Investigation of the electron paramagnetic resonance signal response in gamma-irradiated poly(lactic acid) for high-dose dosimetry

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Received 1 March 2018; accepted 15 June 2018

This paper is concerned with the investigation of the Electron Paramagnetic Resonance (EPR) signal response to Co60 gamma-ray radiation on poly(L-lactic acid) (PLA). The aim of this study is to assess the usefulness of PLA as a high-dose dosimeter. The EPR-signal response of PLA has been investigated to determine some of its dosimetric characteristics such as: signal intensity versus gamma dose received, zero-dose response, signal fading, signal repeatability, batch homogeneity, detection threshold, and stability under simulated sunlight exposure. It is concluded that PLA might be used as a high-dose dosimeter (10-500 kGy), with a very good reproducibility although its signal fading is about 9% in the first 5 hrs.

Keywords: Poly(lactic-acid); gamma-irradiation; high-dose dosimeter; EPR ESR dosimetry.

Este trabajo se ocupa de la investigación de la respuesta de la señal de Resonancia Paramagnética Electrónica (EPR) a la radiación de rayos gamma Co60 sobre ácido poliláctico L (PLA). El objetivo de este estudio es evaluar la utilidad del PLA como un dosímetro para dosis altas. La respuesta de señal EPR del PLA ha sido investigada para determinar algunas de sus características dosimétricas tales como: intensidad de señal versus dosis gamma recibida, respuesta a dosis cero, desvanecimiento de señal, repetibilidad de señal, homogeneidad del lote, umbral de detección y estabilidad bajo exposición solar simulada. Se concluye que el PLA se puede usar como un dosímetro para altas dosis (10-500 kGy), con una muy buena reproducibilidad, aunque su pérdida de señal es alrededor del 9% en las primeras 5 hrs.

Descriptores: Ácido poliláctico; irradiación gama; dosímetro de altas dosis; dosimetría EPR ESR.

PACS: 76.30.Rn

1. Introduction

Nowadays the application of high-dose, high-energy ionizing radiation for a variety of industrial processes has become a common global practice. Radiation-induced modifications improve important qualities of packaging materials, plastic films, protective insulation on wire and cables. Possibly the major use of high-dose irradiation is the sterilization of disposable, single-use medical products (*e.g.*, syringes, bandages, sutures). A related application is the irradiation of food products to reduce pathogens (e-coli, salmonella, listeria, etc.), this with the purpose of dealing with the risks of food-borne illnesses. In addition, high-dose irradiation is also used in agricultural pest control. All these mentioned applications require the provision of reliable, low-cost, readily-available dosimeters to support radiation- processing applications by assuring that the absorbed dose to the product, often prescribed or limited by regulatory agencies, is traceable to national measurement standards.

Poly (Lactic-acid) hereafter PLA, is one of the plastics that have significantly increased its worldwide presence (Carus 2017). This polymer is nowadays widely used by the food-packing industry to encase fresh foodstuff. In addition, PLA is employed in the manufacturing of diverse biomedical devices used in surgical repairs, drug-delivery systems, and tissue engineering (Gupta 2007). Given the fact that many of these objects are made of PLA (*e.g.* foodstuff boxes), and some are exposed to high radiation treatments (mainly for sterilization purposes), in the present paper we are considering that these irradiated objects could be concurrently used as self-dosimeters. Therefore, the intention of the present study is to evaluate the suitability of PLA as a high-dose Electron Paramagnetic Resonance (EPR) dosimeter.

The fundamental block of PLA is lactic acid, which is found in two enantiomeric forms D and L which are optically active (Fig. 1). The properties of PLA vary depending on the content proportion of its enantiomers D or L, in a given sample. Since the world production of the material comes from starch, obtained from vegetable products, the most common variety found in the market is that with a high levorotatory PLA content, *i.e.* PLA-L. One of the world's largest producer of polylactides is currently NatureWoks™ which markets PLA under the brand INGEO®. Among its products we have chosen for our experiments, PLA Biopolymer 2003D®

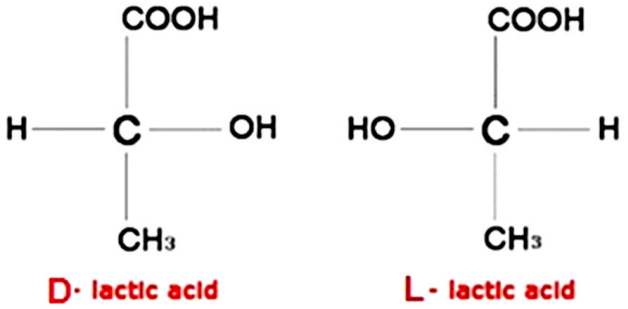

FIGURE 1. Chemical structure of lactic acid enantiometers.

PLA-L. This polymer is currently used for packaging fresh foodstuff and for food serviceware (Ingeo, 2003).

In this work our objective is to evaluate the possibility of using PLA Grade 2003D® as a high-dose dosimeter. For this purpose we have investigated the relevant dosimetric characteristics of EPR response of PLA to Co^{60} gamma radiation: the signal amplitude dependence on gamma dose, zero-dose response, dose threshold, signal fading, reading repeatability, batch homogeneity and signal stability when exposed to simulated sunlight. In addition, we have identified the free radical responsible for the EPR signal.

2. Material and Methods

2.1. Samples and Irradiation

PLA-L samples (polymer 2003D, Natureworks™), consisted of strips: 1 mm thick, 30 mm long and 3 mm wide, directly cut off from fresh food containers supplied by PLAFUSA Mexico.

Irradiations were performed using a Co^{60} gamma ray source (Transelektro LGI-01). Samples were open-air irradiated in PE sample vials, SCIENCEWARETM. To establish its dose rate, a Farmer ionization chamber model 2570 was used to calibrate the rate. The dose rate value turned out to be 1.153 kGy/h. Radiation exposures to which the PLA samples were subjected ranged from 0.1 kGy, up to 600 kGy.

Samples batches were selected as follows: to establish the calibration curve, 5 sample batches per irradiation. For batch homogeneity evaluation, 20 samples were irradiated at a dose of 200 kGy; for signal fading appraisal, 8 samples were irradiated at a dose of 100 kGy and 15 other samples, irradiated at the same dose were employed for stability studies. A set of 5 samples was not irradiated to measure the zero-dose signal response. To investigate signal stability to sunlight, an additional 10 sample batch was irradiated at a dose of 100 kGy and subsequently, 5 of these samples were exposed to a solar light simulator model 16S-150-007 (Solar Light Company, Inc.) at a controlled temperature of 25°C. The first sample was exposed 1 hour, the next one 2 hours and so on till the last sample was subjected to a 5 hours expesure For comparison purposes, the other five irradiated samples were kept stored at the same regulated temperature. To determine the dose threshold five samples per dose were irradiated in a range of 0.1 kGy to 1 kGy.

2.2. EPR readings

The EPR measurements were made immediately after irradiations of samples and were done with a Varian E-15 EPR Spectrometer operating at X-band microwave frequency. The relative concentration of the free radicals produced in the irradiated samples was compared with that of a standard synthetic ruby sample. A dual-resonance cavity (Varian E-323) operating in the TE104 mode was used for this purpose. Double integration of the derivative of the absorption spectra was used to obtain areas under of the absorption signal. One cavity held the standard S and the other the sample D. In this way, the relative concentration of spins in irradiated samples can be evaluated by comparing the ratio of the areas under the absorption signals (D/S) regardless of possible variation in the spectrometer sensitivity.

EPR operational settings were: central magnetic field 330 mT, microwave power 2.0 mW (nominally 1.0 mW per cavity), modulation frequency 100 kHz, magnetic field modulation amplitude 0.1 mT, scan range 40 mT, scan time 8 min and time constant 3.0 s. The received gain parameter was adjusted to optimize EPR signals. All EPR signals were obtained at room temperature and recorded as first derivatives of the absorption spectra.

3. Results and Discussion

3.1. EPR spectra

Figure 2 shows a representative spectrum of irradiated PLA at 200 kGy (solid line). In principle, it can be observed that the spectrum apparently consists of either: a broad line with a small singlet at its middle or else, a pair of closely intersecting lines. However a pair of previous studies (Babanaldi, 1995, Nugroho, 2001) suggests that the only free radical that has a relative long life at room temperature (in vacuum irradiated PLA samples), is derived from H atom abstraction from the quaternary carbon atom (see Fig. 3). As shown in the cited previous studies, this radical produces a well-defined narrow-line EPR quartet whose presence is not evidently discernible in our experimental spectrum (see Fig. 2).

However, for a start, we can presuppose that the same radical species is formed in our air irradiated samples. To check the possibility of this assumption, we performed computer simulations of spectra assuming that the signal is indeed

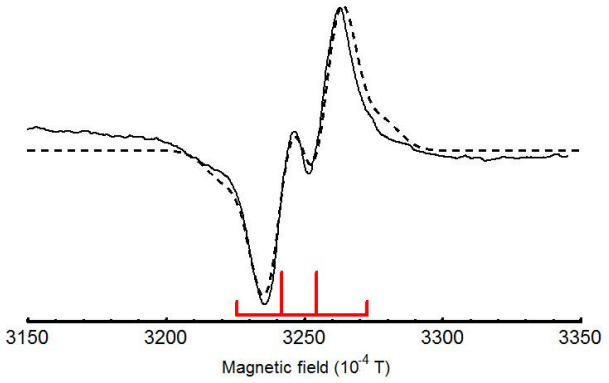

FIGURE 2. Representative EPR first derivative absorption spectrum of gamma–irradiated PLA at 200 kGy (solid line) and simulated spectrum (dashed line).

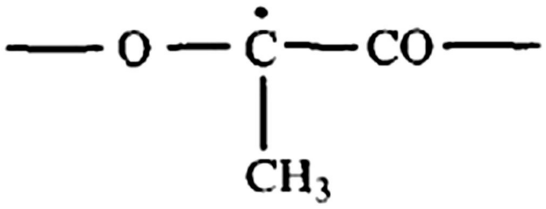

FIGURE 3. Radical formed by Hydrogen abstraction. (Babanaldi, 1995, Nugroho, 2001).

produced by the aforementioned free radical. In this case considering second-order hyperfine coupling, resonance fields are given by second order perturbation theory as (Carrington and Mclachlan, 1967),

$$H = H_0 - (A/g\beta)m - \left[\frac{(A/g\beta)^2}{2H_0}\right] \times [I(I+1) - m^2 + m(M-1)] \quad (1)$$

where H is the resonance field in mT, H0 is the central field in mT, M, m are electron and nuclear spin magnetic quantum numbers, with spins S and I respectively with allowed transitions $\Delta M = \pm 1$ and $\Delta m = 0$. Figure 2 shows the simulated spectrum (dashed line). A hyperfine coupling constant ($A/g\beta$) of 2.3 mT, with a Gaussian linewidth of 0.87 mT, were used to adjust the four-line signal simulation (Intensity ratio of 1:3:3:1) to the experimental spectrum. For clarity, the resultant "stick bar spectrum" shown in Fig. 2 was placed under both spectra. The coupling constant is in good agreement with the previously measured value for the hyperfine constant obtained for y-irradiated PLA samples, irradiated under low vacuum conditions (0.1 mPa). (Babanaldi, 1995, Nugroho, 2001). This good agreement allows us to infer that in both cases we are in the presence of the same free radical.

Nevertheless we must remark that the Gaussian line width (0.85 mT) obtained in the present work, (equivalent to a $\Delta Hpp = 1.44$ mT), is much larger than the value previously reported of $\Delta Hpp = 0.35$ mT by Babanaldi (Babanaldi, 1995). This large difference is due to the fact that our samples were irradiated in open atmosphere while in the two previous studies, samples were irradiated and recorded under low vacuum conditions (0.1 mPa) (Babanaldi, 1995, Nugroho, 2001).

On other hand, linewidth is influenced by the interaction of the electron spin with its environment inside the sample. In our case a possible cause for the observed line broadening could be that molecular rearrangements due to an oxidative degradation process are responsible for producing local field variations that distribute resonance frequencies over a broader range (Weil *et al.* 1994). Yet, finding the exact origin of the observed line broadening is a complex task and does not fall within the scope of the present work. It will be subject of future research.

3.2. Gamma-irradiation response

EPR spectra of the five batch un-irradiated PLA samples, recorded at the spectrometer maximum receiver gain (8×10^4) showed no discernible zero-dose signals. The dependence of the EPR signal intensity of gamma-irradiated PLA samples as function of the absorbed dose is shown in Fig. 4. Figure 5 shows the same data as logarithmic plot.

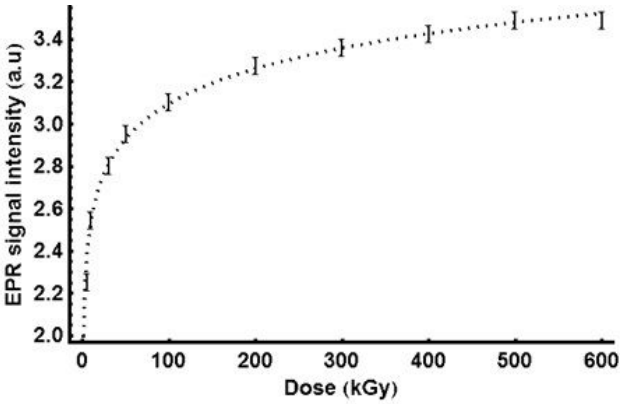

FIGURE 4. EPR signal intensity of irradiated PLA versus absorbed dose.

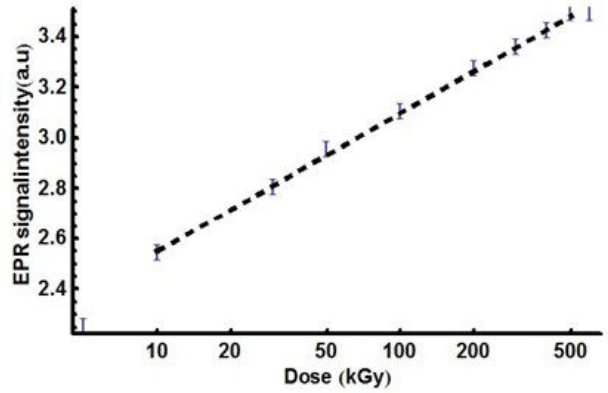

FIGURE 5. EPR signal intensity of irradiated PLA versus the logarithm of absorbed dose.

3.3. Signal Fading

The stability at room temperature of the gamma-induced free radicals in the PLA samples was studied by periodically measuring the signal intensity of a set of eight samples irradiated at 200 kGy. Each one of the eight sample batch was monitored in turn immediately after its irradiation over a period of 24 hours. To minimize error produced by sample repositioning in the cavity, the sample being measured was not removed from the cavity during the whole period of study. The relative humidity during this time interval varied from 45 to 65%. Signal fading results are shown in Fig. 6. As can be noticed, the free radicals produced have medium term stability at room temperature. Figure 7 shows the fading correction factor graph. Experimental fading points were adjusted to a Bézier curve, choosing the 2 hrs. and 24 hrs. points as its two fixed extremes.

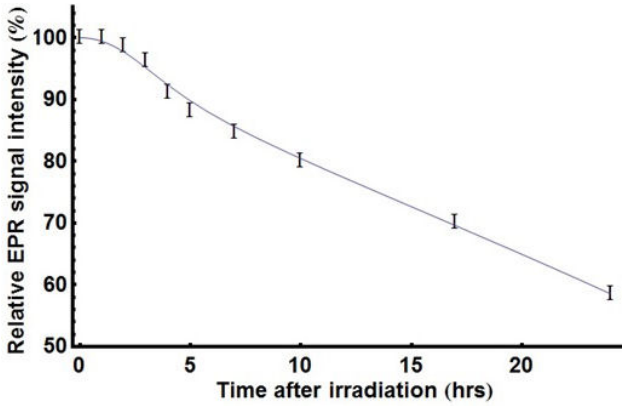

FIGURE 6. Signal fading of PLA samples irradiated at 200 kGy and kept at room temperature.

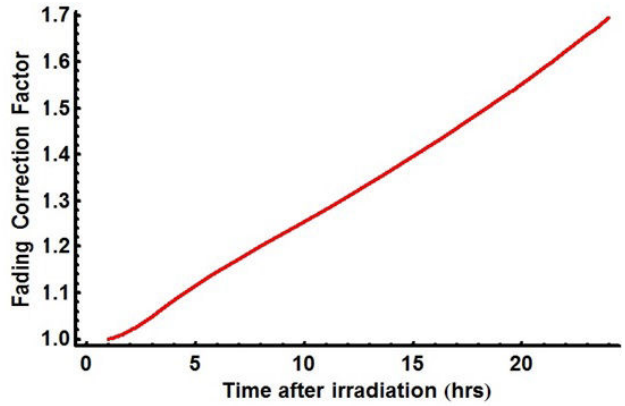

FIGURE 7. Signal fading correction factor.

3.4. Repeatability

The repeatability of the EPR signals indicates the dispersion of the results of repeated measurements carried out under the same conditions. This parameter was evaluated by selecting at random one irradiated sample and 20 replicate measurements of its signal. The sample was reinserted at a different random orientation and the spectrometer parameters reset after each spectrum was taken. As can be seen from Fig. 8, all the readings but one, were within $\pm 2\%$ of the mean.

3.5. Batch homogeneity

The batch homogeneity can be expressed as the standard deviation of the mean value of the samples in the batch (Ranogajec-Komor, 2003). This parameter, also known as inter-specimen signal variation, was determined using 20 samples irradiated at 200 kGy under the same conditions. Their spectra were then recorded under identical conditions. The standard deviation of the results was found to be 1.6%.

3.6. Detection limit

The detection limit is defined as the lowest absorbed dose that produces an EPR signal. From the signal to noise ratio and

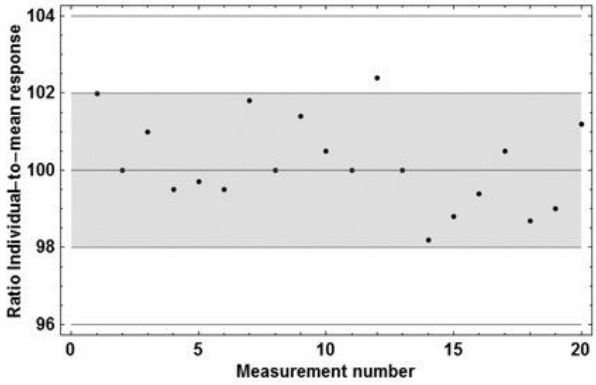

FIGURE 8. Scattering of 20 recordings of the EPR-signal amplitude of a PLA sample irradiated at 200 kGy.

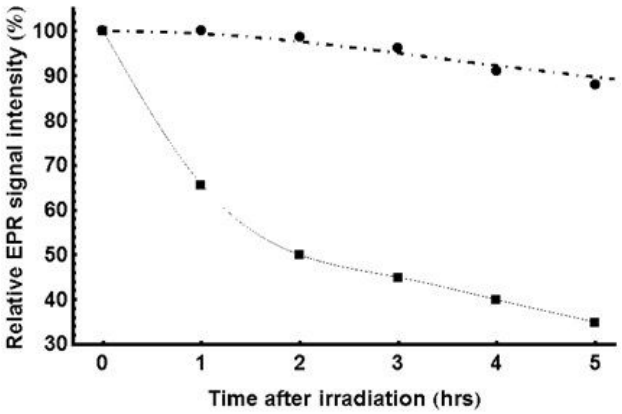

FIGURE 9. Fading curves: exposed to solar simulated light (squares) and non-exposed (dots).

and the calibration curve, the minimum detection limit was obtained, the value of which was revealed to be 0.5 kGy.

3.7. Signal fading under simulated sunlight exposure

The purpose of exposing irradiated samples to simulated sunlight, was to investigate the dosimetric stability of irradiated PLA, which, in the case that irradiated samples were stored out in the open, its received dose can still be assessed if dose corrections can be applied. The commercial equipment used for our investigation is designed to examine the effect of solar radiation on samples at the surface of the Earth. Samples were exposed in accordance to IEC 60068-2-5 (ISO, 2010). Figure 9 shows a comparison of the fading curve of samples irradiated at 100 kGy and subsequently exposed to a solar light simulator, together with the curve for non-exposed samples but irradiated at the same dose.

3.8. Comparison to other dosimetric systems

Table I shows a comparison of PLA-EPR system with other selected currently used high-dose systems. In this table it can be viewed that the proposed system offers the highest upper limit (5×10^5 kGy). One disadvantage with respect to the

TABLE I. Dosimetry systems in present practice versus PLA-EPR system.

Dosimeter systems	Method of analysis	Measurement lapse after irradiation	Useful dose range Gy	Nominal Precision limits	References ISO / ASTM
Fricke solution	Uv-spectro-photometry	immediately	$3 \times 10^1 - 4 \times 10^2$	1%	E 1026-04
Perspex systems	Vis- spectro-photometry	24 h	$1 \times 10^3 - 5 \times 10^4$	4%	51276
Calorimetry	Resistance/temperature	immediately	$1.5 \times 10^3 - 5 \times 10^4$	2%	51631
Alanine	EPR spectroscopy	months	$1 \times 10^0 - 1 \times 10^5$	0.5%	51607
PLA	EPR spectroscopy	Within an hour	$5 \times 10^2 - 5 \times 10^5$	2%	This work

the alanine-EPR system is that the PLA-EPR system must be measured preferably within an hour after exposure to avoid applying fading corrections. However, this disadvantage does not hamper PLA use as a dosimetric system. As can be seen in Table I, there are some other dosimetric systems whose reading should be done as swiftly as possible or even at the moment of exposure. Fast fading of PLA under direct solar light exposure is neither a setback, as sunlight can always be blocked by covering dosimeters inside envelopes. It is pertinent to remark that currently used PERSPEX systems must also be isolated from sunlight. Regarding the accuracy of the PLA-EPR system, this is comparable with other systems.

Finally, we must warn that at high doses PLA becomes fragile and brittle since its mechanical properties degrade. This is due to the fact that under irradiation at doses greater than 60 kGy, the polymer chains break down into shorter sections and smaller structures (Madera-Santana *et al*. 2016). So irradiated PLA should be handled with some care.

4. Conclusions

As part of our Institute's program on high-dose assessment, we have made a complete dosimetric outline of commercial PLA, a material of widespread use for packing purposes, with the purpose of evaluating its possible use as a high-dose dosimeter.

This work has confirmed, by the use of EPR spectroscopy that gamma-irradiation of PLA samples gives rise to the formation of a free radical, namely that resulting from hydrogen abstraction from methine groups located on the backbone of the polylactic acid chain.

Results here presented, indicate that EPR signal response of PLA samples as a function of the absorbed dose is linear in a logarithmic scale graph within a wide range of values (10 to 500 kGy). Other dosimetry characteristics, here reported, show that EPR-PLA system has promising potential to be used as a self-dosimeter for high-doses. However, it must be pointed out that, due to the limited stability of the free radical ions to u.v. radiation (simulated solar light), it is reminded to avoid exposing samples to direct sunlight and to perform measurements within an hour after exposure.

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