Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (3): 599-607

(International Peer Reviewed Journal)

Dose-Dependent Effect of Gamma Radiation on Structural, Thermal and Electrical Properties of Lexan Polymer

Parimal Chandra Bhomick[1], Biswajit Kakoty[2], Susmita Ghosh[1] and Dipak Sinha[1]*

1. Department of Chemistry, Nagaland University, Lumami Campus, Nagaland 798627, **INDIA**
2. Department of Chemistry, Darrang College, Tezpur, Assam 784001, **INDIA**

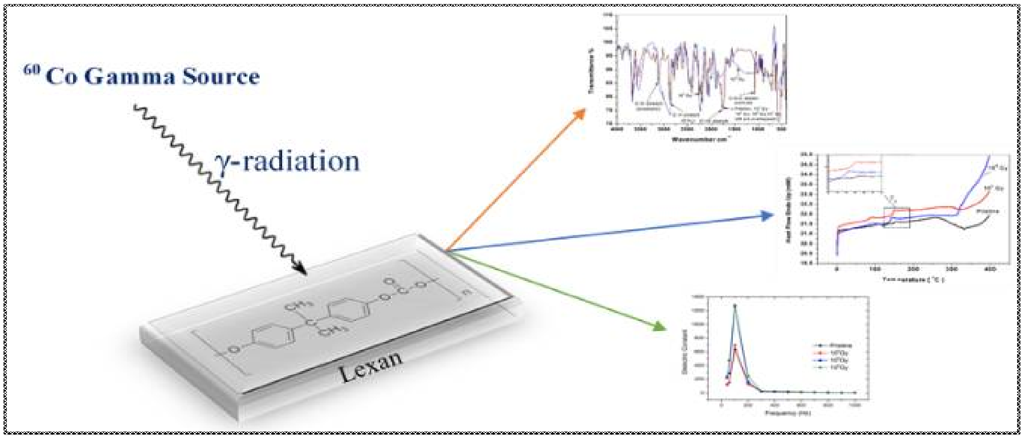
Email: dipaksinha@gmail.com

Accepted on 20th April, 2018

ABSTRACT

Lexan polymer was irradiated with gamma radiation of 10^1-10^6 Gy dose with a ^{60}Co gamma source having a dose rate of 3k Gy h^{-1} at room temperature. The structural, thermal and electrical properties of Lexan polymer irradiated with gamma radiation had been investigated using different analytical techniques. FT-IR studies evidences chain scission and cross-linking at higher gamma dose. TGA and DSC studies reveal that due to gamma exposure, the polymer loses its weight in a single step pattern in comparison to a double step decomposition pattern observed for pristine polymer. Glass transition temperature of the polymer was also found to follow a decreasing order from 150°Cto140°C with increasing gamma dose. Dielectric constant was found to be much higher for their radiated samples in comparison to the pristine Lexan polymer at lower frequency.

Graphical Abstract



Keywords: FT-IR, Gamma Dose, Glass Transition Temperature, Dielectric constant

---

INTRODUCTION

The rapidly expanding use of polymers as materials in hostile environments, in microlithography, and in medical fields makes an understanding of the fundamental processes involved in radiation induced polymer degradation an incumbency [**1-10**]. The degradation of polymer upon irradiation by gamma dose is a universal fact which leads to changes in the chemical and physical properties of the irradiated polymer either through chain- scission or by cross linking brought upon by photo-dissociation of the polymer into radical which is most quintessential, leading to cross-linking process. When these form a network, formation of carbon clusters, liberation of volatile species and, in some cases, even formation of new chemical bonds in the polymeric matrix is observed [**1-6, 9-12**]. Lexan polycarbonate is an amorphous, colorless polymer used extensively for engineering and optical applications. Lexan polycarbonate is widely used for ion track recording and to prepare track-etched membrane as micro filters. Polycarbonate particle track etch membranes are used as templates in the manufacture of nano-tubes and nano-wires [**4, 13**]. Myriad studies have been reported on the radiation-induced degradation of polymers by various researchers [**7-9, 14-16**].

Materials response to high energy ion-beam is expected to be considerably different from those induced by γ-rays. Several works have been reported on gamma irradiation effects on polymers in recent years [**8, 9, 14-17**]. Chowdhury *et al.*, 2017 studied the effect of gamma radiation on the transport and structural properties of polyacrylonitrile-lithium bis (oxalato) borate films, while Stajanca *et al.*, 2016 reported the effects of gamma radiation gamma radiation on per fluorinated polymer optical fibers [**18, 19**]. Our group have been working on modifications of polymers by high doses of gamma radiation for last couple of years and works on PADC, polycarbonate, polyvinylchlorid, poly propylene are reported earlier [**20-24**]. It has been observed that in some cases, modifications induced are very significant, but again in some case the changes not so significant. In continuation of the work, in this present study also, we are reporting a work on gamma induced effect on Lexan polymer.

Polycarbonates are essentially those polymers in which dihydric or polyhydric phenols are joined through carbonate linkages. These polymers which are non-toxic in nature are considered to be the toughest of all the thermoplastics and have the following general structure [**7**]. Lexan polymer is one of the promising polymers which is being utilized in numerous fields of science and technology such as optical, medical, electronic, in space applications and also as nuclear track detectors due to its low cost, easy process ability and low weight [**2,25**]. There have been some reports about gamma irradiation effects on Lexan polycarbonate, however most of the studies have so far been limited to low doses of gamma radiation [**26–28**]. For example, Tayel *et al.*, studied gamma irradiation effect on polycarbonate polymer in the dose range of 20 to 1000 KGy, while Fares studied in the range of 10 to 200 KGy [**27, 28**].Though works related to effect of high doses of gamma radiation on polycarbonate polymer is not very common, however some results have been reported by Navarro-Gonzalez *et.al.*, based on studies in the gamma dose range of 0.25 to 1MGy [**25**]. Understanding the need for a more comprehensive study on radiation effects on Lexan polymer, an effort has been made to study the effect of high doses of gamma radiation on this polymer and this paper presents the results of the study. Accordingly, the dose dependent modifications of different physical and chemical properties of irradiated Lexan polymer have been studied in detail in the range of 10^1 Gy upto 10^6 Gy. Different analytical techniques like FT-IR (Fourier transform infrared Spectroscopy), TGA (Thermo gravimetric Analysis), DSC (Differential Scanning Calorimetry) and Dielectric measurements are used to understand the modifications that took place in the polymer matrix due to gamma irradiation.

MATERIALS AND METHODS

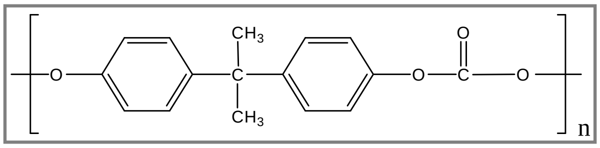
For this present study, Lexan polymer (which is a trade name of polycarbonate polymer) having thickness 600 µm and manufactured by GEC, USA was used. Samples of size s of $2.5\times2.5\text{cm}^2$ of (seven samples) were prepared from commercially available sheets. They were then irradiated with a

^{60}Co gamma source having a dose rate of 3kGy h^{-1} at room temperature. The polymers were exposed to various doses of gamma radiation in the dose range of 10^1-10^6 Gy. The exposure time varied from12 seconds to nearly 14 days in order to deliver the required doses. The errors in doses range from 8% for low dose (10Gy) to about 1% for high doses (10^6Gy).

FT-IR spectra of the irradiated and pristine polymers were taken in the solid state keeping air as the reference. The spectra were recorded using a Nicolet Impact 410 Fourier transforming instrument in the range between 4000 cm^{-1} to 400 cm^{-1}. TGA and DSC measurements were done using Perkin Elmer thermal analyzer, STA 6000 and DSC 6000 at a heating rate of 10°C min^{-1} respectively. Dielectric measurement was done with HIOKI 3532-50 LCR HITESTER meter in the frequency range of 60 to 1000 Hz.

RESULTS AND DISCUSSION

The chemical structure of Lexan, which is a polycarbonate polymer, is given below:



The modifications that took place due to gamma irradiation of different doses are discussed systematically below under different sub headings.

FTIR studies: Figure 1 illustrates the FT-IR spectra of pristine and irradiated polymer at a dose of 10^1 Gy to 10^6Gy. Some of the important characteristics peaks of pristine polymer (Table 1) like aromatic C-H stretching, aromatic C-O-C asymmetric stretching, CH_3 symmetric stretching, are in CH_3 stretching and C=O bondstretching are shown in the spectra. It has been observed that even though the polymer is irradiated with different doses of gamma radiation, the significant modifications occur only at the highest dose of 10^6 Gy as evident from the IR spectra.

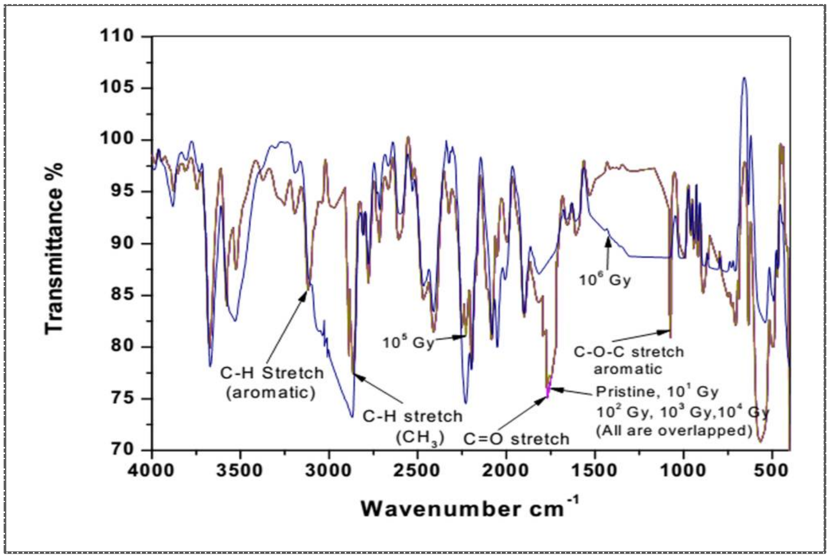


Figure 1. FT-IR spectra of Pristine and gamma irradiated Lexan Polymer at different doses

The comparison of IR spectra at different doses, which is shown in figure 1, has been made to understand the changes in the irradiated polymer in comparison with the pristine one. From the comparison, it can be observed for example that the existing peak at 3118 cm^{-1} (C-H stretching for benzene group) and 2863 cm^{-1} (C-H stretching for -CH_3 group) of the pristine polymer almost disappears at the dose of 10^6 Gy. This disappearance of the above mentioned peaks are due to scissioning of the C-H bonds for both benzene and CH_3 groups. Scissioning of C-H bond of CH_3 group has been observed by Semwal *et al.*, 2013 due to O^{+8} ion irradiation for Lexan polycarbonate [**7**]. Similarly scissioning of C-H bond at a high gamma dose has also been reported earlier for Makforol-E polycarbonate **[24]**.

Table 1. Major absorption peaks of pristine Lexan polymer

CH_3 symmetric stretching	~2863 cm^{-1}
Aromatic C-H stretching	~3100-3000 cm^{-1}
Aromatic C-O-C Asymmetric stretching	~1074 cm^{-1}
C=O bonds	~1768 cm^{-1}
C- H Stretching/ Arene CH_3 stretching	~3118 cm^{-1}

It is also observed that at a frequency of 2228 cm^{-1} a strong peak appears for the irradiated polymer at the dose of 10^6 Gy. On minutely comparing this peak with the peaks of the pristine sample, it is observed that there were two peaks existing at 2249 cm^{-1} and 2227 cm^{-1} for the pristine sample. On the other hand, the spectrum of Lexan which is has been irradiated at a dose of 10^6Gy shows appearance of only one very strong peak at a frequency of 2228 cm^{-1}. Mechanistically, it can be assumed that this peak at 2228 cm^{-1} might be due to formation of some triple bonds in the polymer matrix due scissioning and rearranging of polymer chain induced by gamma irradiation [**29**]. Interestingly this observation is only seen in the IR spectra of that polymer which has been irradiated at a dose of 10^6 Gy. From this observation, some probable explanation about the structural modifications might be drawn, suggesting that gamma irradiation at a dose of 10^6 Gy causes scissioning of C-H bond for both CH_3 group as well as aromatic C-H bond to take place, thereby leading to the formation of aryne groups in the polymer matrix, causing the strong IR peak to appear at a frequency of 2228 cm^{-1}.

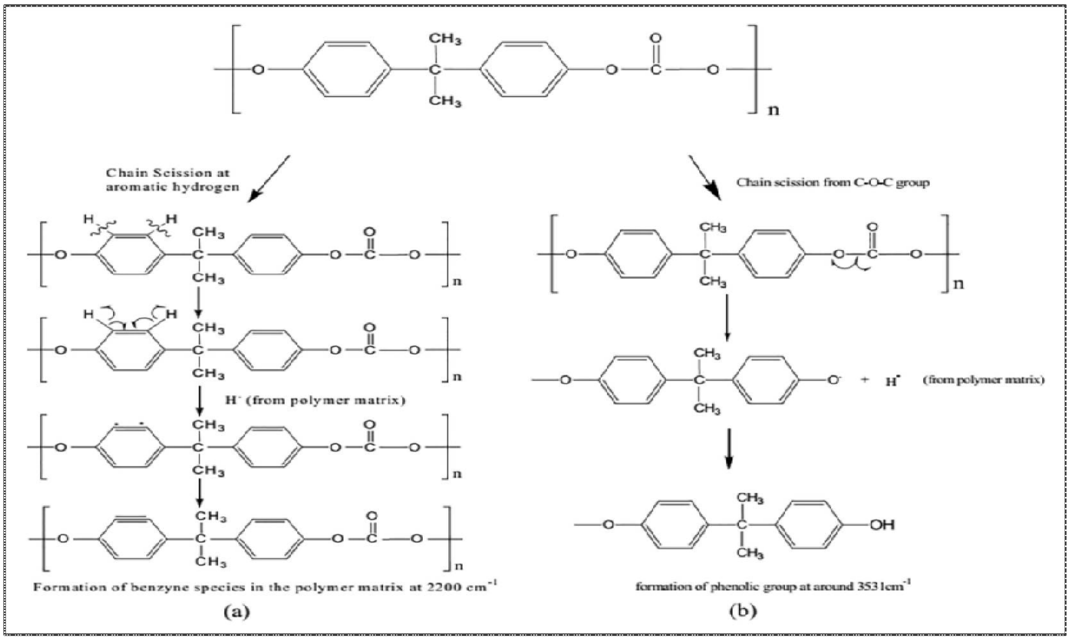


Figure 2. Plausible mechanism showing formation of (a) benzyne (b) phenolic groups in the irriadaiated Lexan polymer

Further, it is also observed that there is a disappearance of the carbonyl peak at 1768 cm^{-1} in their radiated polymer at a dose of 10^6 Gy which was not observed at lower doses of gamma radiation. This disappearance of the carbonyl peak might be due scissioning of ester linkage resulting probable release of carbon dioxide/carbon mono oxide [7]. At the same time, a new broad peak at around 3531 cm^{-1} appears. The appearance of the peak at 3531cm^{-1} might be due to O-H stretching bonds in the irradiated sample. The occurrence of O-H stretching could be due to the formation of a phenolic group in the polymer matrix through breakage of ester group. Scissioning of ester linkage leads to the formation of oxygen radicals which easily combine with hydrogen radicals and form phenolic groups [20, 29]. The probable chemical mechanism for the formation of phenolic group as well as arynes in the irradiated polymer is given in figure 2.

Thermal Studies: TGA thermogram of pristine and irradiated Lexanpolymer was obtained by heating the samples with a heating rate of 10°C min^{-1} and is shown in figure 3. The pristine lexan shows a double step decomposition pattern, in which the first step is a major step and the second step of weight loss is aminorone. The first step of decomposition takes place in the range from 377^{0}C-550°C and the second step of decomposition starts around 600°C and continues till 674^{0}C. Similar pattern of weight loss have been observed till the gamma dose of 10^4 Gy but at gamma dose 10^5 Gy and above, this weight loss pattern totally changes. At a dose of 10^5 Gy and10 Gy, the second step of decomposition disappears signifying the fact that the irradiated polymer loses its weight in a single step. Further, it is observed that at both 10^5 Gy and 10^6 Gy, thermal stability of their radiated polymer increases and the weight loss process continues till 750°C.

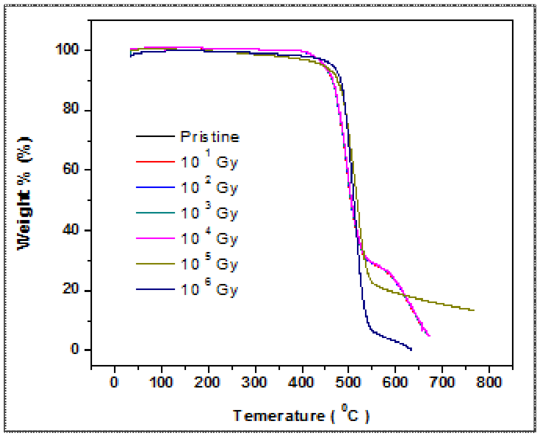


Figure 3. TGA thermogram of Lexan film irradiated with different doses of gamma radiation

DSC thermograms for pristine Lexanpolymer have been recorded in the temperature range 0°C to 400°C, with heating rate of 10°C min^{-1} (Fig. 4). From the figure it is clear that one prominent broad exothermic peak starts around 250^{0}C and finishes around 400°C. This exothermic peak is due to melting of the Lexanpolymer **[23, 30]**. Morphology of Lexanpolymer is such that it has both amorphous and crystalline arrangement of chain in the polymermatrix. The broad melting behavior of the polymer signifies the partial amorphous nature of the polymer. Comparing the DSC thermograms of pristine and irradiated samples (Fig. 4), it is observed that the board exothermic behavior of the polymer remains still the dose of 10^5 Gy. Only at the dose of 10^6 Gy, the board melting peak of the polymer reduces and almost ceases to exist. This disappearance may be due to the fact that due to Scissioning of the chainsand rearrangement of the broken segments, amorphous behavior of the polymer reduces and the polymer becomes more crystalline in nature. However, if one compares the TGA thermogram with DSC thermogram, it is observed that just after the exothermic transition, the weight loss of the polymer starts which highlights the fact that weight loss process starts after melting of the polymer.

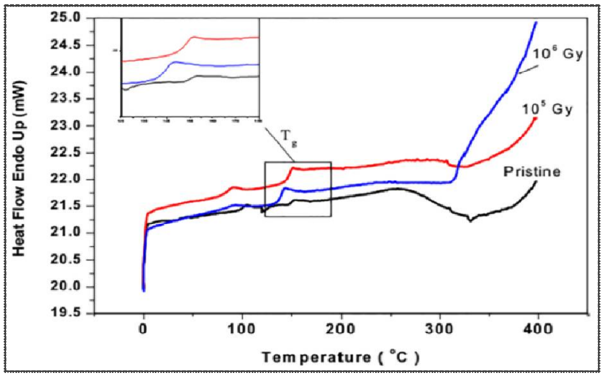


Figure 4. DSC curve at different dose showing T_g of Lexan polymer

Glass transition temperature of the pristine polymer is found to be around 150°C for the pristine Lexanpolymer. However on comparing the glass transition temperature (T_g) of the pristine polymer with their radiate done, it can be seen that the T_g decreases with increasing gamma dose. This decrease in T_g is observed only above the gamma dose of 10^4 Gy. A plot of decrease in T_g due to gamma exposure is shown in Figure 5, where it is observed that the T_g decreases from 150°C for pristine sample to140°C at the highest does of 10^6 Gy. The decrease in the T_g might be due to the increase in molecular mobility as a result of scissioning of the polymer chain which leads to decrease in the average molecular length of the polymer chain [23].

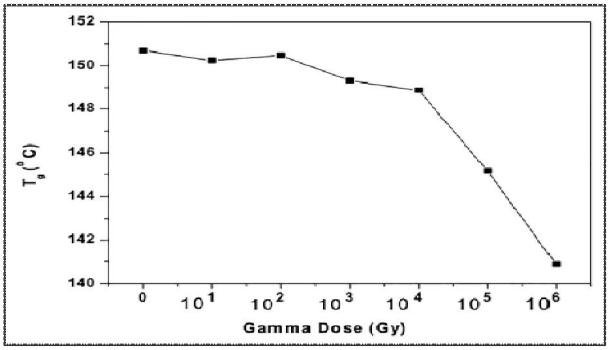


Figure 5. Dose dependent variation of T_g gamma irradiated Lexan polymer

Dielectric Studies: Dielectric constant for the pristine Lexan polymer along with irradiated polymer has been measured in the frequency range 42 to1000Hz and shown in figure 6.

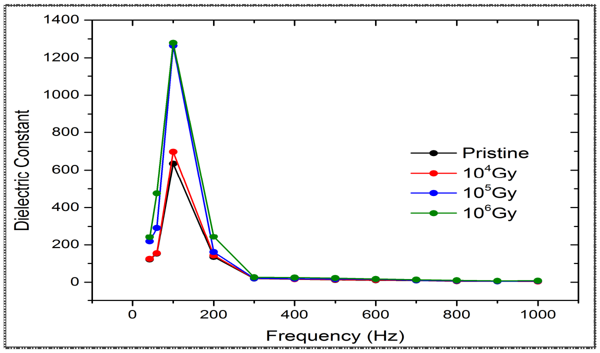


Figure 6. Comparison of dielectric constant of Lexan polymer irradiated at different doses with Pristine

Table 2. Dielectric Constant value of Pristine and irradiated at different doses

Frequency	Pristine	10^1 Gy	10^2 Gy	10^3 Gy	10^4 Gy	10^5 Gy	10^6 Gy
42	121.56	121.65	121.09	120.96	124.45	217.85	241.60
60	152.97	151.71	151.22	152.77	155.14	292.12	475.31
100	634.57	631.43	629.59	632.11	697.12	1264.34	1278.97
200	135.09	132.19	136.74	135.43	143.11	161.57	243.46
300	19.49	19.11	19.43	19.65	19.97	20.83	26.32
400	15.89	15.05	14.99	15.11	16.66	18.44	24.85
500	12.34	12.87	12.64	12.74	13.99	16.77	21.86
600	9.96	9.08	9.36	9.74	11.43	15.81	17.21
700	9.36	9.38	9.65	9.44	9.96	10.26	13.45
800	5.34	5.65	5.98	5.76	6.05	7.75	9.96
900	4.53	4.87	4.53	4.67	4.99	5.57	7.79
1000	4.00	4. 64	3.11	2.54	3.75	5.92	7.86

It is observed that dielectric constant of the polymer increases initially with increasing frequency and becomes highest at around 100 Hz and there after slowly decreases with increase in frequency. This decrease in dielectric constant is due to the fact that as the frequency increases, the charge carrier migrates through the dielectrics and gets trapped against a defect site, there by inducing an opposite charge in the vicinity which results in slowing down the motion of charge carriers, thereby decreasing the value [29]. A decrease in the dielectric constant with increasing frequency is expected in most dielectric materials due to dielectric relaxation, caused because the speed of dipole rotation at high frequency is insufficient to match the shift in the applied AC bias [22]. However, when the polymer is irradiated with gamma radiation of different doses, it is observed that the dielectric constant increases. This increase suggests that polarization in the polymer increases with gamma exposure (Fig. 6). Due to irradiation an increase in carrier polarization takes place indicating that charge carriers move by discontinuous hopping movements between localized sites. Their regularity in the polymerchains due to irradiation gives rise to a hopping mechanism which enhances the polarization in the polymer matrix. The dielectric constant values for pristine and irradiated polymer have been given in table 2. From the table, it is apparent that dielectric constant increases with irradiation and this increase is significant at a dose of higher than10^4 Gy.

CONCLUSIONS

From this present study, it can be concluded that due to gamma exposure, structural modifications of Lexan polymer take place due to gamma irradiation and these modifications are significant mostly at the highest dose of 10^6 Gy with random destruction of the polymeric chain taking place with the probable formation of aryne and phenolic groups in the polymer matrix. It is also found that glass transition temperature (T_g) of the Lexan polymer decreases with increasing gamma dose due to increase in mobility of the polymer chains caused by scissioning of the polymer chains. Dielectric constant increases with gamma exposure at lower frequency region at dose of higher than 10^4 Gy.

ACKNOWLEDGEMENTS

This work has got financial support through UGC Major Research Project (Project No: 42-267/2013). Author, Susmita Ghosh is grateful to UGC Major Research Project and Parimal Chandra Bhomickis grateful to DST- INSPIRE Fellowship for financial assistance.

REFERENCES

[1]. A. A. Abdel-Fattah, H. M. Abdel-Hamid, R. M. Radwan, Changes in the optical energy gap and ESR spectra of proton-irradiated unplasticized PVC copolymer and its possible use in radiation dosimetry, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms,* **2002,** 196, 279-285.

[2]. D. Fink, Fundamentals of ion-irradiated polymers, Springer Ser. Mater. Sci. v. 65. **2004.**

[3]. D. Fink, P. S. Alegaonkar, A. V. Petrov, M. Wilhelm, P. Szimkowiak, M. Behar, D. Sinha, W.R. Fahrner, K. Hoppe, L.T. Chadderton, High energy ion beam irradiation of polymers for electronic applications, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*., **2005,** 236, 1-20.

[4]. C. Gavade, N. L. Singh, A. Sharma, P. K. Khanna, F. Singh, The effect of SHI irradiation on structural, thermal and dielectric properties of a silver nanoparticle-embedded polystyrene matrix, *Radiat. Eff. Defects Solids*., **2011,** 166, 585-591.

[5]. L. Singh, K. S. Samra, Structural characterization of swift heavy ion irradiated polycarbonate, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*., **2007,** 263, 458-462.

[6]. G. B. V. S. Lakshmi, A. M. Siddiqui, M. Zulfequar, Structural, optical and electrical properties of 60MeV C5+ ion-irradiated poly(3-methylthiophene) films, *Radiat. Eff. Defects Solids*., **2011,** 166, 427-434.

[7]. A. Semwal, A. Negi, V. Joshi, T. Sehgal, F. Singh, R. C. Ramola, Modifications induced by O+8 ion beam to Lexan polycarbonate, *Radiat. Eff. Defects Solids*., **2013,** 168, 594-600.

[8]. K. Hareesh, A. K. Pandey, Y. Sangappa, R. Bhat, A. Venkataraman, G. Sanjeev, Changes in the properties of Lexan polycarbonate by UV irradiation, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, **2013,** 295, 61-68.

[9]. C. Agarwal, P. C. Kalsi, A. Ramaswami, Gamma-irradiation effects on track etching characteristics of polyester nuclear track detector, *Radiat. Eff. Defects Solids*., **2006,** 161, 131-133.

[10]. S. A. Nouh, M. M. Abutalib, Effect of gamma irradiation on the structural, thermal and optical properties of Makrofol BL 2–4, *Radiat. Eff. Defects Solids*, **2014,** 169, 817-827.

[11]. N. L. Singh, D. Singh, A. Qureshi, Swift heavy ion-induced modification of the physical properties of polymethyl methacrylate/carbon black composites, *Radiat. Eff. Defects Solids*., **2011,** 166, 640-647.

[12]. A. Tidjani, Y. Watanabe, Study of the Effect of g-Dose Rate on the Oxidation of Polypropylene, *J. Appl. Polym. Sci*., **1996,** 60, 1839-1845.

[13]. T. Yamauchi, R. Barillon, E. Balanzat, T. Asuka, K. Izumi, T. Masutani, K. Oda, Yields of CO2 formation and scissions at ether bonds along nuclear tracks in CR-39, *Radiat. Meas*., **2005,** 40, 224-228.

[14]. S. K. Gupta, P. Singh, R. Kumar, Modifications induced by gamma irradiation upon structural, optical and chemical properties of polyamide nylon-6,6 polymer, *Radiat. Eff. Defects Solids*., **2014,** 169, 679-685.

[15]. N. L. Mathakaria, V. N. Bhoraskar, S. D. Dhole, A comparative study on the effects of Co-60 gamma radiation on polypropylene and polyimide, *Radiat. Eff. Defects Solids*., **2014,** 169, 779-790.

[16]. Neerja, S. Prasher, S. Singh, The effect of gamma irradiation on the activation energy of bulk and track etching in Lexan track detector, *Radiat. Meas*., **2007,** 42, 135-137.

[17]. S. A. Nouh, M. H. Abdel-Salam, Y.E. Radwan, S.S. Fouad, Thermal, electrical and optical properties of proton-irradiated Makrofol de 7-2 nuclear track detector, *Radiat. Eff. Defects Solids*., **2011,** 166, 37-41.

[18]. F.I. Chowdhury, M.U. Khandaker, Y.M. Amin, A.K. Arof, Effect of gamma radiation on the transport and structural properties of polyacrylonitrile-lithium bis(oxalato)borate films, *Solid State Ionics*, **2017,** 304, 27-39.

[19]. P. Stajanca, L. Mihai, D. Sporea, D. Neguţ, H. Sturm, M. Schukar, K. Krebber, Effects of gamma radiation on perfluorinated polymer optical fibers, *Opt. Mater. (Amst)*., **2016,** 58, 226-233.

[20]. D. Sinha, K. L. Sahoo, U. B. Sinha, T. Swu, A. Chemseddine, D. Fink, Gamma-induced modifications of polycarbonate polymer, *Radiat. Eff. Defects Solids*., **2004,** 159, 587-595.

[21]. D. Sinha, T. Swu, S.P. Tripathy, R. Mishra, K.K. Dwivedi, D. Fink, Gamma-photon induced modification of Polyvinylchloride (PVC) film, *Radiat. Eff. Defects Solids*., **2003,** 158, 593-598.

[22]. T. Swu, C.A. Pongener, D. Sinha, N. Sen Sarma, Effect of gamma radiation on dielectric properties of polyacetate polymer, *Der Chem. Sin*., **2013,** 4, 132-136.

[23]. D. Sinha, A comparative study of gamma radiation effects on track properties of different PADC detectors, *Radiat. Eff. Defects Solids* [Internet]., **2009,** 164, 604-610.

[24]. D. Sinha, S. Ghosh, K.K. Dwivedi, D. Fink, Structural modifications and track registration response of some gamma irradiated polycarbonate detectors, *Radiat. Eff. Defects Solids*., **1998,** 145, 45-56.

[25]. R. Navarro-González, P. Coll, R. Aliev, Pyrolysis of γ-irradiated bisphenol-A polycarbonate, *Polym. Bull.*, **2002,** 48, 43-51.

[26]. S. Singh, S. Prasher, The optical, chemical and spectral response of gamma-irradiated Lexan polymeric track recorder, *Radiat. Meas*., **2005,** 40, 50-54.

[27]. A. Tayel, M.F. Zaki, A.B. El Basaty, T.M. Hegazy, Modifications induced by gamma irradiation to Makrofol polymer nuclear track detector, *J. Adv. Res*., **2015,** 6, 219-224.

[28]. S. Fares, Frequency Dependence of the Electrical Conductivity and Dielectric Constants of Polycarbonate (Makrofol-E) Film under the Effects of γ-Radiation Armenia, *Am. J. Mater. Sci*., **2011,** 1, 52-56.

[29]. B. Smith, Fundamentals of Fourier transform infrared spectroscopy, **2006.**

[30]. Z. Qiu, M. Komura, T. Ikehara, T. Nishi, DSC and TMDSC study of melting behaviour of poly(butylene succinate) and poly(ethylene succinate), *Polymer (Guildf)*., **2003,** 44, 7781-7785.