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# Effect of gamma irradiation on physicochemical properties of commercial poly(lactic acid) clamshell for food packaging



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#### HIGHLIGHTS

- The gamma irradiation effects on PLA clamshells were studied.
- DSC, XRD, NMR and FTIR analysis were used for PLA clamshell characterization.
- The  $M_w$ ,  $T_m$ , strength and elongation of the irradiated PLA clamshells decreased.
- The tensile modulus increased with increasing gamma doses.
- The Surface of PLA clamshell showed scratches and minor cracks.

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# ABSTRACT

Poly(lactic acid) (PLA) is a well-known biodegradable polymer with strong potential application in food packaging industry. In this paper, samples of PLA clamshell for tomatoes packaging were exposed with  $^{60}$ CO  $\gamma$ -ray's source (1.33 MeV) at different dose levels (0, 10, 60, 150, 300, and 600 kGy), at room temperature and in presence of air. The physicochemical properties of neat PLA and sample exposed to gamma irradiation were investigated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and tensile measurements. Results show as the dose increases, the molecular weight ( $M_w$ ), melting temperature ( $T_m$ ), tensile strength and elongation at break decreased. However, the tensile modulus increased with increasing doses. The surface of PLA clamshells was degraded (scratches and minor cracks) when samples were exposed to doses greater than 60 kGy.

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### 1. Introduction

Food irradiation is an effective technology for reducing postharvest food losses and ensuring hygienic quality of foods. It is known that gamma irradiation is the most widely-used cold sterilization technique because of its high penetration power (George et al., 2007). The food is packaged during irradiation processing of foods, and a wide variety of packaging configurations such as single or multi-layered films, trays, clamshells, etc. are employed in food packaging. It is well known, that ionizing

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radiation produces physical and chemical changes in packaging materials. Traditionally, petroleum-derived plastics have been used as food packaging materials. However, the growing accumulation of petro-polymers in the environment is a global environmental issue and has spurred interest in replacing these with biodegradable polymers from renewable resources (Mohanty et al., 2002; Wang and Huang, 2007). Among the group of biodegradable polymers, polyesters and their derives, poly(ɛ-caprolactone), poly(3-hydroxy butyric acid), polymalic acid and polylactic acid have been studied extensively (Lunt, 1998; Nugroho et al., 2001). The poly(lactic acid) (PLA) offers the potential for an attractive combination of mechanical properties, thermal plasticity, high degree of transparency, biocompatibility and cost. Therefore, PLA has tremendous potential for several applications

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in the biomedical, household, and agricultural industries. The US Food and Drug Administration have approved the use of PLA for food contact and is widely used in rigid and flexible food packaging (FDA, 2005).

There are published studies reporting on the thermal, hydrolytic or oxidative stability of this polymer, which has been shown to undergo random chain scission (Nugroho et al., 2001; Zaidi et al., 2013). Moreover, Gupta and Desmukh (1982) have demonstrated that the isothermal degradation of PLA is a random chain scission in which two kinetically independent units take part in the degradation. There are, however, only few reports on radiation-induced degradation of PLA, even though it is known to be highly sensitive to ionizing radiation (Nugroho et al., 2001: Yovcheva et al., 2013). Some of these papers have reported the optical thermal, morphological, structural among other properties of modified PLA (blends, crosslinked, filled with nanoparticles, etc.) (Zaidi et al., 2013; Razavi et al., 2014). To our knowledge, the physical properties of PLA clamshells designed for food packaging when subjected to different doses of gamma irradiation have not been reported so far. In this research, laminates of clamshell based-on PLA have been subjected to different doses, from 0 to 600 kGy. The molecular characteristics, mechanical, thermal, structural and morphological properties were studied as a function of irradiation dose and the mechanism of radiation induced degradation is discussed.

#### 2. Experimental

#### 2.1. Materials

Clamshells were manufactured from PLA pellets (NatureWorks LLC. Ingeo<sup>TM</sup> biopolymer 2003D), and were used as received. The material has a number average molecular weight  $(M_n)$  of 150,500 g/mol, melt flow rate of 5.92 g/10 min and density of 1.2 g/cm. The PLA samples were cut from clamshells into  $5 \times 5$  cm<sup>2</sup> sheets having the thickness of 400  $\mu$ m.

#### 2.2. Methods

#### 2.2.1. Gamma irradiation exposure test

The PLA samples were irradiated in a self-contained gamma research irradiator Gammacell 220 Excel (GC-220E) of MDS Nordion (4.9 kCi). Target doses of 0, 10, 60, 150, 300 and 600 kGy were performed at 3.86 kGy/h dose rate by a  $^{60}\text{Co-}\gamma$  source, under ambient conditions (25 °C).

# 2.2.2. Optical properties

Film opacity was determined using procedures described by Zhang and Han (2006). Briefly, the film samples were cut into rectangles and placed on the internal side of a spectrometer cell. The absorbance spectrum (200–800 nm) was recorded for each sample using a Varian Cary-50 Bio UV-visible spectrophotometer (Palo Alto, CA). The opacity of the PLA samples was determined by measuring the absorbance at 600 nm ( $A_{600}$ ). The opacity at unit light path length was calculated using the following equation described by Han and Floros (1997):

Opacity measurement = 
$$\frac{A_{600}}{T}$$
 (1)

where  $A_{600}$  is the absorbance at 600 nm, and the thickness T is in mm. The measurement was performed in three replicates for each film, and the average value is reported.

The irradiated samples were measured for their color values. Color was read using the Commission International de L'Eclairage (CIE) Lab parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) with a spectrophotometer–

colorimeter Konica Minolta model Chroma Meter CR-300 (Ramsey, NJ). The scanner was calibrated with a white standard tile (Y=93.2, X=0.3133, Y=0.3192). In this coordinate system, the  $L^*$  value is a measure of the lightness (brightness), ranging from 0 (black) to 100 (white); the  $a^*$  value is a measure of the redness, ranging from -100 (green) to +100 (red), and the  $b^*$  value is a measure of the yellowness, ranging from -100 (blue) to +100 (yellow). The color differences ( $\Delta E$ ) were calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$
 (2)

where  $\Delta L^* = L^* - L_o$ ,  $\Delta a^* = a^* - a_o$ , and  $\Delta b^* = b^* - b_o$ .  $L_o$ ,  $a_o$  and  $b_o$  represent the color parameter values of the standard, and  $L^*$ ,  $a^*$  and  $b^*$  represent the color parameters of the sample. Measurements were performed by placing the PLA sample over the standard. All of the samples were analyzed by recording six measurements of each sample.

# 2.2.3. Mechanical properties

The irradiated samples were cut into rectangular pieces  $(6 \times 1 \text{ cm}^2)$  and evaluated using an universal testing machine United model SSTM-5 (Houtivigton Beach, CA). The thickness of each specimen was measured using a micrometer Mitutoyo Digimatic MDC-1SB (Kawasaki, JP) with a precision range between 0.001 mm and average values were determined. The initial grip separation was set at 30 mm, and the crosshead speed was set at 10 mm/min. A minimum of five specimens were used to determine the average of mechanical parameters (tensile strength, elongation at break, and tensile modulus).

#### 2.2.4. Structural analysis

The infrared spectra in the attenuated total reflection mode (FTIR-ATR) were obtained at room temperature using Thermo Nicolet spectrometer model Nexus 670-FTIR (Madison, WI). The samples were analyzed in the range of 4000-600 cm<sup>-1</sup>, with 4 cm<sup>-1</sup> of resolution, and 100 scans. To determine the crystalline structure of the irradiated samples, a sample of  $1 \times 1 \text{ cm}^2$  was placed in a sample holder for X-ray diffractometry. The X-ray diffraction patterns were recorded in the reflexion mode in an angular range of 5-60° (2 $\theta$ ) at room temperature using a diffractometer Siemens model D5000 (Karlsruhe, Germany), with a Bragg Brentano geometry and monochromatic CuKα radiation  $(\lambda = 1.5418 \text{ Å})$ , at 34 kV, and 20 mA. The molecular weights of PLA samples were determined by gel permeation chromatography (GPC) an Agilent PL-GPC 50 system (Santa Clara, CA) was used in combination with a differential refractive index detector Agilent 1260 Infinity. The column set consisted of two PLgel columns of 5 μm Mixed D with 300 mm of length and 7.5 mm of diameter. The eluent was analytical grade tetrahydrofuran (THF) at a flow rate of 1 mL/min at 40 °C. PLA samples were previously dissolved in THF for 24 under stirring. Solutions were filtered through 0.45 µm stainless steel frits and heated at 40 °C for 1 h prior to injection. The quantitative <sup>1</sup>H solution NMR spectra were recorded at 25 °C on a Varian/Agilent 600 MHz Premium Compact NMR spectrometer (Santa Clara, CA) at 599.78 MHz, 8.7  $\mu$ s, 10 s and 1.5 s for  $^{1}$ H frequency,  $\pi/2$  pulse, recycle delay and acquisition time respectively. Deuterium-chloroform 99.8% (CDCl<sub>3</sub>) from Cambridge Isotope Laboratories, Inc. was used as solvent and chemical shifts  $(\delta)$ were determined relative internal TMS ( $^{1}$ H,  $\delta$  0.00).

#### 2.2.5. Thermal analysis

The differential scanning calorimetry (DSC) thermograms of irradiated samples were performed on a Discovery DSC from TA Instruments (New Castle, DE) under nitrogen atmosphere. A sample of 5 mg was heated to 200 °C at 10 °C/min, isothermal for

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