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Novel, VOC-Free-Renewable Solid-State Biopolymer Detector for Mid-to-Extreme Radiation Field Monitoring

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Abstract: A novel, VOC-free-renewable solid-state biopolymer detector is presented for applications pertaining to mid-to-extreme gamma-electron beam dosimetry applications. Polylactic-Acid (PLA) based "green" biopolymer was used to derive PLAD – a renewable, inexpensive solid-state radiation detector that promises to offer significant potential benefits over when compared with state-of-art detectors for detecting gamma-electron and also other forms of ionizing radiation. Experimental data are presented on well-correlated measurements of ionizing radiation in the mid-to-extreme dose range to readily discernible physical property changes such as relative viscosity, embrittlement, and molecular bonding.

Keywords: Polylactic Acid, PLA, Radiation, Gamma, Electron, FTIR, Detector, Dose.

1. Introduction

Nuclear safety is of paramount concern in worldwide nuclear and radiation-based facilities – especially, for those handling and reprocessing involving extreme radiation doses, and esp. for actinides (e.g., Pu/Am/U) that are also high-impact alpha-spontaneous fission neutron emitters; as also, medical and sterilization facilities deploying high energy photon and e-beam accelerators. As such, nuclear radiation instrumentation for safety and optimal functioning of such facilities with varying missions is always an important factor [1]. For the past over 80+y, radiation monitoring technology has remained largely the same [2-4] – relying primarily on sensor technologies which require monitoring for the tell-tale charge buildup in ionized gases/solids (e.g., fission chambers using HEU and compensated ion chambers), or monitoring of light flashes from scintillation or thermoluminescence. At the high cost end, complex radiation spectrometers can cost in the $M range (as may be deployed at high powered accelerator driven spallation sources or research reactor facilities and requiring skilled scientific staff), down to a range of $1-10K for portable survey meters, and even at as low as $10 for commonly used personnel dosimeters (e.g., TLDs) the aggregate personnel monitoring costs for complex-wide needs can rise to several $M/y.

In addition, present day nuclear instrumentation is varied in construction and deployment according to its application; i.e., different individual systems for neutron/gamma/beta/alpha/fission radiation detection. This paper provides results from scoping studies that address the need for improvements to present-day nuclear instrumentation by means of development and testing of a novel, ultra-low cost, solid state polylactic acid (PLA) bio-polymer based nuclear detector instrumentation referred to herein, as PLAD.

2. Methodology & PLAD Sensor Overview

At Purdue University (PU), we have researched [5-7] the potential for inexpensive, renewable (cornsoy derived) "green" PLA-based polymers to be used for radiation detectors we call "PLAD". PLA is a biopolymer (derived from dextrose sources such as corn/soy/..) that appears to offer significant potential benefits as a detector for various forms of ionizing radiation, as well as for dosimetry. Fig. 1 shows a typical commercially-purchased PLA (MW ~10^5) resin bead (~2-3 mm OD) from Natureworks, LLC. Effectively, each such resin bead serves as a solid-state ionizing radiation detector.

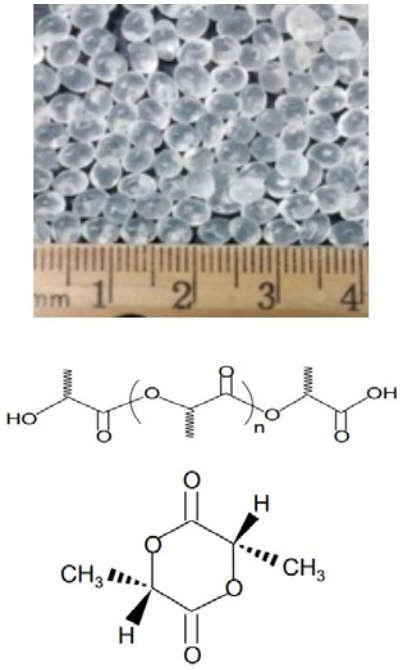

Fig. 1. PLA resin beads (Natureworks, LLC) and molecular structures (repeat and dimer) [6].

2.1. What May be so Compelling for PLAD as a Potential Radiation Detector?

It is well-known that ionizing radiation interaction will produce atom dislocations and other effects in virtually every material to varying extents for example via neutron irradiation of steels leading to embrittlement. However, such dislocations and property changes are not readily discernible for monitoring in real-time using commonly available devices and techniques. What is needed is a material that responds well even in harsh environments to varied forms of ionizing radiation to produce well-correlated property changes to simple physical properties (e.g., density, relative viscosity, hardness, molecular weight, etc.) that are amenable to rapid-fire and cost-effective measurements using common laboratory equipment. This is where PLAD technology appears to show significant potential. Successful implementation may provide for ultra-low cost (10-100x lower than even TLDs), safety-security-environment friendly alternate to expensive nuclear instruments such as HEU-fission chambers and compensated ion chambers.

2.2. Preparation of Irradiated Resin

Approximately 2 kg of NatureWorks™ 4043D resin was placed into a Gammacell™ 220 ^{60}Co irradiator to irradiation dose uptake of up to 110 kGy. At intervals of 10 kGy, 110 g of resin was removed from the irradiator for subsequent testing. Simulation using MCNP was performed previously to determine the dose profile in the main chamber of the Gammacell™. Fig. 2 shows this variation with axial and radial position in the Gammacell™ [6].

2.3. B. Preparation and Testing of Fourier Transformed Infrared (FT-IR) Spectroscopy Samples

FT-IR is a well-established technology which can identify chemicals using an infrared light source to measure absorption or emission of light from solid, liquid or gas phase materials at various wavelengths – collecting high-spectral resolved data over a wide spectral range, and consequently providing a molecular fingerprint. The irradiated samples were heated to just above each respective melting temperature to avoid further structural changes and rolled into thin films. A Nicolet™ FT-IR spectrometer from Thermo Electron Corp. was used. Resin beads were placed directly onto an Attenuated Total Reflectance (ATR) diamond window in the FT-IR instrument with no preforming. After obtaining a Fourier Transform on the interferogram, each scan was corrected, by establishing a baseline and then normalizing to the strongest signal for a given wavenumber. This was used as a metric for comparing relative molecular bond composition variations amongst a range of irradiated samples.

2.4. Preparation and Testing for Relative Viscosity (RV)

The irradiated samples were dissolved in a 1.0 g dl^{-1} chloroform solvent and measured in a size 25 Cannon-Ubbelohde viscometer. The relative viscosity of a sample is determined by measuring total flow time for a dissolved sample to traverse a set distance. These measurements were performed for the untreated resin and the samples that were irradiated up to 100 kGy..

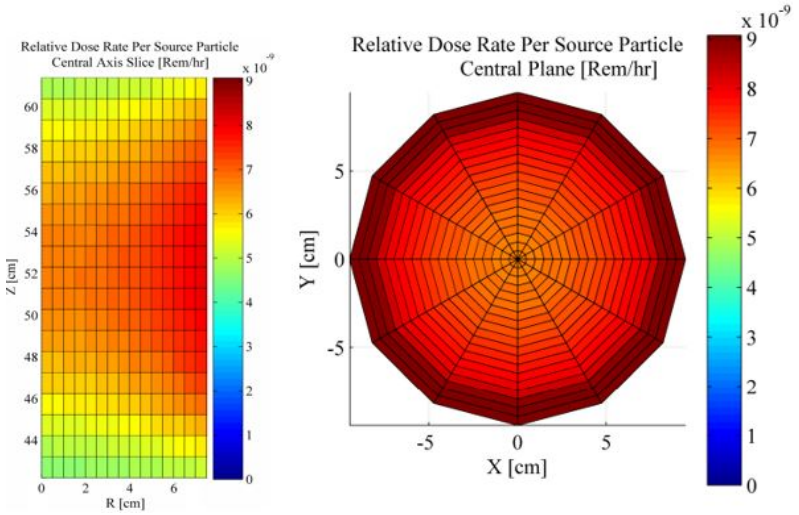

Fig. 2. Simulated Axial (Left) and Radial (Right) dose profiles in Gammacell™ [6].

2.5. Preparation and Testing for Grinding Efficiency

The irradiated samples were ground using an off the shelf commercial blender for up to 90 min. The resulting powder was then sieved using HumboldtTM ASTM E-11 sieves with <250 and <500 µm mesh sizes. The untreated resin was subjected to the same process. The fractional mass in each sieve bin for the irradiated samples was compared with the mass remaining for the untreated resin, in order to arrive at the grinding efficiency.

3. Results

3.1. FT-IR Results

The FT-IR scans show dominant wavenumber peaks of 867, 956, 1043, 1081, 1127, 1181, 1264, 1361, 1382, 1452 and 1747 cm^{-1}. For two given samples, the absorbances of each peak were compared with one another to measure relative increase or decrease in normalized intensity. Fig. 3 plots the FT-IR scan of PLA resin against 100 kGy irradiated PLA resin (PLAI-100). This allows for a visualization of the change in relative absorbance for the maximum irradiated sample investigated in this study.

The vibrational assignments for each number are shown in Table 1. Wavenumbers 1081 and 1043 were compared to determine the percent change in COC to COH bonds. Wavenumbers 1081 and 1747 were compared to determine the percent change in COC to C=O bonds. Wavenumbers 1081, 1382 and 1452 were compared to determine the percent change in COC to CH3 bonds. Finally, wavenumbers 1043 and 1747 were compared to determine the COH to C=O bonds. Fig. 3 shows the FT-IR scans of irradiated sample PLAI-100 versus the unmodified PLA Resin 4043D. It shows a clear relative increase for bands at 1453 cm^{-1}, 1380 cm^{-1} and 1129 cm^{-1}. These peaks have been assigned to $–CH_3$ [8].

Table 1. Wavenumber and bond trait assignments for PLA [7].

Wavenumber cm^{-1}	Stretch/Bend
860-875	ν C-COO
925-960	$\Gamma CH_3 + \nu CC$
1043	C-OH
1090-1100	$\nu_s COC$
1127	$\Gamma_{as} CH_3$
1185-1215	$\nu_{as} COC + \Gamma_{as} CH_3$
1264	$\delta CH + \nu COC$
1360-1368	$\delta_l CH + \delta_s\ CH_3$
1348-1388	$\delta_s CH_3$
1452	$\delta_{as} CH_3$
1747	$\nu C{=}O$

Fig. 4 shows the relative percent change of bonds in the irradiated PLA. These bonds were correlated with certain wavenumbers taken from Table 1, and compared with each other to determine the presence and change in bonds and their compositions. The colors in the legend correspond to changes in bond prevalence; these changes were calculated by normalizing wavenumbers to the strongest signal and comparing the relative change in reference to unmodified 4043D resin.

Fig. 4 shows an increasing trend in COC to COH bonds, this is likely due to the formation of carboxylic acid during the irradiation process. The carboxylic acid group is formed after the bonds between the carbon and oxygen atom is broken by the thermal energy. The carbon to oxygen bond has the second lowest bond dissociation energy, $350\frac{\text{kJ}}{\text{mol}}$, which allows for a large increase in carboxylic acid groups [9].

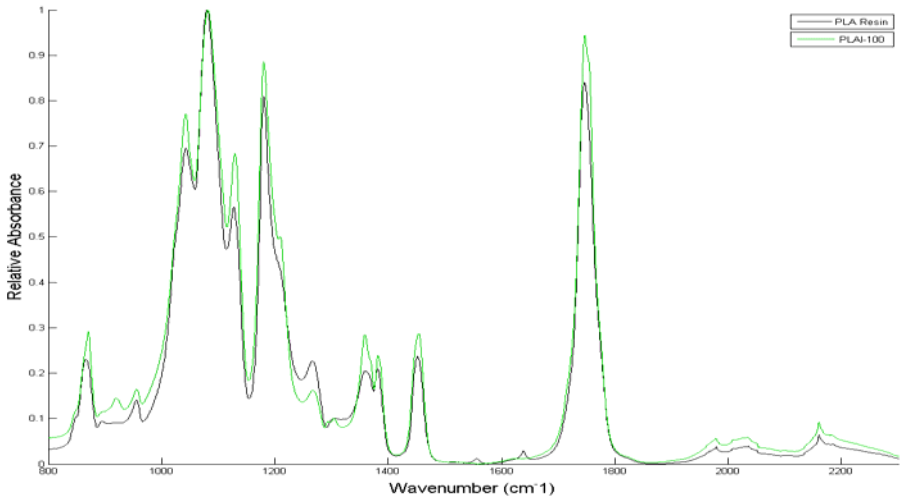

Fig. 3. Relative absorbance of FT-IR scans for irradiated 100 kGy PLA (green) against PLA Resin 4043D (black).

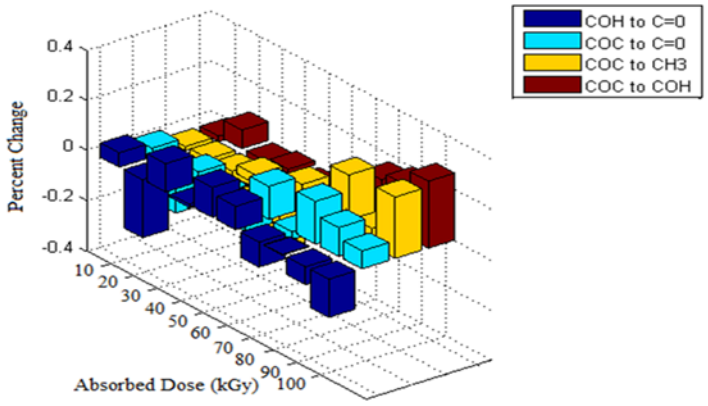

Fig. 4. Relative percent change in bond compositions of irradiated PLA.

3.2. Relative Viscosity Results

The relative viscosity of irradiated PLA was measured with varying dose up to 100 kGy. Fig. 4 depicts the results of these measurements.

In Fig. 5, a first order linear variation is observed for doses ranging from 0 kGy to about 40 kGy (40,000 Rad). Beyond this 40 kGy the slope of the linear variation changes. This slope change indicates a deviation from the rapid breakdown of the polymer. Although Fig. 5 seems to indicate a stagnation in RV changes with doses above 100 kGy, further experiments have been performed indicating a dose response in the RV up to 220 kGy.

3.3. Grinding efficiency Results

The grinding efficiency of irradiated PLA was compared with doses for two sieve bins, the results of this experiment are depicted in Fig. 6.

Once again, the grinding efficiency was determined by simply measuring the mass of irradiated powder that was collected. This grinding was performed in a commercial (off-the-shelf) grinder, implying ease of use and rapid results with this dose measurement. Fig. 6 indicates a linear variation of grinding efficiency over 0 – 100 kGy (0-100,000 RAD) ranges which is relevant for high dose environments such as encountered commonly for medical sterilization and also in the vicinity of spent nuclear fuel (SNF) wherein the radiation field intensity can readily reach ~10^4 R/h even 2y post-shutdown [3].

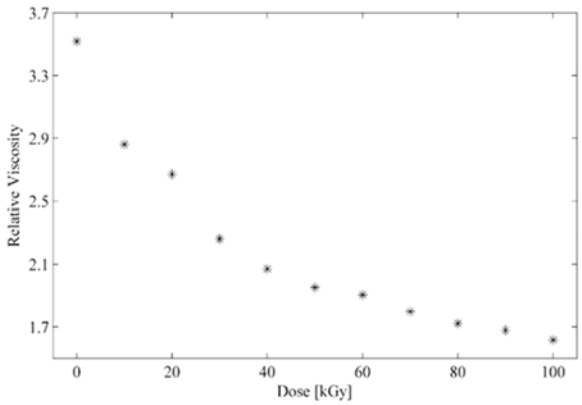

Fig. 5. Variation of Relative Viscosity vs Irradiation Dose [6].

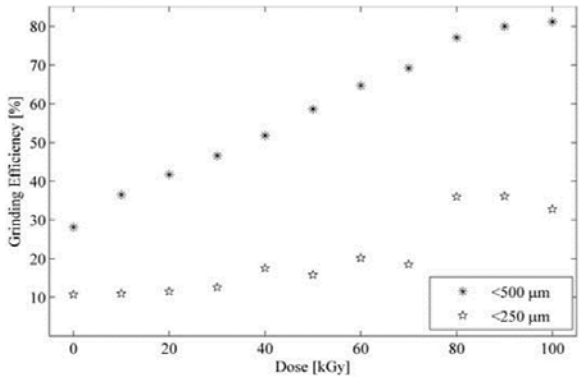

Fig. 6. Embrittlement/ Grinding efficiency vs Dose [6].

4. Conclusions

Systematic experimentation was performed to characterize the mid-to-extreme gamma and/or electron beam dose response of PLA resin. The results of these experiments reveal a significant correlation of delivered radiation dose (through 100 kGy) with RV, grinding efficiency, and FTIR molecular bond changes. Additional experimentation has shown such response for even up to 220 kGy of gamma/e-beam dose. Other parameters such as melting temperature as well as material hardness also appear to provide first-order monitoring enablement to varying extents for correlating to the subjected radiation dose [6].

Acknowledgements

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