



Electron Beam Radiation Modification on Chemical, Thermal and Crystalline Properties of Poly (L-lactic acid)

N Rajeswara Rao^{a,*}, T Venkatappa Rao^b, B Sanjeeva Rao^c, & P S V Shanmukhi^a

^aDepartment of Physics, Aditya College of Engineering and Technology, Surampalem, A.P, 533 291 India.

^bDepartment of Physics, National Institute of Technology, Warangal, Telangana, 506 001 India.

^cDepartment of Physics, Govt. Degree College, Warangal, Telangana, 506 345 India.

Received 7 April 2019; accepted 17 September 2021

The paper presents the effect of electron beam (EB) irradiation on poly (L-Lactic acid) (PLLA). The resultant physicochemical properties were investigated using Electron spin resonance spectrometer (ESR), Fourier transform infrared spectrometer (FTIR), Differential scanning calorimetry (DSC), X-ray Diffraction (XRD) and Scanning electron microscopy (SEM). The results suggest that PLLA undergoes random chain scission producing two types of free radicals $\sim\dot{C}(\text{CH}_3)\sim$ (I) and $\dot{\text{C}}\text{H}(\text{CH}_3)\sim$ (II) at room temperature. Presence of these free radicals has been confirmed by the ESR method and computer simulation studies using *easyspin* tool. FTIR results depict that the intensity of the absorption band 1745 cm^{-1} is reduced by 12% for 90 kGy dose. DSC studies indicate that both glass transition temperature (T_g) and melting temperature (T_m) of PLLA decrease following radiation dose. However melting enthalpy (ΔH) and degree of crystallinity (X_c) increased initially up to 30 kGy of radiation dose followed by a decrease after 30 kGy. These results confirm the existence of two types of crystalline lamellar are present in PLLA. Measurements of X_c by XRD also confirm the same aspect. The surface of PLLA is composed of micro-cracks when exposed to higher radiation doses.

Keywords: Electron beam, Component spectra, Glass-Transition temperature, Degree of crystallinity, Micro-Cracks

1 Introduction

Bio-decomposable plastics have become alternative agents for petroleum based plastics due to their environmental friendliness. Poly (L-lactic acid) (PLLA) is one of such materials which is an aliphatic polyester made up of 2-hydroxy propionic acid building blocks. The PLLA is biodegradable due to its susceptibility to microbial enzyme degradation, hydrolytic degradation and biocompatibility derived from renewable sources like corn starch, tapioca roots and sugarcane¹. PLLA has occupied second place in consumption of any bioplastics in the world. FDA has approved PLLA for clinical usage such as sutures, bone fixation device, tissue scaffolds and drug delivery systems². Conventionally the uses of PLLA have confined to biomedical industry due to its bioresorbable properties, but recently the usage of PLLA has expanded its limits to consumer goods and packaging applications. The unique physicochemical properties of PLLA makes it a potential material for packaging applications in food and beverages³. PLLA is a good packing material with minimal greenhouse gas emissions and with environmental benefits⁴.

Although PLLA is biodegradable, some of its properties like brittleness, high gas permeability, low heat distortion temperature and low melt viscosity restrict the applicability of neat PLLA while processing⁵.

So to overcome such problems, the physicochemical properties of PLLA have to be modified by treating it with high energy radiations. The effects of radiation on biopolymers are well established and have been utilized to tailor the key properties of material for specific applications. Irradiation effects on PLLA were first investigated by Gupta et al⁶ and reported the radiation chemical yield for chain scission and crosslinking of polymer. Thermal and hydrolytic of degradation of PLLA was investigated by several authors⁷⁻⁹. The degradation processes is characterized by reduction in molecular weight, change in structural configuration, lower thermal stability and loss of mechanical properties. Loo et al¹⁰ have irradiated PLA and poly(lactic-co-glycolic acid) with EB in the dose range of 2.5-50 Mrad. New crystalline phases were formed, degree of crystallinity (X_c) increased upon irradiation and also the authors have predicted the accurate manner to control rate of hydrolytic degradation for biomedical devices.

*Corresponding author (E-mail: rajeshn9@gmail.com)

Recently studies on electret stability of PLLA films irradiated upto 100 kGy of gamma radiation dose have been reported by Yovcheva *et al*¹¹. The surface potential values of the irradiated PLLA were higher than the non-irradiated samples. As a potential material for food packing industry, PLLA clamshells were exposed to gamma rays up to 600 kGy¹². It is observed that molecular weight, melting temperature, tensile strength and elongation at break decreased with radiation dose while tensile modulus increased. PLA films were irradiated with EB to doses between 0 to 120 kGy¹³ and reported that the molar mass, glass transition temperature and mechanical properties were affected significantly. They evidenced that at 45 kGy of radiation dose, the physicochemical and mechanical properties changed for PLA. Treatment of PLA with various ions and EB irradiation was carried out to study its surface physico-chemical properties. Decrease in micro-hardness and increase in surface conductivity was noticed after irradiation¹⁴.

The objective of this investigation was to study the effect of electron beam on some physico-chemical properties of PLLA. Thermal and crystalline properties of processed PLLA play a key role in packaging industry. Hence the radiation induced thermal and crystalline properties of PLLA were studied. ESR spectra are also analyzed using computer simulations to identify the actual free radicals formed at room temperature.

2 Materials and Methods

The PLLA polymer is gifted from CIPET, Bhubaneswar with an average Molecular weight $M_n \sim 50,000$ in form the granules. Electron beam irradiation was accomplished using electron beam accelerator which is ILU-6 type, pulse linear accelerator from BRIT, INDIA operating at power of 2MeV. The actual doses delivered to the polymer samples are 30, 60 and 90 kGy. Irradiation exposure was performed batch-wise in order to avoid significant rise in temperature of PLLA. The packets of the samples were kept on conveyer belts and the speed is adjusted to 3.00 m/minute. The successive pass of the conveyer belt in radiation area determines the actual dose absorbed by the samples. Also the irradiation was performed in air and the dose rate chosen is 5 kGy/minute. ESR spectra are recorded on JES-FA200 ESR JOEL spectrometer operating at X-band frequency, 100 kHz modulation. The ESR spectrometer was setup with variable temperature facility to study the stability of the radicals at higher

temperatures. FTIR spectra are recorded on Perkin Elmer spectrometer in the pellet form along with KBr. Spectra was scanned with a resolution of 4 cm^{-1} over the range of $3400\text{--}400 \text{ cm}^{-1}$. DSC measurements were implemented on a DSC-TA Q10 model calorimeter. The samples were sealed tightly in aluminum crucibles and heated from 25°C to 200°C at a heating rate of $10^\circ\text{C}/\text{minute}$. The melting enthalpy of 100% crystalline PLLA was taken as 93.6 J/g to calculate the degree of crystallinity¹⁵. The X-ray diffractograms were recorded on Bruker D8 Advance X-ray diffractometer (XRD). The wavelength of X-ray used was 0.154 nm . The morphology of the polymer surface was investigated under TESCAN VEGA 3 LMU Scanning electron microscope at an accelerating voltage of 10kV and $2000\times$ magnification was used.

3 Results and Discussion

3.1 ESR Studies

3.1.1 Effect of radiation dose

ESR spectra of PLLA irradiated with electron beam to radiation doses of 30, 60 and 90 kGy are as shown in Fig. 1. The spectra are doublet of quartet

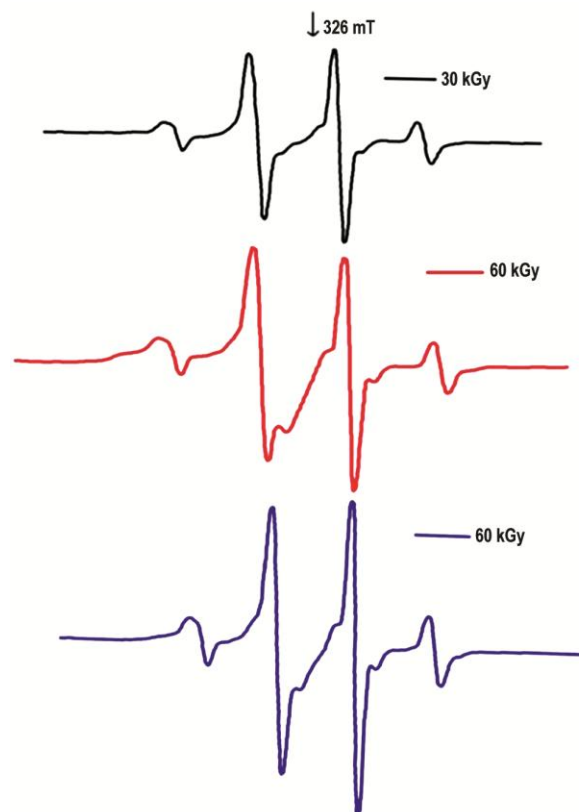


Fig. 1 — ESR spectra of EB irradiated PLLA irradiated to doses 30, 60 and 90 kGy.

with hyperfine splitting of 1.5 mT & 2.3 mT and are poorly resolved hyperfine pattern due to anisotropy of the polymer matrix. As the radiation dose is increased, intensity of the spectra gradually increased. Increase in spectral area corresponds to formation of more number of free radicals on radiation exposure. Free radicals produced in PLLA due to irradiation have been identified by various authors¹⁶⁻¹⁸ using ESR technique. Babanalbandi *et al.* have recorded the ESR spectra of irradiated PLLA at various temperatures from 77K – 350K. They have proposed the existence of three types of free radicals. They are (i) free radicals produced due to cleavage of proton from methine group of PLA backbone $\sim\dot{C}(CH_3)\sim$ (I) (ii) free radicals produced due to homolytic cleavage of C-C bond near ester carbonyl group of PLA backbone $\dot{C}H(CH_3)\sim$ (II) (iii) free radicals formed by cleavage of bonds adjacent to carbonyl group of PLLA backbone $\dot{C}O\sim$ (III). Later Kantoglu *et al.*¹⁷ have recorded the ESR spectra of PLA copolymer irradiated to sterilized doses and the spectrum is assigned to be due to radical (I). In addition to radical (I), (II) and (III), Nugroho *et al.*¹⁹ have postulated the presence of two more radicals in irradiated PLLA. They are $\sim CO\dot{O}$ (IV) and $\sim CH\dot{O}CH_3$ (V).

The studies indicate that PLLA preferably undergo random chain scission when exposed to high energy radiation. Consequently the ESR spectra are assigned to different types of free radicals I, II & III under different conditions. However component spectra corresponding to each of these free radicals have not been shown in literature. The authors have generated component spectra corresponding to each free radical species and superposed them in different proportions to get resultant spectrum. The simulation studies indicate that the observed ESR spectrum of EB irradiated PLLA at RT could be simulated with the component spectra arising due to two different free radicals. Component-1 is simulated with the values of $n_i=2$ (one interacting α -proton) & $m_i=4$ (three interacting β -proton) and total number of hyperfine lines is $2 \times 4=8$ i.e. octet or doublets of quartets assigned to be due to the free radical of type $\dot{C}H(CH_3)\sim$ (II). The other one is component quartet simulated with the values of $n_i=1$ & $m_i=4$ i.e. three alpha protons of the radical $\sim\dot{C}(CH_3)\sim$ (I). The corresponding component spectra of both the radical species are as shown in Fig. 2. To estimate the goodness of fit, experimental and simulated (superposed) spectra are overlapped as shown in Fig. 3. It is also to be noted that the two radicals

$\dot{C}H(CH_3)\sim$ & $\sim\dot{C}(CH_3)\sim$ are superposed in the ratio of 3:1 respectively. Therefore presence of radical (I) & (II) is proposed at room temperature for EB irradiated PLLA. The presence of radical (III) might be seen at temperatures below RT. Magnetic properties employed to simulate the spectra of EB irradiated PLLA are as listed in Table 1.

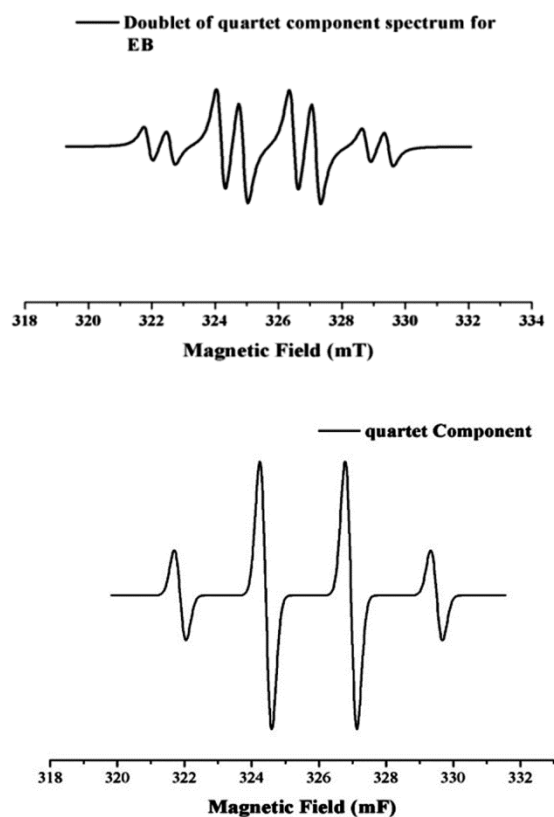


Fig. 2 — (a) Component doublet of quartet spectrum due to radical-II (b) Component quartet spectrum due to radical-I of EB irradiated PLLA.

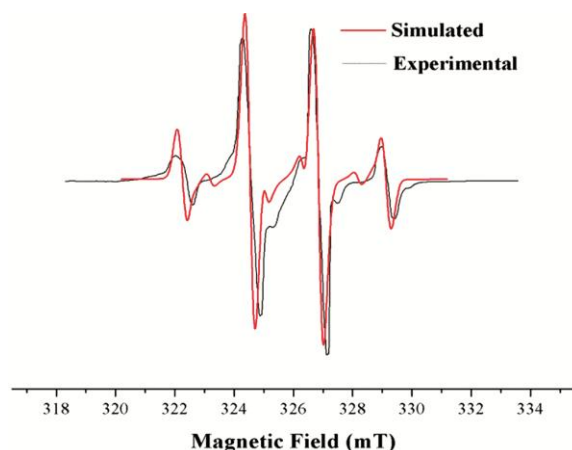


Fig. 3 — Overlapping of experimental and simulated (superposition of two component spectra) of EB irradiated PLLA.

Table 1 — Magnetic parameters of component spectra of EB irradiated PLLA

S.No	Dose kGy	component	Line width H_{pp}	hyperfine Splitting (mT)		number of interacting protons		g-value
				A	B	n_i	m_i	
1	90	quartet	0.35	2.3	0	0	3	2.0061
		doublet of quartet	0.35	2.3	0.7	1	3	2.0057
2	60	quartet	0.35	2.3	0	0	3	2.0061
		doublet of quartet	0.35	2.3	0.7	1	3	2.0057

The main event of degradation of PLLA is rupturing of proton at quaternary carbon forming radical $\sim\dot{C}(\text{CH}_3)\sim$ (I), which gives the component quartet spectrum. The other cleavages occur at the ester carbonyl group of PLLA back bone forming radical $\dot{\text{C}}\text{H}(\text{CH}_3)\sim$ (II), which gives component doublet of quartet or octet. Since irradiation is performed in air, diffusion of oxygen takes place forming peroxy radicals. But diffusion of oxygen is controlled by the morphology of the polymer. Also ESR spectrum due to peroxy radical is characterized by its anisotropic shape. Such type of ESR spectra is not observed in EB irradiated PLLA

3.1.2 Effect of Temperature

To study the thermal stability of free radicals produced in PLLA, variable temperature ESR spectra of EB irradiated PLLA are recorded at different temperatures 323d, 353d and 393 K are shown in Fig. 4. As the temperature is increased the doublet of quartet remains stable upto temperature 353 K and it assumes a doublet like structure at 363 K. Though the spectrum appears to be a doublet, enlarged spectrum indicates that the spectrum is quartet. Similarly the spectrum appearing at 393 K is appears to be doublet but it contains two more latent lines in the wings. Main lines of the doublet/quartet shows latent doublet like structures. Therefore doublets of quartet are likely to be present at 363 K.

The ESR signal totally vanished by heating the irradiated PLLA beyond 393 K. The melting temperature (T_m) of PLLA is 428 K (155°C)²⁰. The disappearance of ESR signal below melting temperature of PLLA depicts that the free radicals are trapped in amorphous region of PLLA. This type of phenomena is observed in other semi-crystalline polymers like Polyglycolic acid²¹, Polyethylene terephthalate²² etc.

3.2 FTIR Studies

To ascertain the chemical changes induced by EB irradiation in polymer, FTIR spectra are recorded for unirradiated and irradiated PLLA are shown in Fig. 5.

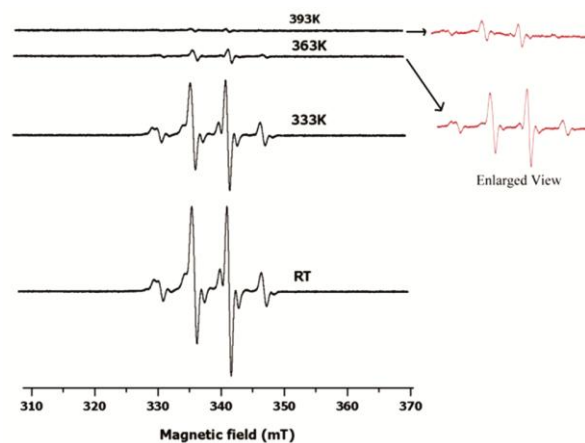


Fig. 4 — Temperature dependent ESR spectra of EB irradiated PLLA.

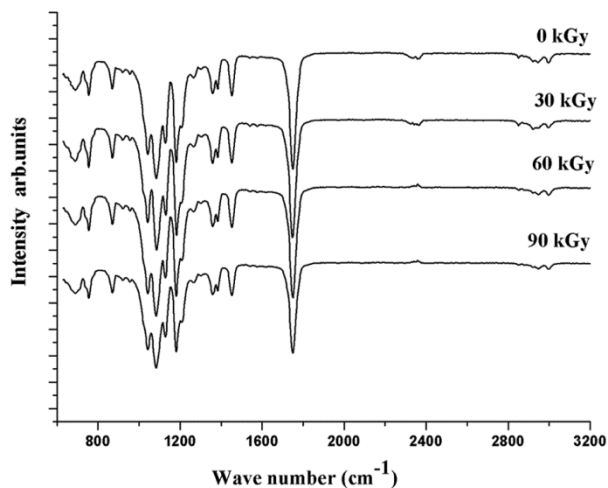


Fig. 5 — FTIR Spectra of unirradiated and EB irradiated PLLA.

FTIR spectra of unirradiated and irradiated PLLA exhibit absorption bands at 2997 cm^{-1} and 2945 cm^{-1} due to asymmetric and symmetric stretching of $-\text{CH}_3$, $-\text{CH}$ functional groups. The absorption band 1745 cm^{-1} is due to valance vibrations of the carbonyl group ($-\text{C}=\text{O}$)¹⁴. Absorption bands at 1453 cm^{-1} , 1353 cm^{-1} are indicative of asymmetric and symmetric stretching of $-\text{CH}_3$ groups. Other absorption bands at 1183 cm^{-1} , 1080 cm^{-1} and 1043 cm^{-1} are reported to be associated with asymmetric bending of (COC), symmetric bending of (COC) and vibrations of (C- CH_3)

respectively in PLLA chains²³. New chemical bond formation following irradiation was not detected. On irradiation the following changes are observed. (i) Decrease in intensity of 1745 cm^{-1} band is observed (ii) Intensity of band 2340 cm^{-1} is due to trapped carbon dioxide gas. (iii) No change in the intensity of absorption bands 1453 cm^{-1} and 1350 cm^{-1} indicates that the cleavage does not occur at C-CH₃ band. The intensities of valance carbonyl group bands of unirradiated and irradiated PLLA were compared by the base line method. The results depict that the intensity of the absorption band 1745 cm^{-1} is reduced by 12% for 90 kGy dose. No significant change in intensity of 1745 cm^{-1} band was observed for other doses *i.e.* 30 and 60 kGy. The reduction is associated with decarbonylation and decarboxylation processes of PLLA macro-molecular chains.

3.3 DSC studies

3.3.1 Glass Transition and Melting behavior

Thermograms of non-irradiated and EB treated PLLA are as shown in Fig. 6. The thermal parameters are as listed in Table 2. Glass transition temperature (T_g) and melting temperature (T_m) of pure PLLA 61° C and 155° C respectively²⁰. The variation of T_g and T_m following radiation dose are as shown in Fig. 7. This type of variation in T_g and T_m for gamma and EB irradiated PLLA was also observed by Loo *et al*^{9,24}.

Though the T_g and T_m have decreased with the dose of irradiation, both the melting enthalpy (ΔH) and degree of crystallinity (X_c) have followed a different trend. Both ΔH and X_c increased initially upto 30 kGy dose of irradiation and then started decrease after 30 kGy (but the decreased value is greater than the unirradiated value of ΔH and X_c). PLLA is a semi-crystalline polymer comprising of crystalline domains dispersed in amorphous phase of polymer matrix. Molecular chains are compact and orderly orientation in crystalline domains while the chain orientations are loose and irregular in amorphous regions. On irradiation, the cleavage of molecular chains takes place in amorphous region where the chains are less dense and disordered which results in lesser degree of molecular entanglement, causing a decrease in T_g . As

the radiation dose is increased further, cleavage of more number of chains takes place reducing the T_g further. Therefore in the event of radiation exposure, chain cleavages occur in amorphous region rather than crystalline region.

Further appearance of a small shoulder in low temperature side of melting thermogram indicates formation of new crystalline phase for PLLA irradiated to a dose of 30-60 kGy.

Development of shoulder on the melting thermogram of irradiated PLLA has also been

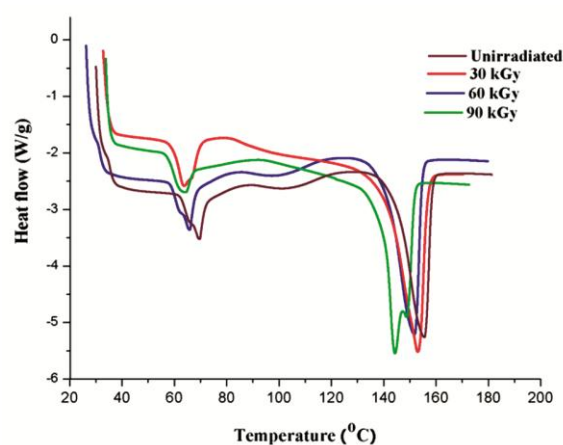


Fig. 6 — DSC thermograms unirradiated and EB irradiated PLLA.

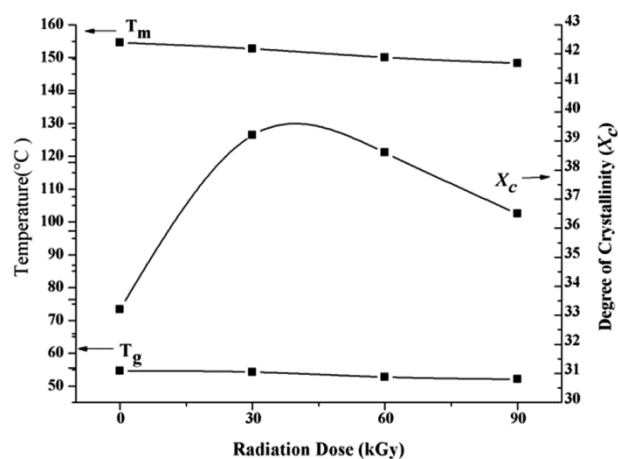


Fig. 7 — Variation of T_m , T_g and X_c with radiation dose of EB irradiated PLLA.

Table 2 — Thermal parameters of EB irradiated PLLA

Dose kGy	Melting Temperature (°C)	Glass Transition (T_g) °C	Enthalpy (ΔH) J/g	Degree of crystallinity (X_c) DSC	Degree of crystallinity (X_c) XRD
0	154.6	61.9	34.1	36.6	33.2
30	152.8	59.4	36.6	39.3	38.2
60	151.4	58.8	36.1	38.8	36.7
90	142.2	58.1	31.2	33.5	34.9

reported by few authors^{9,19}. This indicates that there are two types of irregularities in PLLA on irradiation. Further the onset of melting transition begins at 137° C for unirradiated PLLA where as the process begins at an early temperature in case of irradiated PLLA. The transition process advanced by a temperature of 12° C for 90 kGy irradiated polymer.

3.3.2 Variation of Degree of Crystallinity (X_C)

The radiation induced increase in crystallinity at lower doses can be attributed to scission of stiff molecules and increase in lamellar thickness. The molecular chain mobility was improved significantly with low degree of molecular entanglement of cleaved chains. Crystallization process takes place when the cleaved polymer chains align themselves orderly and increases X_C at initial doses. Such type of increase in X_C has also been reported in PGA²¹. X_C increased upto 30 kGy and decreased for subsequent doses. The decrease of X_C above 30 kGy is due to recombination of radicals within the crystalline region due to close packing structures of crystalline region in PLLA. This results in branching and non-uniformity of chains.

Variation of X_C with radiation dose is as shown in Fig. 7. Such type of variation in degree of crystallinity for gamma and EB irradiated PLLA was also observed by Milicevic *et al*^{9,24}.

The ΔH values gradually increases and then decrease with radiation dose confirming the crystallinity behavior of irradiated PLLA. These views are further strengthened by particle size measurements of XRD technique using Scherrer equation. Full width at half maximum (FWHM) corresponds to the mean dimension of crystallite (t). FWHM is strongly affected by damages occur in crystalline region, causing the broadening of peaks. Increase of ' t ' confirms the radiation induced crystallite damage of crystal region.

3.4 XRD Studies

X-ray diffraction profile of unirradiated and irradiated PLLA are shown in Fig. 8. The diffractograms show two prominent peaks centered around 2θ of 16.5° and 18.5°. They are assigned to 100/200 and 203 planes of PLLA crystal²⁵. PLLA is reported to exist in three different crystalline states namely α , β and γ forms. Among them, α -form is more prominent and reported to have a pure left handed 10_3 helix which packs into an orthorhombic unit cell²⁶. Degree of crystallinity from XRD is calculated and the values are listed in Table 2.

Before and after irradiation the prominent peaks are appeared at $2\theta = 16.5^\circ$ & 18.5° for PLLA which

remained almost in the same position. Inter-planer spacing (d) corresponding to 16.5° peak is calculated using Bragg equation and variation of inter-planer spacing against radiation dose is as depicted in Fig. 9. Full width at half maximum (FWHM) of XRD peaks represent the domain or crystallite size distribution of the semi-crystalline polymer. The average crystallite size (t) is calculated using Scherrer equation and variation of crystallite size with radiation dose is shown in Fig. 9. It is observed that the values of ' d ' decreased while ' t ' increased following the radiation dose. This is assigned to damage of crystalline structure and increase of domain or crystallite size. The degree of crystallinity is measured from DSC and XRD methods however small variations are observed in both the methods but followed the same trend. Diffractograms are obtained from the sample surfaces which are influenced by polymer processing and shear zones thus leading to higher degree of crystallinity.

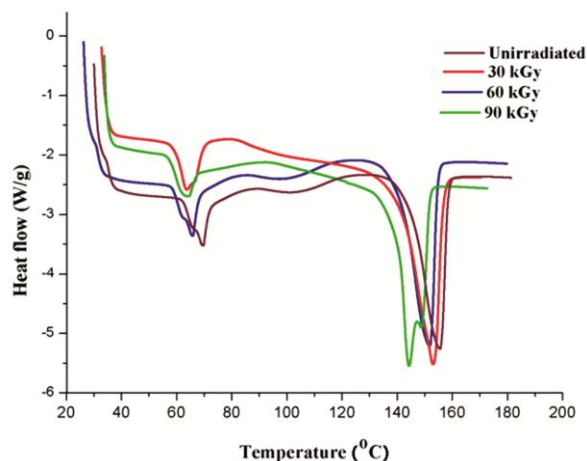


Fig. 8 — XRD diffractograms of unirradiated and EB irradiated PLLA.

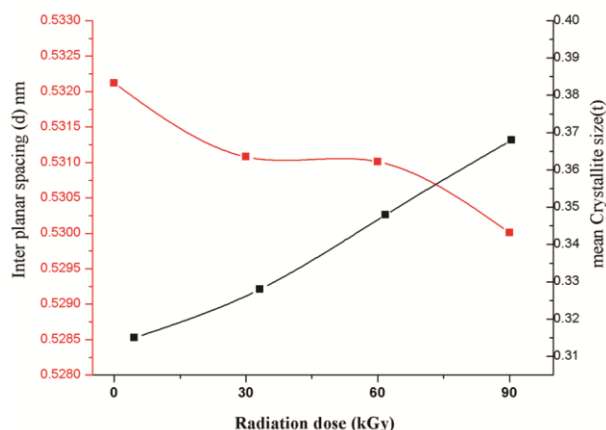


Fig. 9 — Variation of inter planar spacing (d) and mean crystallite size (t) with radiation dose of EB irradiated PLLA.

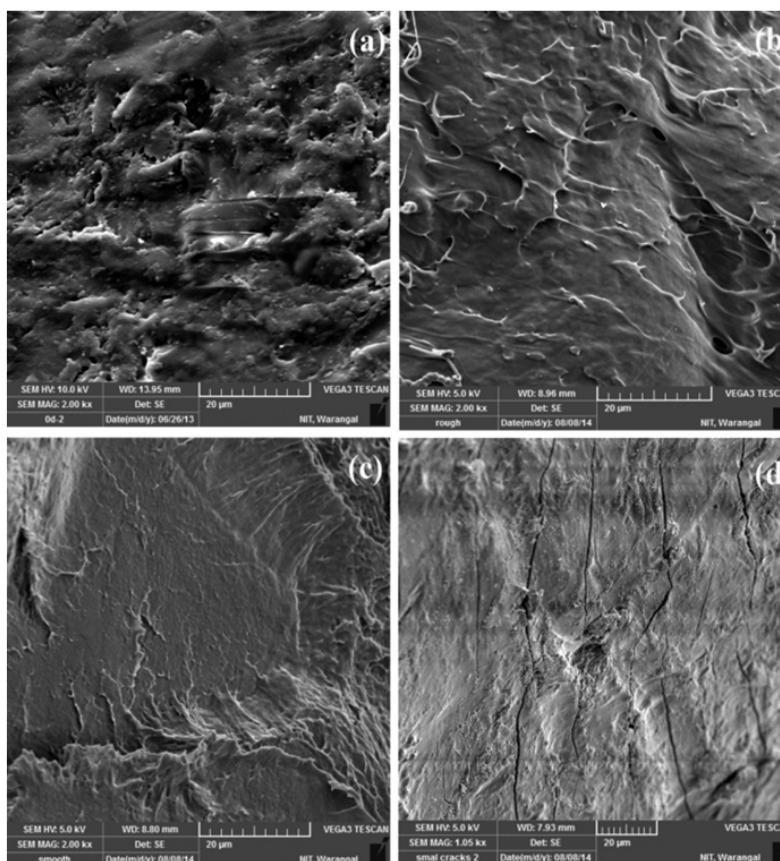


Fig. 10 — SEM images of EB irradiated PLLA of doses (a) unirradiated (b) 30 kGy (c) 60 kGy (d) 90 kGy.

This phenomenon is observed in case of other semi-crystalline polymers²⁷.

3.5 SEM studies

The SEM Micrographs of unirradiated and electron beam irradiated PLLA are as shown in Fig. 10(a-d) respectively. The surface morphology of irradiated PLLA is dose dependent. The surface of PLLA became irregular/damaged following irradiation and at 90 kGy of dose micro cracks are generated, which depicts the surface effect of electron beam radiation. The modification of surface by irradiation is attributed to degradation of polymer.

Conclusions

EB irradiation of PLLA leads to random chain scission producing two types of radicals $\sim\dot{C}(\text{CH}_3)\sim$ (I) and $\dot{\text{C}}\text{H}(\text{CH}_3)\sim$ (II). Radical (I) gives component quartet spectrum while radical (II) gives component doublet of quartet at RT as confirmed by simulation studies. With the increase of temperature, ESR spectral intensity gradually decreases and signal totally decays around 380 K *i.e.* below the melting temperature of PLLA which depicts that the free radicals are captured in amorphous

region. FTIR spectroscopy reveals that new chemical bonds weren't formed upon electron beam treatment. It was established that there is a 12% reduction in the intensity of $-\text{C}=\text{O}$ band by giving off CO/CO_2 on irradiation. DSC studies indicate that both T_g and T_m have decreased following radiation dose. However degree of crystallinity increased initially upto 30 kGy of radiation dose followed by a decrease after 30 kGy dose. In the present studies the dose range 30-60 kGy acts as a crucial transition zone between chain scission and recombination of the free radicals. In this dose range the degree of crystallinity has changed significantly which confirmed the existence of two types of crystalline lamellar present in irradiated PLLA. SEM studies indicate that the degradation process is predominant in PLLA on irradiation. The use of biopolymers in packaging industries depends on thermal, crystalline properties of polymer and electron beam irradiation has successfully tailored these properties of PLLA.

Acknowledgements

The authors would like to thank BRIT, Mumbai for extending the Electron beam facility. We would also

like to thank Dr. Mukhul Gupta, UGC- DAE CSR, Indore for XRD measurements. Thanks to SAIF, IIT Mumbai for ESR spectrometer facility.

References

- 1 V Krikorian & D J Pochan, *Chem Mater*, 15 (2003) 4317.
- 2 Ito H, Minami A, Tanino H & Matsuno T, *Acta Orthop Scand*, 73 (2002) 60.
- 3 Melski K, Kubera H & Gluszewski W, *Nukleonika*, 56 (2011) 65.
- 4 Vargas L F, Welt B A, Pullammanappallil P, Teixeira A A, Balaban M O & Beatty C L, *Packag Technol Sci*, 22 (2009) 97.
- 5 Fortunati E, Puglia D, Iannoni A, Terenzi A, Kenny J M & Torre L *Materials (Basel)*, 10 (2017) 809.
- 6 Gupta M C & Deshmukh V G, *Polymer*, 24 (1983) 827.
- 7 Gupta M C & Deshmukh V G, *Colloid Polym Sci*, 260 (1982) 514.
- 8 Athanasiou K A, Niederauer G G & C M Agrawal, *Biomaterials*, 17 (1996) 93.
- 9 Milicevic D, Trifunovic S, Galovic S & Suljovrujic E, *Radiat Phys Chem*, 76 (2007) 1376.
- 10 Loo S C J, Ooi C P & Boey Y C F, *Polym Degrad Stab*, 83 (2004) 259.
- 11 Yovcheva T, Marudova M, Viraneva A, Gencheva E, Balabanov N & Mekishev G, *J Appl Polym Sci*, 128 (2013) 139.
- 12 Madera-Santana T J, Meléndrez R, González-García G, Quintana-Owen P & Pillai S D, *Radiat Phys Chem*, 123 (2016) 6.
- 13 Mansouri M, Berrayah A, Beyens C, Rosenauer C, Jama C & Maschke U, *Polym Degrad Stab*, 133 (2016) 293.
- 14 Vasenina I V, Savkin K P, Laput O A, Lytkina D N, Botvin V V, Medovnik A V & Kurzina I A, *Surf Coatings Technol*, 334 (2018) 134.
- 15 Saëdlou S, Huneault M A, Li H & Park C B, *Polymer (Guildf)*, 54 (2013) 5762.
- 16 Babanalbandi A, Hill D J T, Donnell J H, Pomery P J & Whittaker A, *Polym Degrad Stab*, 50 (1995) 297.
- 17 Kantoglu O, Ozbey T & Guven O, *Kinetics of free radical decay reactions in lactic acid homo and copolymers irradiated to sterilization dose*, (1995) 837.
- 18 Nugroho P, Mitomo H, Yoshii F & T Kume, *Polymer*, 72 (2001) 1.
- 19 Nugroho P, Mitomo H, Yoshii F & T Kume, *Polym Degrad Stab*, 72 (2001) 337.
- 20 Martin O & L Avérous, *Polymer (Guildf)*, 42 (2001) 6209.
- 21 Nakka R R, Thumu V R, SVS R R & Buddhiraju S R, *Radiat Eff Defects Solids*, (2015) 1.
- 22 Campbell D & Turner D T, *J Polym Sci Part A-1 Polym Chem*, 5 (1967) 2199.
- 23 Kister G, Cassanas G & Vert M, *Spectrochim Acta Part A Mol Biomol Spectrosc*, 53 (1997) 1399.
- 24 Loo J S C S C, Ooi C P P & Boey F Y C Y C, *Biomaterials*, 26 (2005) 1359.
- 25 Brizzolara D, Cantow H J, Diederichs K, Keller E & Domb A J, *Macromolecules*, 29 (1996) 191.
- 26 Okihara T, Tsuji M, Kawaguchi A, Katayama K-I, Tsuji H, Hyon S H & Ikada Y, *J Macromol Sci Phys*, 30 (1991) 119.
- 27 Cairns M L, Dickson G R, Orr J F, Farrar D, Hawkins K & Buchanan F J, *Polym Degrad Stab*, 96 (2011) 76.