INVESTIGATION OF PBAT DOSIMETRIC PROPERTIES FOR HIGH GAMMA DOSE DOSIMETRY

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ABSTRACT

Poly(butylene adipate-co-terephthalate) (PBAT) is an aliphatic-aromatic copolyester which is biodegradable. It is a non-photoluminescent copolyester that becomes photoluminescent after previous exposure to gamma doses higher than 100 kGy. After the previous high energy irradiation, the material shows the highest photo-stimulated luminescence emission when excited with a LED source at wavelengths ranging from 370 to 405 nm. In this work we investigated the enhancement of the photoluminescence (PL) and dosimetric properties of PBAT, after exposure to high doses of gamma radiation ranging from 50 to 4,000 kGy. In this investigation we demonstrate that increasing the PBAT film thickness by 100 μm enhances the PL output by 3.5 times, when irradiated with 500 kGy. Also, besides the already known color green brightness, the PL intensity can also be used for high dose dosimetry purposes for doses ranging from 50 to 750 kGy. The FTIR analysis has demonstrated that the there is a linear relationship between peak intensity and dose for doses ranging from 100 and 2,000 kGy for the absorbance peaks at 3,241 cm^{-1} and 3271 cm^{-1}, with linear correlation coefficients of 0.9981 and 0.9992, respectively. The results indicate that PBAT has great potential for applications in bio-imaging devices and high gamma dose dosimetry.

1. INTRODUCTION

High dose dosimetry systems are generally required to achieve international standards in determining the dose distribution patterns and the delivered absorbed dose over a wide range of industrial products and process which make use of ionizing radiation. Examples can be found in food irradiation, surgery devices sterilization and gemstone treatment. However, most of the commercially available standard reference high dose dosimeters find application only for very limited dose ranges and radiation qualities, as for instances alanine-EPR and calorimetric systems (IAEA [1] and ISO [2]).

Polymer-based dosimetry systems have been employed in high gamma dose dosimetry for more than 60 years [3–6]. Some examples are polyester, vinyl and acrylate based dosimeters. The most frequently studied copolyester is poly(butylene adipate-co-terephthalate) (PBAT), which is biodegradable. Widely known as Ecoflex®, their typical applications are in the

production of compost bags for organic waste, films in the agricultural sector and coating materials for starch-based products (e.g., plates), within the fast-food and catering industries. Recently, we have chosen Ecoflex to perform an investigation about its radio degradation after exposure to high gamma doses. Particularly, we were interested in polymeric materials that show an unambiguous relationship between optical absorption and the delivered gamma dose, or even radio-induced photoluminescence features, for applications in high dose dosimetry [7].

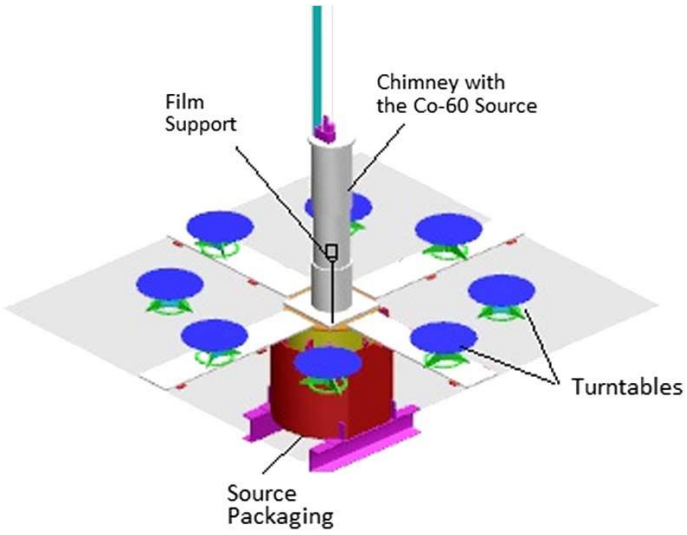
In this work we report the investigation about the improving of the radio-induced photoluminescence (PL) regarding to the thickness increasing of PBAT films and also to the infrared absorbance variation of two radio-induced peaks, both applied to radiation dosimetry. We shall see in this report that it is possible to hardly enhance the PL output by increasing the film thickness and an interesting possibility of using infrared absorption spectrometry applied to high-dose dosimetry.

2. Experimental

Films of PBAT were prepared from commercial resins named Ecoflex (BASF-Brazil) (Fig. 1, left) by "casting" from trichloromethane at room temperature. The process is performed by using the "wire-bar coating" technique that allows producing good samples in the form of transparent films (Fig. 1, right), with thickness varying from 4 to 64 μm, depending on the chosen wire rod. The device also allows the production of films with several layers in order to investigate the PL output as a function of the number of layers.

Figure 1: PBAT pellets as purchased from Basf-Brazil (left) and transparent PBAT film samples prepared by casting from trichloromethane using the "wire-bar coating" technique.

The samples were irradiated using a Co-60 gamma ray source at a constant dose rate (12 kGy/h), with doses ranging from 0.0 to 4.0 MGy, as shown in the schematic drawing–irradiation setup bellow.



Schematic drawing–irradiation setup.

The photoluminescent signal was produced by exciting samples with a LED light source (405 nm). Optical emission spectra were collected in a USB2000 Ocean Optics spectrometer. FTIR spectra were collected in a BOMEM 100 spectrometer for wavenumbers ranging from 350 to 4000 cm.

3. Results and Discussion

3.1. Photoluminescence of PBAT

The radio-induced photoluminescence features of PBAT has been reported by Schimitberger T., et al. (2014) [7]. In a first step the PBAT film is exposed to high gamma doses. In a second step, the polymer is excited with a 405-nm LED source and shows a high quantum yield of photo-stimulated luminescence. In this sense, unlike scintillator materials, it occurs that, after the gamma irradiation process, PBAT copolymer is transformed into a PL material. Until nowadays it is considered the only biodegradable photoluminescent aliphatic-aromatic polymer. The PL output can be observed exciting the films with wavelengths ranging from 320 to 420 nm. However, the maximum PL output is obtained when the excitation is performed at 405 nm.

The mechanisms behind the radio induction of the photoluminescence phenomenon in PBAT copolymers involves the production of aromatic amines by the attachment of NH_2 molecules in the aromatic hydrocarbons present in the main chain, via chain scission [7].

For comparison purposes, the photoluminescence of a PBAT film 70 μm thick, irradiated with 1.0 MGy and pos-exited at 405 nm, is seven times higher than the PL of the well-known MEH-PPV films excited and measured at the same conditions. The radio-induced PL in biodegradable PBAT is a very interesting result because it involves the development of a new cheap biodegradable photoluminescent polymer, which may have applications in biological imaging.

Figure 2 displays the PL emission spectra for 70 μm thick PBAT films irradiated with gamma doses ranging from 100 to 1750 kGy and also for pristine PBAT. It is observed an increasing PL output at 490 nm for increased gamma doses. For gamma doses bellow 100 kGy the PL signal is practically undetectable. The PL emission at 490 nm gives to the film a very dark

green color when irradiated with 100 kGy. This dark green color is gradually transformed into a very bright green (1.75 MGy) as the gamma dose increases. This feature permits to create a green color legend associating its intensity with the applied gamma dose [7].

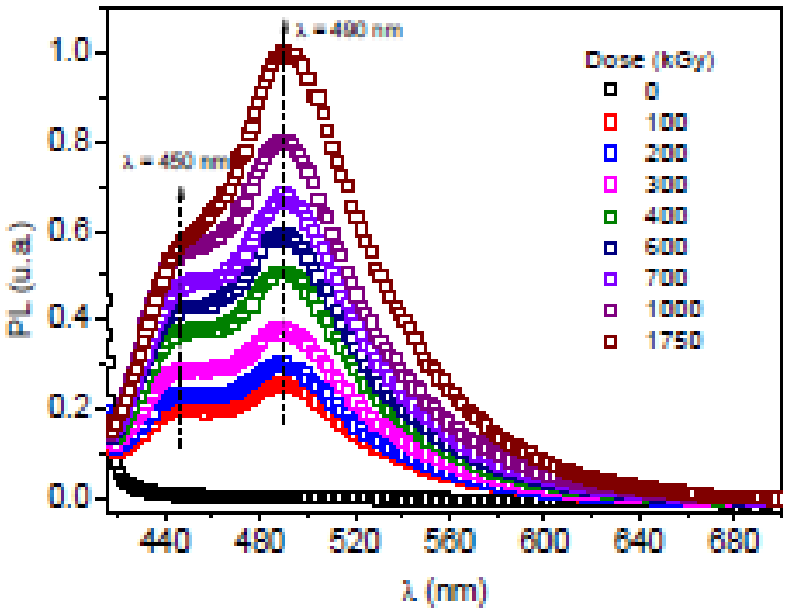


Figure 2: Photo-stimulated luminescent emission spectra of Ecoflex excited with a LED source at 385 nm, for doses ranging from 0.0 to 1.75 MGy.

In order to investigate the relationship between PL output and film thickness we have produced films with 3 layers (38 μm thick), 4 layers (49 μm), 5 layers (61 μm), 6 layers (75 μm), 7 layers (106 μm) and 8 layers (130 μm) by using the *wire-bar coating* technique. In Fig. 3 we display the PL intensities at 490 nm provoked by photo-excitation at 405 nm, for gamma doses ranging from 50 kGy to 750 kGy. We see that, for the sample with thickness of 130 μm and irradiated with 500 kGy, the quantum yield of photo-stimulated luminescence increases around 3.5 times. Also, we see an important feature in these curves: the unambiguous relationship between dose and PL intensity for all thickness and dose range studied, except for sample with 130 μm irradiated with 750 kGy. In other words, besides the color green brightness [7], the PL intensity can also be used for high dose dosimetry purposes.

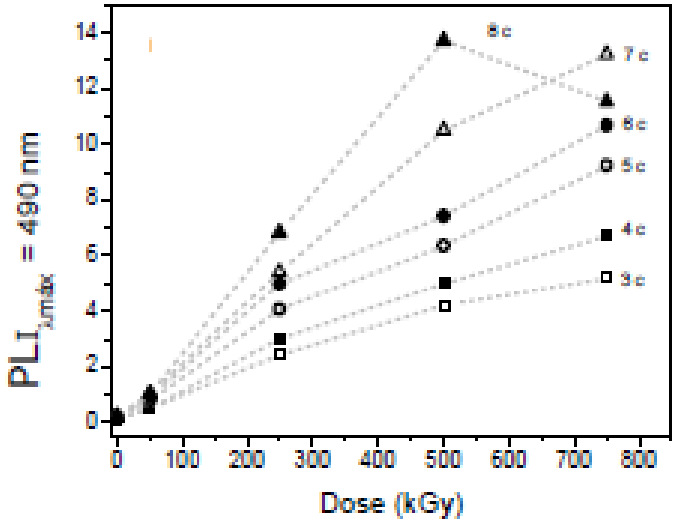


Figure 3: PL output as a function of gamma doses for samples with with 3 layers (38 μm thick), 4 layers (49 μm), 5 layers (61 μm), 6 layers (75 μm), 7 layers (106 μm) and 8 layers (130 μm), produced by using the *wire-bar coating* technique.

3.2. FTIR Analysis

As observed before, polymer-based dosimetry systems have been employed in high gamma dose dosimetry for more than 60 years. Particularly, radio-induced absorbance peaks in the UV-Vis and IR region have been reported to have unambiguous relationship with gamma doses in the range of 1.0 kGy to 1,000 kGy [8-10]. The same relationship has been observed for gamma doses and the melting latent heat associated to the disruption of the crystalline volume in these semi-crystalline polymers [11].

In this work, besides the PL features associated with high dose gamma dosimetry, we intended also to investigate the behavior of the absorption peak intensities in the infrared region with respect to the delivered gamma dose. Thus, we collected the FTIR spectra of the irradiated PBAT films, previously used to the photoluminescent study. The FTIR spectra for pristine PBAT film and films irradiated with gamma doses ranging from 100 kGy to 4,000 kGy are displayed in Fig. 4. For clarity purposes, the spectra are plotted for wavenumbers ranging from 3,000 cm^{-1} to 3,800 cm^{-1}. We note the appearing of a wide radio-induced peak at 3,256 cm^{-1}, which gradually increases for increased gamma doses. This absorption peak is attributed to the antisymmetric stretch vibration of NH_2 molecules. These molecules are created after the radio-induced chain scission during the irradiation process performed in the air. As observed previously, the NH_2 molecules are linked to the aromatic benzene rings, creating the aromatic amines, which in turn are photoluminescent. This process is illustrated in Fig. 5.

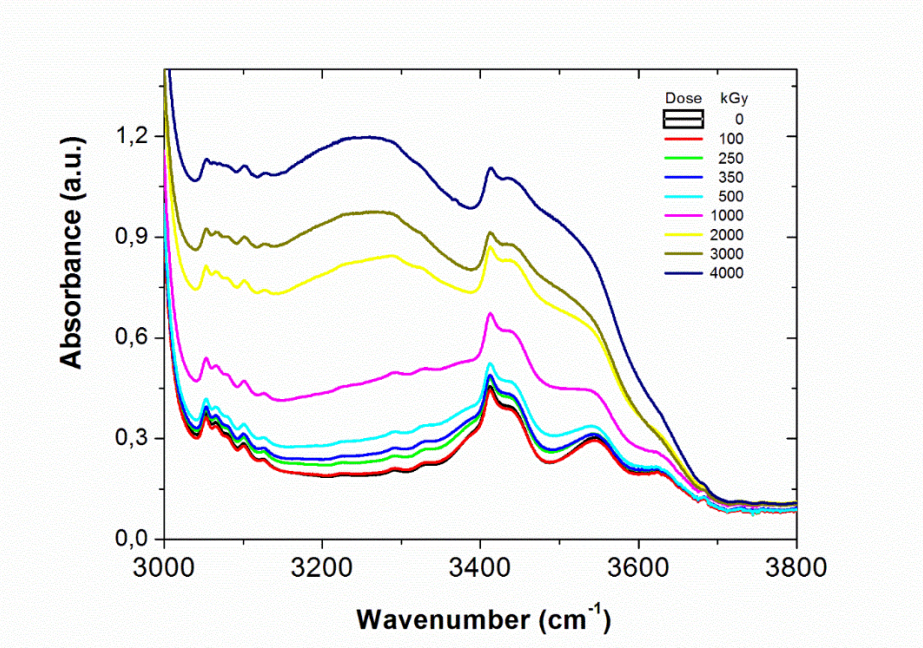


Figure 4: FTIR spectrograms of Ecoflex films irradiated with gamma doses ranging from 0 to 4.0 MGy in the 3,000 to 3800 cm^{-1} wavenumber range.

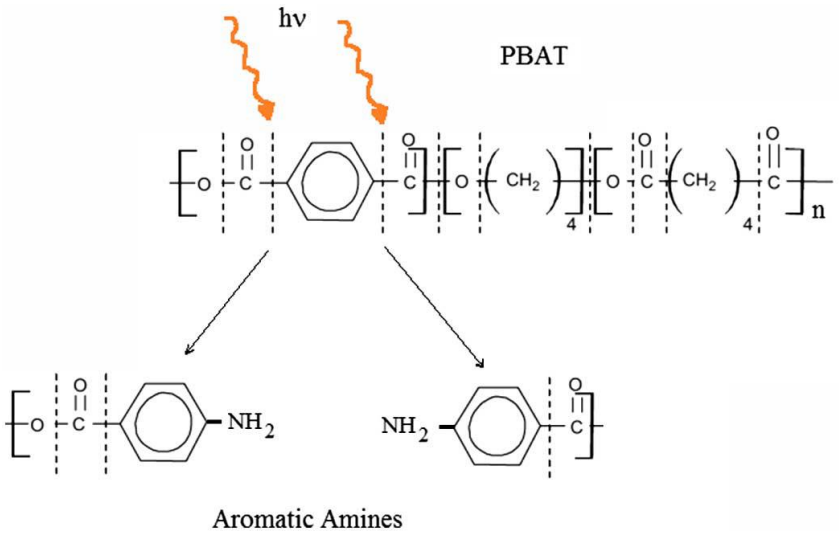


Figure 5: Structure of PBAT and chemical bonds that could be broken by gamma radiation, provoking chain scission. Photoluminescent aromatic amines could be formed by linking a hydrocarbon ring with an NH_2 molecule

The gradual increase of the wide radio-induced peak at 3,256 cm^{-1} provokes a gradual increase in the intensities of all adjacent peaks. At this point we may focus our attention to the absorbance peaks at 3,241 cm^{-1} and 3271 cm^{-1} that belongs to pristine PBAT. They seem attractive to be explored for dosimetry purposes. In fact, when we plot their intensities as a function of the exposed gamma dose, it becomes very clear that they really are. There is a linear relationship between peak intensity and dose for dose ranging from 100 and 2,000 kGy, as shown in Figures 6 and 7. The linear correlation coefficient is 0.9981 for the peak centered at 3,241 cm^{-1} and 0.9992 for the peak centered at 3271 cm^{-1}, as shown in the inset of Figures 6 and 7, respectively.

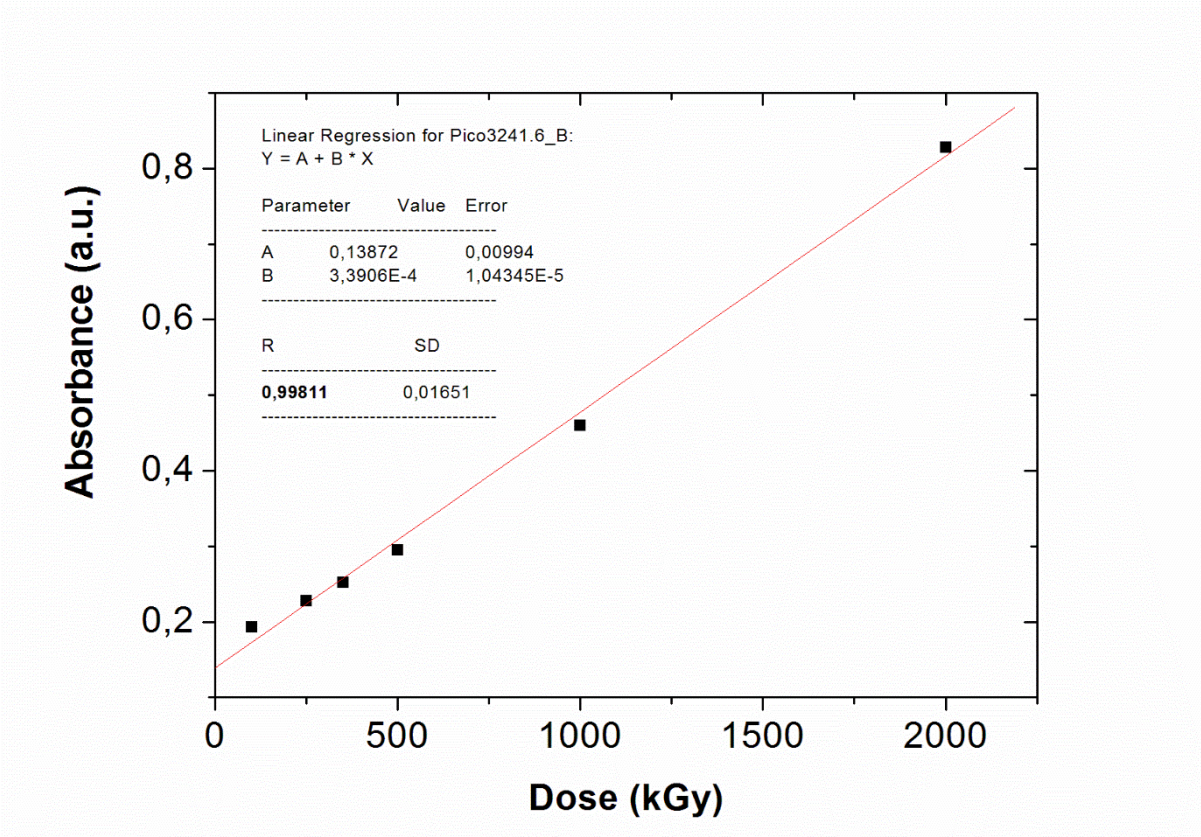


Figure 6: Plot of the absorption peak intensities at 3241 cm^{-1} as a function of the delivered dose, taken from Fig. 4. The linear regression data are displayed in the inset, with the correlation coefficient of 0.9981.

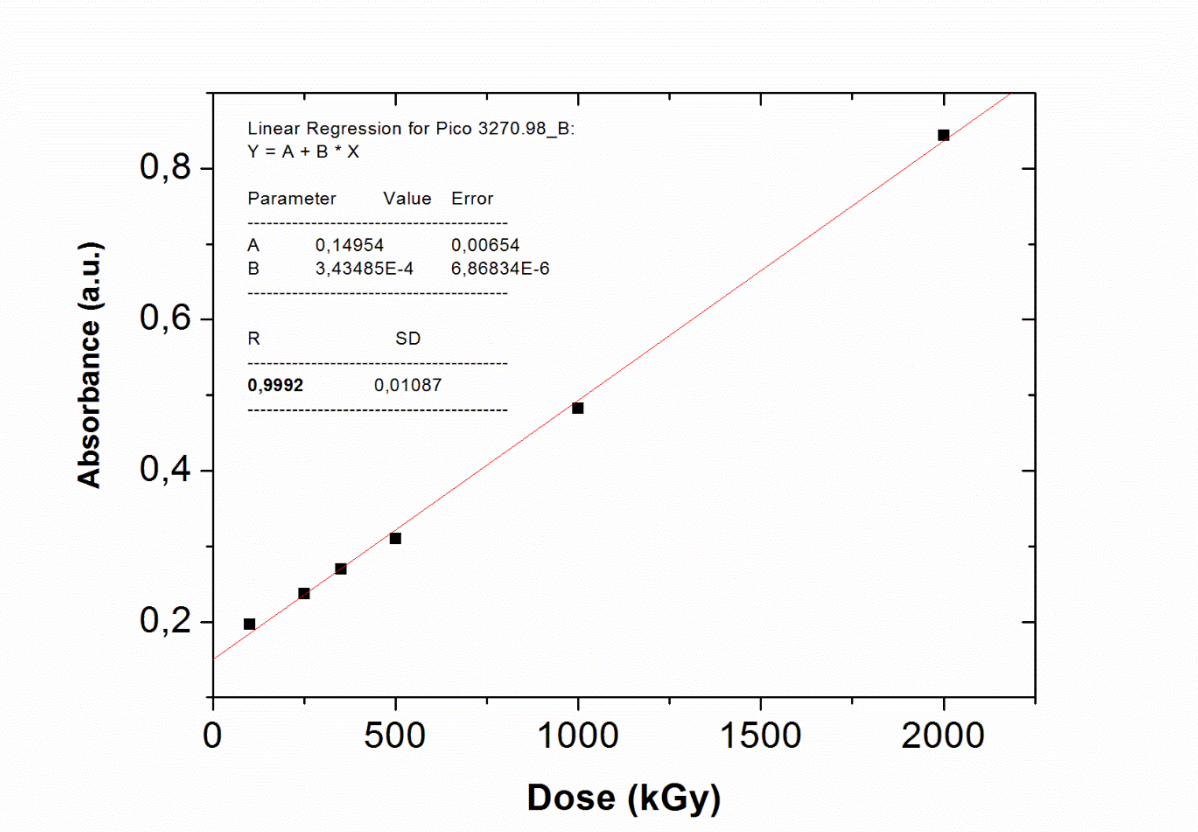


Figure 7: Plot of the absorption peak intensities at 3271 cm^{-1} as a function of the delivered dose, taken from Fig. 4. The linear regression data are displayed in the inset, with the correlation coefficient of 0.9922.

We remark that, once the small measuring dose range is an intrinsic limitation of most of high dose dosimetric systems, the data provided by the linear fitting in Figures 6 and 7 indicate that PBAT copolymer should be further investigated for high-dose dosimetry in order to provide more experimental points, mainly in the range of 500-2,000 kGy. This would make PBAT a potential candidate for use as a commercial dosimeter in the high dose range.

3. CONCLUSIONS

In this work we report the investigation of photoluminescence (PL) and dosimetric properties of poly(butylene adipate-co-terephthalate) (PBAT), an aliphatic-aromatic copolyester, after exposure to high doses of gamma radiation. Concerning the investigation about the dependence of the film thickness with the PL output, it was found that increasing the thickness from 38 μm to 130 μm enhances the PL output around 3.5 times, when the film is irradiated with 500 kGy. Also, besides the color green brightness reported earlier, the PL intensity can also be used for high dose dosimetry purposes for doses ranging from 50 to 750 kGy. The FTIR analysis has demonstrated that the there is a linear relationship between peak intensity and dose for doses ranging from 100 and 2,000 kGy for the absorbance peaks at 3,241 cm^{-1} and 3271 cm^{-1}, with linear correlation coefficients of 0.9981 and 0.9992, respectively. These results indicate that PBAT has great potential for applications in high gamma dose dosimetry and bio-imaging devices.

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