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An attempt for application of γ-irradiated poly glycolic acid (PGA) as new solid state/ESR dosimetry system

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ABSTRACT

In several laboratories all around the world, electron spin resonance (ESR) dosimetry is a well-established reference dosimetric system in industrial applications of ionising radiation, and its use is also proposed in radiation therapy and accident dosimetry. In the present experimental work, PGA solid state dosimeters (SSD) has been investigated using ESR Spectroscopy to study the gamma radiation response of this material and to evaluate its dosimetric characteristics: dose response, room temperature fading, Heat treatment effect during post-irradiation storage. Results obtained up to now confirm that PGA seems to be suitable material for ESR dosimetry.

KEYWORDS

Dosimetry;
Solid state dosimeter (SSD);
Poly glycolic acid (PGA);
Electron spin resonance (ESR);
Post-irradiation thermal treatments;
Fading behaviour.

INTRODUCTION

Electron spin resonance (ESR) Electron or paramagnetic resonance (EPR) spectroscopy has been the standard technique in the characterization of radicalic species, their stabilities and decay kinetics. Semiconductors and polymers are examples of materials that have been studied by EPR spectroscopy through the detection of paramagnetic species[1-3]. It has therefore been the main experimental technique in understanding the effect of ionizing radiation on polymers. Radiation-induced radicals, provided that radicals having long-term stability can be used in the establishment of radiation dose-radical concentration relations.

The more used material in Dosimetric applications[4-6] for EPR dosimetry is the alanine due to its good dosimetric properties, such as sensitivity, stability of the EPR signal with time[6]. Alanine has been accepted as standard and reference radiation dosimeter material by International Atomic Energy Agency (IAEA), its sensitivity however is not high for low doses.

In radiation technology applications, it is very

important to adjust precise and accurate integral dose and dose rate. Many attempts to characterize a new material[7-9] has been discussed and have shown that they have great potential of ESR dosimeters they are more sensitive than conventionally available ones. The new material should have a stable radical per radiation energy; a sharp linewidth and thermal stability at room temperature.

Nevertheless, there are present investigations to find new materials with better radiation sensitivity to substitute alanine[10-12]. One of these new materials already studied by X-Band EPR measurements is Poly Glycolic Acid (PGA) used for many years in medical and surgical applications[13-16]. The molecular structure of PGA and the free radicals formed by its interaction with radiation are shown in Figure 1. The free radical produced by radiation in PGA which is predominant at room temperature is the molecular species -CH°—COO- Radical I[13]. In ESR Spectrum it's traduced by a doublet signal (Figure 2) and it is formed by Hydrogen abstraction from a Methylene group located adjacent to Carbonyl group in the polymer backbone[13]. At room Temperature there is essentially no contribution to the spectrum from radicals II and III.

In spite of its good dosimetric properties, PGA may be applied to dosimetry in radiotherapy. One of the goals of the present work was to analyze the response of PGA dosimeter for possible application in ESR dosimetry.

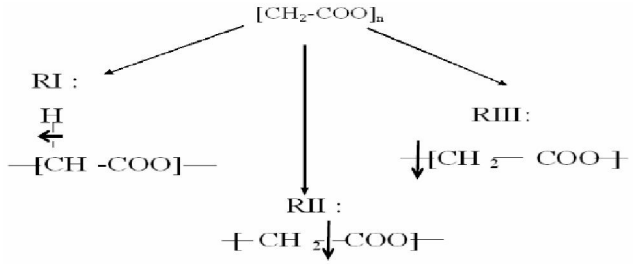

Figure 1 : Molecular structure of PGA and the most probable free radicals formed.

EXPERIMENTAL

Poly glycolic acid polymer

Poly Glycolic Acid was obtained from Boehringer Ingelheim of Germany. The characteristics of the materials, according to the supplier, are given in TABLE 1.

TABLE 1 : Physical and chemical proprieties of PGA

Polymer	Melting Point (°C)	Glass Transition (°C)	Approximate Strength	Processing Method
Polyesters: Poly(Glycolic Acid)	225-230	35-40	7.0 GPa (Modulus)	E, IM, CM, SC

E = extrusion, IM = injection moulding, CM = compression moulding, SC = solvent casting

Irradiation

The irradiations have been performed in air at the Tunisian semi-industrial ^{60}Co gamma-irradiation facility[17]. The dose rate was established with the alanine/ EPR dosimetry system in term of absorbed dose traceable to the National Physical Laboratory, UK. Before the experiment the dose rate was verified by the standard Fricke dosimeter. Three dosimeters were irradiated for each point of measurement.

EPR measurement

EPR measurements at 9.837 GHz (X-band) were performed at 25 °C using an EMX Bruker spectrometer. The microwave power used, 316 mW, were determined by considering the saturation properties of PGA EPR lines at 25°C. The samples were accommodated in quartz sample tubes and kept up from the bottom. The different EPR spectra presented in this paper have been normalized to the same receiver gain (10^3) and sample weight (mg) in order to get quantitative comparison of the EPR lines intensities between the different samples. All samples were fixed in the cavity center and flat ones were oriented to lie in the cavity nodal plane. In the present work it is thus very difficult to compare theses spectra to determine the absolute number of radical spins. Then, in this study, we will only use arbitrary units (arb.u.) to analyze the evolution of Radical concentration in PGA Polymer content as a function of the integrated dose.

Determination of important EPR parameters

The PGA dosimeter was fixed in the cavity and measured 30min after switching on the EPR spectrometer. Every spectrum was recorded in about 61 s and delay time was 300 s. Microwave power, modulation amplitude, time constant, conversion time and modulation frequency were also studied, but are not shown here in detail. The operating EPR parameters were

set as following: center magnetic field 351.5 mT, sweep width 5 mT, microwave power 316 mW, modulation amplitude 1G, modulation frequency 100 kHz, time constant 163. 84 ms and conversion time 60 ms.

RESULTS

ESR spectra of gamma- irradiated PGA

Before gamma-irradiation, the PGA used in this study has small signal at about 348mT which can be related to impurity in PGA matrix. The X-Band EPR spectra were subsequently recorded at R.T. (Room Temperature, 25°C). The resulting EPR spectrum of PGA sample after exposure to 25 kGy is shown in Figure 2. All PGA samples, regardless of radiation dose produced similar EPR spectra varying only in the intensity of the observed signals.

The radiolytic degradation mechanism of PGA and it's copolymers due to irradiation of samples has been investigated previously[13,18-20] and it's well known that chain scission processes dominate at low temperature. This results in a wide range of relative primary and secondary radical species which are visible by EPR. However at temperatures (R.T.), as in ambient conditions studied here, Hydrogen abstraction reaction by the primary radicals occurs extensively at secondary C-H bonds on the polymer backbone. This produces a narrower range of relatively stable radicals, such as -CH°-COO- which is visible at ambient temperature (25°C)[13].

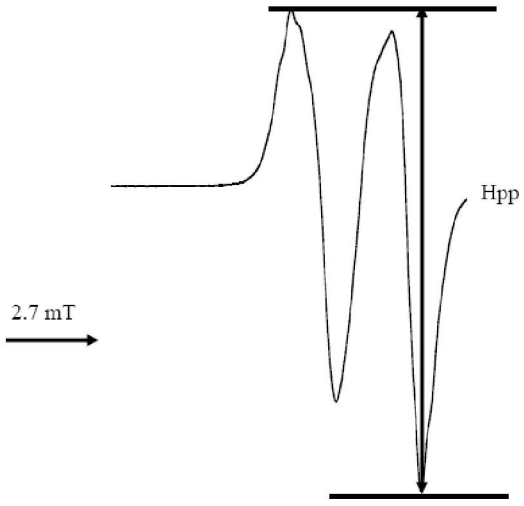

Figure 2 : Peak to peak higher (Hpp) of ESR spectra related to PGA irradiated at a dose of 25 kGy.

Dose response

In order to find out the useful dose range for this Polymer, the response curve (specific higher Peak to Peak (Hpp) versus dose) was measured in the dose range 0.1–200 kGy (Figure 3). All data for the dose response curve were immediately acquired after irradiation. As expected in (Figure 3) the radical concentration increases linearly as function of applied dose in the dose range 0.1–200 kGy with the linear regression coefficient better than 0.99 (Figure 3). At higher doses the specific Hpp continued to grow slowly up to 200 kGy which was the upper dose level of the present experiments. The PGA response had not yet reached saturation at this dose level. There was linear growth of the Hpp as function of the dose because at room temperature only one radical contribute to the ESR spectrum which is formed by hydrogen abstraction (Figure 1) RI -CH°-COO-[13]. In the dose range 0.1 to 10kGy there was also linear growth of the Hpp as function of the dose see (Inset Curve).

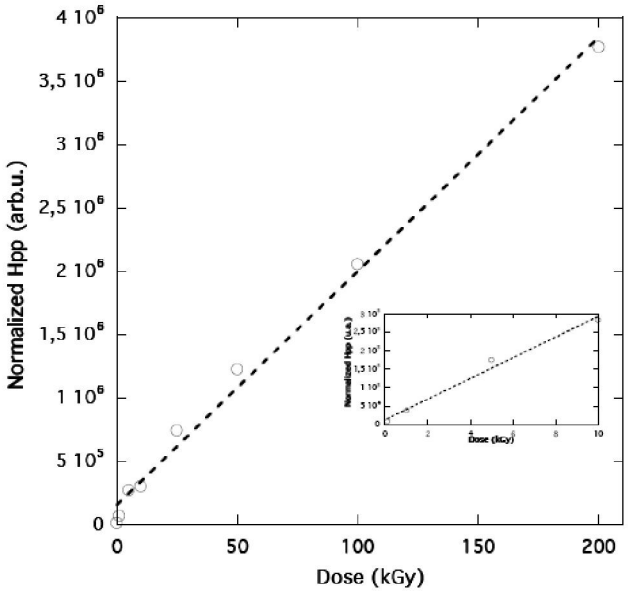

Figure 3 : Dose response curve of PGA dosimeter in the dose range of 0.1–200 kGy, experimental (°) and calculated by a linear function (dashed line).

Post-irradiation stability

As a transfer dosimetry system, it is very important to have good stability after irradiation. There are many factors that affect post-irradiation stability such as temperature, humidity, dose, light, crystallization degree[13].

Fading characteristics of radical concentration at room temperature

The main disadvantage presented by majority types of dosimeters is the undesirable strong post-irradiation fading at room temperature. In order to examine the stability of radical, three replicate samples PGA were irradiated with ^{60}Co gamma rays to 25 kGy. After irradiation PGA samples were stored at room Conditions: 25°C, 40-60% RH (RH, Relative Humidity). The resulting radical concentration was then followed up to 60 days via ESR technique.

The result concerning long-term room temperature variation in signal intensity was given in Figure 4. The signal intensity was found to be non stable at room temperature in the range of storage time. A function was used to fit signal intensity decay as shown in Figure 4. The coefficient of correlation (R^2) was 0.999. The stability of radiation-induced radical at room temperature was mainly controlled by the fading process. This fading process seems to follow a simple first-order kinetic. All fitting parameters are presented in TABLE 2.

$$y = y_0 + a\, e^{(-xk)} \quad (1)$$

Where k is the first order decay rate constant.

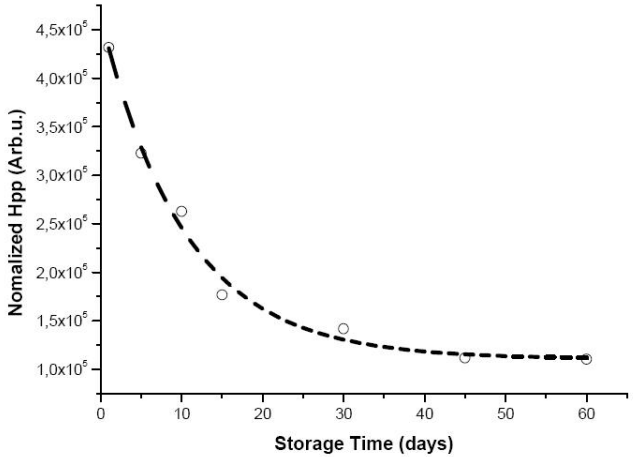

Figure 4 : Experimental and calculated ESR signal intensity decay curves for PGA irradiated at a dose of 25kGy and kept at room temperature. Symbol (experimental) and dashed line (theoretical, calculated by a function describing first- order kinetic).

To overcome the problem of the undesirable strong post-irradiation fading at room temperature. The heating at 140°C for 35 minutes was found to be the most suitable procedure to stabilize the irradiated PGA dosimeter. This procedure did not affect the metrological properties (reproducibility and useful dose range) of the PGA dosimeter.

TABLE 2 : Calculated parameters for a first- order kinetic describing the decay curves of PGA irradiated at a dose of 25kGy.

Fit parameter	Value
y_0	110829,999
a	352107,206
k	0.096
R^2	0.999

Effect of post-irradiation heat treatments on radical concentration at room temperature fading

The effect of post-irradiation heat treatments on the PGA response fading was studied in the temperature range of 60–140 °C using sets of three PGA samples. After gamma irradiation with 25 kGy absorbed dose, samples sets were immediately submitted to the different heat Treatments for 35 min, which was found to be the best treatment time, and stored after irradiation under room condition. ESR measurements were carried out up to 45 days. The radical concentration values were normalized to the first measurements taken 5 min after the heat treatments. The results are presented in Figure 5. The best results have been obtained with heat treatments at 140 °C (35 min). This procedure is very effective for the removal of unstable entities responsible for the strong fading. The standard deviation of PGA dosimeters response measurements is about 1% (1σ)

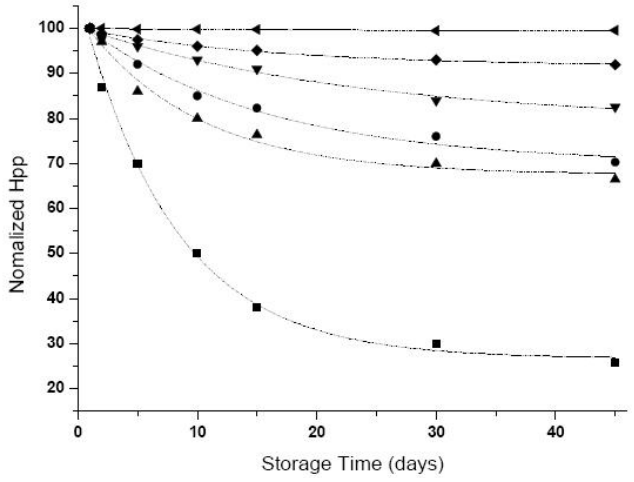

Figure 5 : Variations of the ESR signal intensity with storage time for PGA samples irradiated at a dose of 25kGy and kept at different temperatures: RT (■), 333K (▲), 353K (●) 373K (▼) 393K (◄) 413K (◆); calculated by a function describing first-order kinetic (dashed lines).

within the first 1 day after irradiation. After the heat treatment performed at 140 °C, the response decay of irradiated PGA is about 3% between the first day and 45 days. This means that PGA dosimeters can be evaluated anytime after irradiation and heating.

The decay behaviours at the higher temperatures have been attributed to the semicrystalline nature of PGA, which will influence the mobility of the polymer chains, particularly in the crystalline and crystalline amorphous boundary regions[13]. The fact that most of the radicals formed in PGA decay well below the melting temperature of the crystallites suggests that they are formed in the amorphous regions of the polymer.

CONCLUSION

A PGA has been investigated with ESR technique in order to evaluate this potential as radiation-sensitive material for dose measurements. The response curve was measured in the dose range 0.1 kGy– 200 kGy. The results demonstrated that the influence of post-irradiation storage on the ESR/PGA response might be very significant. The heating at 140°C for 35 minutes was found to be the most suitable procedure to stabilize the irradiated PGA dosimeter. From the detailed studies we conclude that the PGA dosimeter has the potential to be used as a transfer dosimetry system particularly ^{60}Co γ-ray.

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