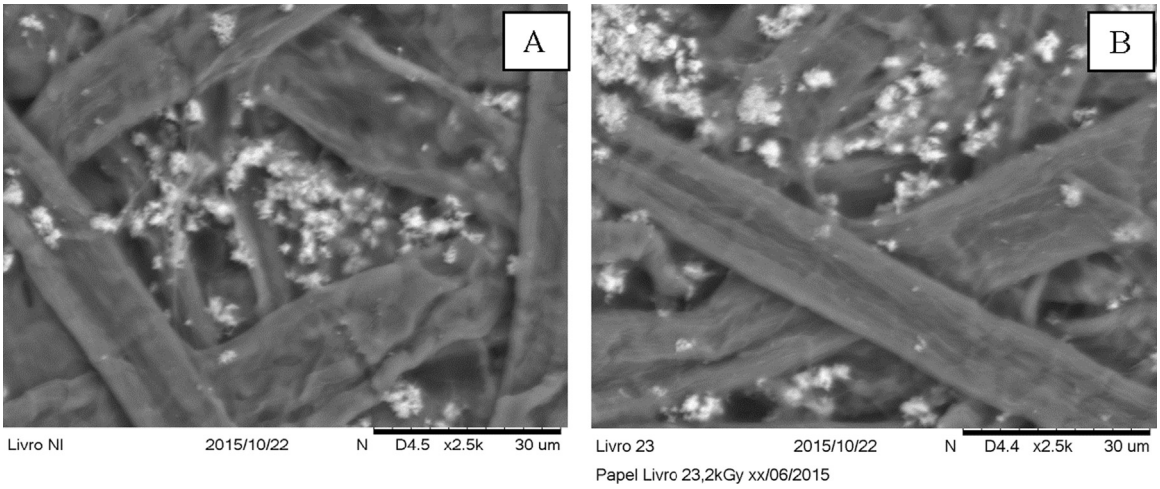

Fig. 1. SEM micrographs of book paper: (A) non irradiated and (B) gamma irradiated with 22 kGy, magnification 2500 ×.

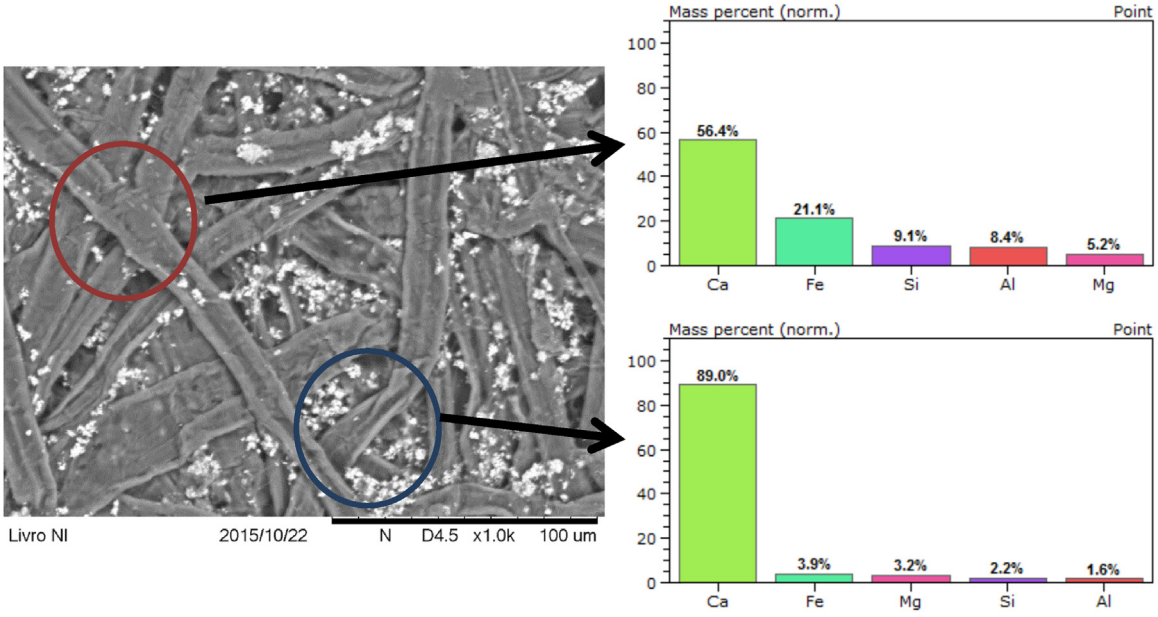

Fig. 2. SEM–EDS analysis of non-irradiated book paper.

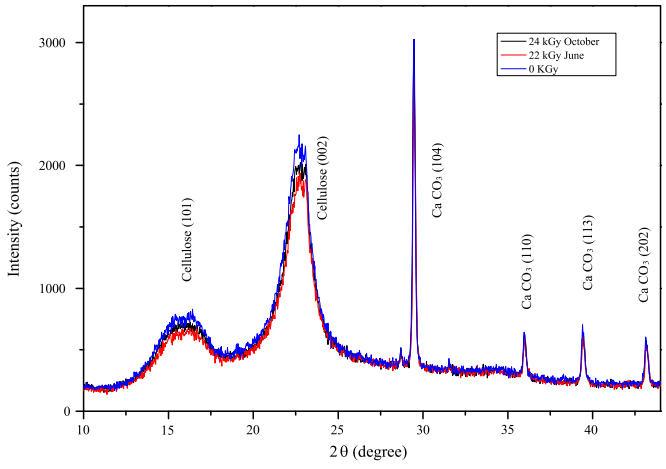

Fig. 3. XRD pattern diffraction of book paper: non-irradiated (blue); irradiated in June (red) and irradiated in October (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Similar XRD patterns of cellulose were obtained from jute fibers by Khan et al. (2006). They observed that the intensities of the crystalline peaks of cellulose gradually decreased with the increase of dose. Overall crystallinity of irradiated fibers decreased from 42% to 31% for 100 kGy of absorbed dose, suggesting that high-energy radiation results in significant changes in physical and chemical properties of cellulose. However, in this case the dose was much higher than in our case.

In this study, the first EPR spectrum of cellulose was acquired at 50 min after irradiation, and a triplet line of cellulose was observed in irradiated paper book (Fig. 4, inset) in accordance with those observed previously in the literature (Kameya and Ukai, 2013; Ranby and Rabek, 1977).

As it has been previously reported the triplet EPR spectrum of cellulose is attributable to the interactions between the two hydrogen atoms at the C(6) position of the glucose unit with the unpaired electron formed by the removal of the hydrogen atom at the C(5) position of the glucose unit by gamma radiation. Glucose unit C(1) is attached to oxygen atom in the ring and C(2) has the hydroxyl group. The stable radical observed at room temperature by Kameya and Ukai (2013) was attributed to a radical at the C

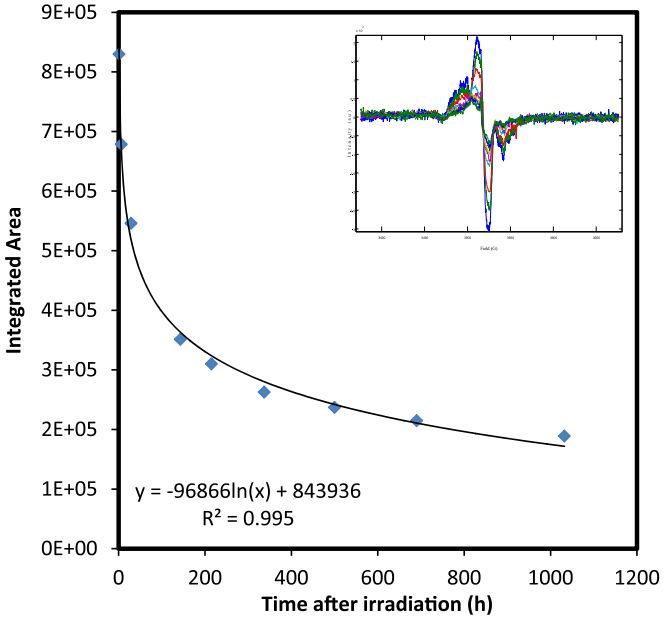

Fig. 4. Spin concentration (C_A) versus time after irradiation. Inset: EPR spectrum of cellulose paper, gamma irradiated in air, measured and irradiated at room temperature, at different times after irradiation.

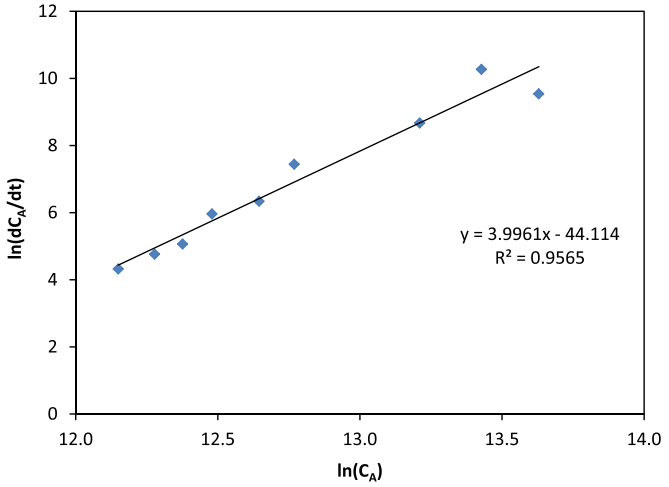

Fig. 5. Linear curve of $ln(-\frac{dC_A}{d_t})$ of cellulose radical (concentration variation) through time after irradiation.

(5) position of the glucose unit in irradiated cellulose. The EPR signal of the radical at the C(5) position of the glucose unit yields a triplet line shape due to hyperfine interactions between the unpaired electron of a carbon atom and two protons (Kameya and Ukai, 2013).

In this study, it was possible to observe the cellulose radicals decay of the irradiated book paper through time after irradiation (Fig. 4). Approximately 50% of radicals reacted roughly in 2 days, continued reacting reducing its rate through time and after 40 days of irradiation approximately 20% of radicals remained. Area et al. (2014) reported that the observed decrease of intrinsic viscosity of cellulose was related to the degree of polymerization and the molar mass decrease. This is characteristic of cellulose degradation and caused possible weakening of interfiber bonds and as consequence, the strength of paper decreased. Therefore, possibly further reactions expected of the cellulose free radicals formed in irradiated paper would be towards to cellulose deterioration. Moreover, Bouchard et al. (2006) had observed that when irradiation is performed in the presence of oxygen, carbonyl groups are formed on the cellulose and carboxylic acid group formation has also been reported.

Bouchard et al. (2006) suggested that under ionizing radiation exposure cellulose radicals were formed primarily by the rupture of C–H bonds in the weakened 1- and 4- positions while rupture of C–OH, C–C, and cyclic C–O–C bonds was discarded. They presumed that it was the secondary reactions that lead to cleavage of cellulose.

Taking into account paramagnetic behavior, each magnetic species has a unique and single *g*-value, many of them have the same value of *g* of the electron. However, there are many systems that present variation far from this value. It would be possible to differentiate organic from inorganic paramagnetic species, for example *g*-value is used in order to take into account the field-induced local magnetic fields. The local field can be induced, for instance, by orbital motion of the unpaired electron (Weil and Bolton, 2006). When magnetic field, *B*, and frequency, ν, varies but the other parameters are constant, *g*-value can be estimated by dividing frequency by field value. It could be observed that *g*-values did not change significantly, 0.02% of variation of the mean value. So, magnetic field locally seemed to be changed very few with radical' decay, it did not affected radical's spin in a significant way.

Calculation of half-life, $T_{½}$ of cellulose observed radical, can be done by using the values obtained from the graph of Fig. 5. Calculated $T_{½}$ is 58.86 h, or 2 days and a half-day, meaning that 50% of radicals reacted within this period of time. Also, it is possible to predict how long the radicals will last. We considered 80% of reacted radicals as the end of reaction. This value is approximately 44 days as it can be observed in Fig. 5.

4. Conclusion

The proposed method using EPR results can be suitably applied to study the fate of radicals on cultural heritage objects. It is advisable that cultural values be irradiated not mixed with low doses to decontaminate paper based cultural products.

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