GAMMA IRRADIATION OF PLOY (L-LACTIDE) BIOPOLYMER

A. Nabipour Chakoli¹, Shahab Shafayyan², M. Amirian Chayjan³, F. Mianji⁴
¹Nuclear Safety and Radiological Protection Research Department, NSTRI, Tehran, Iran.
²Head Of Industrial And Mining Research Center, Tehran, Iran
³Teachers University, Ferdosi Center, Baghestan, Karaj, Iran,
⁴School of Agriculture, NSTRI, Rajaeshahr, Karaj, Iran

SUMMARY: Gamma irradiation is often used to sterilize biomedical devices for medical applications. However, high energy radiation can damage medical devices made from polymers, even at the minimum sterilization dose of 25 kGy. Radiation sterilization is especially damaging to biodegradable polymers, such as Poly(L-lactide) (PLLA) which even decompose when irradiated. In this research, neat PLLA was synthesized and irradiated by gamma irradiation processing. The physical and chemical properties of neat PLLA and irradiated PLLA were checked out using, FT-IR, XRD and SEM. The research results show that 25 KGy gamma irradiation don’t change the physical and mechanical properties of PLLAs. Also, it is found that with increasing the dosage of gamma to 100 KGy, the properties of PLLAs, due to decreasing the mechanical properties, are useless for medical performance.

Keywords: Poly (L-lactide), Sterilization, Gamma Irradiation, Crosslinking, Microstructure.

1. INTRODUCTION

Response of the organism to the implanted composite biomaterial depends on numerous factors. One of the most important is sterility. Different procedures can be utilized for the sterilization of the sensitive polymers like a Poly(L-lactide) PLLA. Radiation and commercially dominated sterilization process by high-energy radiation are successfully utilized for modification and sterilization of sensitive PLLA. The dominant effect of irradiation on PLLA is chain scission, but there are some recent reports concerning irradiation cross linking by introducing cross linking agent [1, 2]. However, because of excellent penetration characteristics of ionizing radiation, radiation sterilization eliminates problems which may appear with other sterilization methods like high sterilization temperature, need for quarantine, problems associated with residuals and ethylene oxide gas penetration, uniformity of sterilization, etc [3, 4].

Radiation cross-linking and radiation grafting are widely used in industrial applications of radiation processing of polymeric materials. In collaboration with the local polymer industry, an effort has been made to demonstrate the advantage of the radiation processing as compared with the conventional chemical process. Radiation has been known to alter the physical properties of polymers through main-chain scission and cross-linking. Usually both these processes take place simultaneously for many polymers. The combination of two radicals leads to cross linking in the amorphous phase or recombination in the crystalline region, whereas chain transfer and the subsequent splitting results in chain scission [5-6]. Radiation is based on the use of high-energy ionizing radiation to induce chemical and biological changes in irradiated systems. Since high energy electromagnetic and particle radiation exhibit properties of controlled penetration and intensities, which are especially suitable for synthesis and modification of polymeric biomaterials without the need of usually toxic additives, the interest to use radiation techniques in biotechnology and biomedicine is growing rapidly. These methods are being used for synthesis of functional polymers in forms of macro gels and micro gels, micro spheres and nano spheres, functionalization of surfaces and radiation processing of naturally derived biomaterials among others [7, 8]. In this
research, the effect of gamma irradiation processing on PLLA are characterized. For this purpose, PLLA are synthesized and then irradiated using gamma radiation.

2. EXPERIMENTAL

2.1 Materials
The L-lactide (LA) oligomer (Xiaogan Esun New Material Co, China) was used as received. Stannous octanoate (St(Oct)2) (Shanghai chemical reagent company, China) was used as a catalyst. Chloroform, ethanol, methanol, toluene, p-amino benzoic acid, poly phosphoric acid and phosphoric penta oxide (P2O5) were purchased from Kernel of China as analytic reagent.

2.2 PLLA Synthesis
To synthesis of PLLA, LA monomers were added into a flask with Sn(Oct)2 as initiator. For uniform dispersion of Sn(Oct)2 in flask, we used toluene as solvent. After degassing the flask to remove toluene, the flask was sealed under vacuum and then placed in an oven at 130 °C for 48 hours. The synthesized materials were dissolved in chloroform and then precipitated using Methanol. Finally, the products were dried in oven at 40 °C.

2.3 PLLA Irradiation
The neat PLLA irradiated in a calibrated 60Co irradiator (Issledovatel type PX-30) with the activity of 4500 Ci and dose rate of 0.1 Gray per second (Gy)/s in air atmosphere and at room temperature. For each kind of samples two different doses of are directd, 5000 Gray (50 KGy) and 100000 Gray (100 KGy). After irradiation the samples are cutted for FT-IR, XRD and tensile test experiments.

2.4 Characterization
The molecular weight and the distribution of the synthesized PLLA was measured by gel permeation chromatography (GPC) using Agilent 1100 series (Agilent, USA). It is found that the $M_w=272625$, $M_n=147641$ and P.I.=1.84. It means that the prepared polymer has a good quality.

The FT-IR spectra of pristine and functionalized MWCNTs were recorded between 500 and 4000 cm$^{-1}$ using a Perkin Elmer Spectrum One FT-IR spectrometer. The samples were mixed with KBr powder and then sample pellets plate prepared with press device. A minimum of 16 scans were averaged with a signal resolution of 4 cm$^{-1}$ within the 500–4000 cm$^{-1}$ range. The X-ray diffraction (XRD) method was employed to investigate the crystalline structure of neat polymer and composites using a Rigaku D/max-rb rotating anode X-ray diffractometer at 50 kV and 40 mA.

To investigate the morphology of prepared materials, a SEM was carried out using a Hitachi S-4700 field-emission system. For sample preparation, samples were dissolved in chloroform separately. Then one drop of the resulting solution was put on aluminum plate. After drying, the samples were coated with gold layer by sputtering to avoid charging under the electron beam.

3. RESULTS AND DISCUSSIONS
It is expected to observe some modification on functional groups of the irradiated PLLA by FT-IR, and the results are shown in Fig. 1. During gamma irradiation some cross-linking and some chain scissoring are created. As can be seen, there is not any significant difference between the FT-IR spectra of primary PLLA and irradiated PLLA. It means that the cross linking or chain scissoring of polymer chain is low.
The FT-IR spectra of neat PLLA before and after gamma irradiation is shown in Fig. 1. The XRD of irradiated PLLA is compared with the XRD of primary neat PLLA in Fig. 2.

As can be seen, the intensity diffraction peaks increases with increasing the gamma dose. Whereas, the FWHM of peaks decrease with the increase of gamma dose. It shows that the size of lamellae increases during irradiation. It means that the gamma irradiation increases the crystallinity of neat PLLA gradually. Of course, the form of crystallinity of PLLA do not change during gamma irradiation. It is predicted that after gamma irradiation the mechanical strength of PLLA increases while the elongation at break of PLLA decreases.

The X-ray diffraction patterns of neat PLLA before and after gamma irradiation is shown in Fig. 2.

Fig. 3 The SEM micrographs of PLLA before irradiation (a), after 50 K Gy irradiation (b) and after 100 K Gy irradiation (c)
It is predictable that the gamma irradiation introduce bulk defect in the PLLA, but it is not possible to observe the bulk defect using SEM. The SEM analysis shows that the 50 KGY gamma radiation slightly change the PLLA surface morphology. Changes in the surface morphology with irradiation are dose dependent. As can be seen, some defects are created on the surface of neat PLLA and its composites. After 100 KGY irradiation is more clear than neat PLLA. The surface morphology of irradiated PLLA predicts that the 100 KGY irradiated PLLA are too brittle. Hence, the mechanical properties of 100 KGY irradiated PLLAs are useless for medical performance.

4. CONCLUSIONS

The effect of gamma irradiation on PLLA during sterilization has been checked out. The gamma irradiation creates defects in neat PLLA. Chain scission of neat PLLA under the gamma radiation is higher than cross-linking. The research results show that 25 KGY gamma irradiation don’t change the physical and mechanical properties of PLLAs. Hence, Gamma irradiation will be useful for sterilization of medical materials and medical devices that fabricated using PLLA. It is necessary to consider that the mechanical properties of 100 KGY irradiated PLLAs are useless for medical performance

5. REFERENCES


