Annexure - VIII

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Final Report of the work done on the Major Research Project.

1.	Project report No. 1st /2nd /3rd/Final	Final
2.	UGC Reference No.F	42-267/2013 (SR); dated 25th March, 2013
3.	Period of report	01-04-2013 to 31st March, 2017
4.	Title of research project	Gamma Induced Modifications of Polymeric Nuclear Track Detectors
5.	(a) Name of the Principal Investigator (b) Department (c) University where work has progressed	Dr. Dipak Sinha Department of Chemistry Nagaland University
6.	Effective date of starting of the project	1st April, 2013
7.	Grant approved and expenditure incurred during the period of the report a. Total amount approved : b. Total expenditure :	a. 8,88,800/- b. 8,44,834/-

7. C. Report of the work done

i. **Brief objective of the project** :

The objective of the present proposal is to study the effect of gamma irradiation on modifications of physical and chemical properties of polymeric track detectors. In general their characterization requires more than just one technique and thus the objectives broadly proposed for this ongoing project was

- Study of modifications on thermal properties of track detectors due to different doses of gamma irradiation
- Study the modifications in track properties due to gamma irradiation
- Gamma irradiation effect on electrical properties of polymeric track detectors
- Study of surface and morphological modifications due to gamma irradiation

All this studies is expected to bring a complete understanding about the modifications that takes place due to irradiation of high doses of gamma radiation.

ii. **Work done so far and results achieved and publications, if any, resulting from the work:**

Attached as **Annexure-I**

iii. **Has the progress been according to original plan of work and towards achieving the objective? If not, state reasons**

Yes, the progress has been according to original plan

iv. **Please indicate the difficulties, if any, experienced in implementing the project**

One of the difficulties has been appointing project fellow under the project. Since the project fellow is given less salary then a JRF, students are reluctant to apply for the post. Secondly release of second installment was not done in time which made the progress of work little slower.

v. **If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet.**

The project is completed however some analysis is still going on. Some more publication are expected to come out from the project. Kindly refer **Annexture-I**

vi. **If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission.**

Attached

vii. **Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any**

Manpower trained: Two

Ph.D. Awarded: Not yet, but one student is registered

Publications of results: Some results are published and some results are yet to be published.

4/6/18

SIGNATURE OF PRINCIPAL INVESTIGATOR

21-06-18

REGISTRAR

कुलसचिव / Registrar
नागालैण्ड विश्वविद्यालय
Nagaland University
लुमामी / Lumami - 798627

Annexure-1

The objective of the present proposal is to study the effect of gamma irradiation on modifications of physical and chemical properties of polymeric track detectors. In general their characterization requires more than just one techniques and thus the objectives broadly proposed for this ongoing project was

- Study of modifications on thermal properties of track detectors due to different doses of gamma irradiation
- Study the modifications in track properties due to gamma irradiation
- Gamma irradiation effect on electrical properties of polymeric track detectors
- Study of surface and morphological modifications due to gamma irradiation

In the first year of study some of the polymeric detectors like Polyallyldiglycol carbonate (PADC), Polycarbonates (PC), Polyethylene terepthalate (PET) Polyvinyl Alcohol, Polyacetate are exposed to gamma radiation of different doses. Once the exposure is done some studies are conducted to analyse the exposed polyemer. Thermal studies had been done for Polycarbonate detectors, Polyethylene terepthalate (PET) and also for PADC detectors. Different types of thermal studies like TGA/DTA/DSC are done for irradiated samples and are compared with the pristine one. IR study for PET, PC and Polyacetate, Macrofol-E are being done for samples irradiated with different doses to understand the structural modifications due to gamma irradiation.

In the second year of studies the dialectic study of the samples started along with other studies like IR, Thermal and XRD. Dielectric measurements had been for five different types of polymer exposed to different doses of gamma radiation ranging from 10^1 Gy to 10^6 Gy. The polymer studied were polycarbonate, PET, PADC (two types) and also polyimide samples. .

In the third year of study, further exposure of the samples are done in Pondichery University. Since the initial results signify the fact that at dose higher than 10^5 Gy, there is s certain change in the polymer properties. Thus in order to under the effect further exposure in the dose range from 105 to 107 Gy is done. The works on exposed samples are continuing. Some studies like IR, TGA-DTA etc. are done for some samples and some studies like XRD is yet to finish.

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A summary of the findings of the study

Certain polymers has being taken for studying modification due to exposure to gamma dose Some of the polymers that have being taken and have studied are Polycarbonate, PET, PADC etc Thermal studies have already been started for Polycarbonate detectors, Polyethylene terepthalate (PET) and also for PADC detectors. Different types of thermal studies like TGA/DTA/DSC are done for irradiated samples and are compared with the pristine one. IR study for PET, PC and Polyacetate are being done for samples irradiated with different doses to understand the structural modifications. Dielectric measurements have already started for PC, PADC and PET. A significant progress has also been made in this regard.

1. **Study of modifications on thermal properties of track detectors due to different doses of gamma irradiation**

Thermal Studies for Polycarbonate:

TGA thermogram of the Lexan polymer was studied which shows a double step decomposition pattern, where the first step is a major step and the second step is a minor step. The pristine polymer is found to be thermally stable till the temperature of around 370^{o}C after which the process of weight loss starts. The first decomposition takes place in the range from 377 ^{0}C – 550^{0}C, where almost 75% of the polymer weight is lost. The second step of decomposition starts around 600^{0}C and continues till 674^{0} C, losing the remaining weight of the polymer. This pattern of weight loss is observed till the dose of 10^{4}Gy..

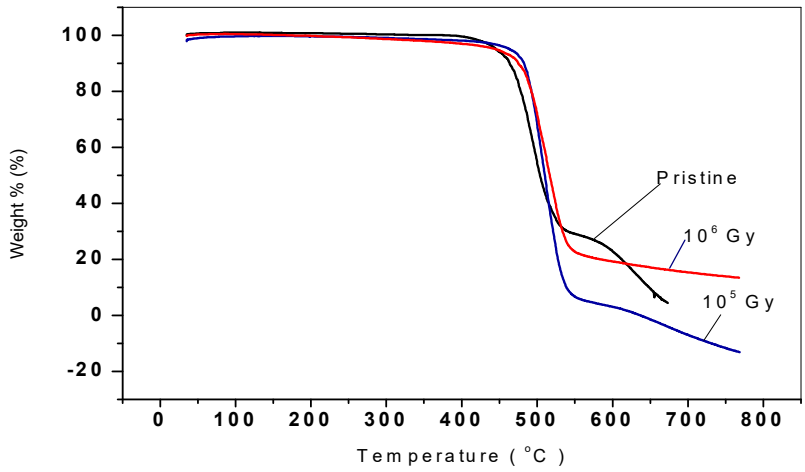


Fig 1: TGA thermogram of Polycarbonate film irradiated with gamma radiation

However, when the gamma dose becomes 10^5Gy and above, this weight loss pattern changes. As can be seen in Figure 5 that at a dose of 10^5Gy and higher, the second step of decomposition disappears. This signifies the fact that the irradiated polymer loses its weight in a single step. Further it is also observed that at a dose of 10^6Gy, that weight loss process starts at much lower temperature i.e. around 168^0C and continues till 750^0C as Shown in the Figure 1

Differential Scanning Calorimetric studies were also investigated. DSC thermograms for pristine Lexan polymer have been recorded in the temperature range 0^0C to 400^0C, with heating rate of 10^0C/min (shown in Figure 2). Fromthefigureitisclearthatoneprominent broad exothermicpeakstarts around 250^0Candfinishesaround400^0C. This exothermic peak is due to melting of the Lexan polymer [27, 28]. Morphology of Lexan polymer is such that it has both amorphous and crystalline arrangement of chain in the polymer matrix. The broad melting behavior of the polymer signifies the partial amorphous nature of the polymer. Comparing the DSC thermograms ofpristineand irradiated samples (Figure 4), it is observed that the board exothermicbehaviorofthepolymerremainstillthedoseof10^5Gy. Only atthedoseof10^6Gy, 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 chains and rearrangement of the broken segments, amorphous behavior of the polymer reduces and the polymer becomes more crystalline in nature.

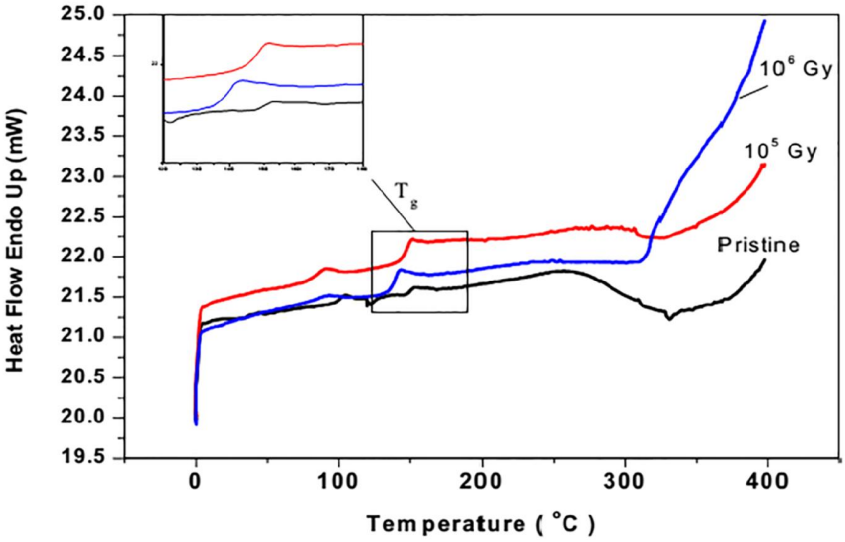


Fig. 2. DSC curve at different dose showing $T_g$of polycarbonate polymer

Glass transition studies were also evaluated which shows that glass transition temperature of the pristine polymer is found to be around 150^0C for the pristine Lexan polymer. However on comparing the glass transition temperature (T_g) of the pristine polymer with the irradiated one, 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 3, where it is observed that the $T_g$decreases from 150^0C for pristine sample to 140^0C at the highest does of 10^6 Gy.

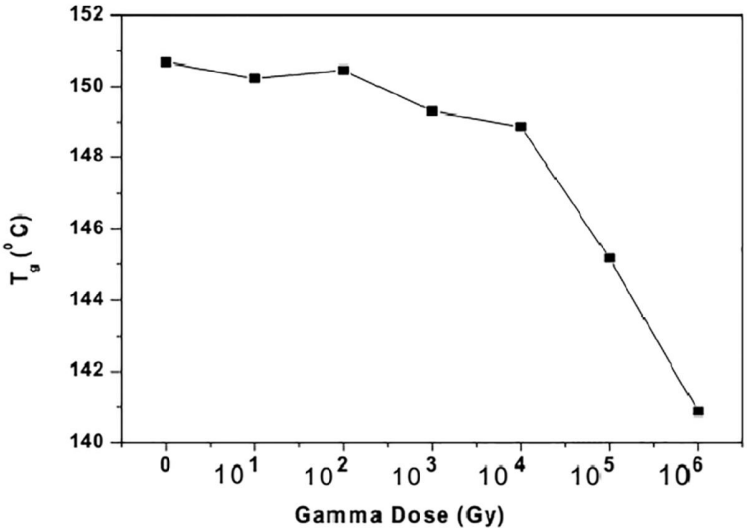


Fig. 3. Dose dependent variation of $T_g$gamma irradiated Lexan polymer

The Thermal studies for PET is also taken which is given below in Figure 4:

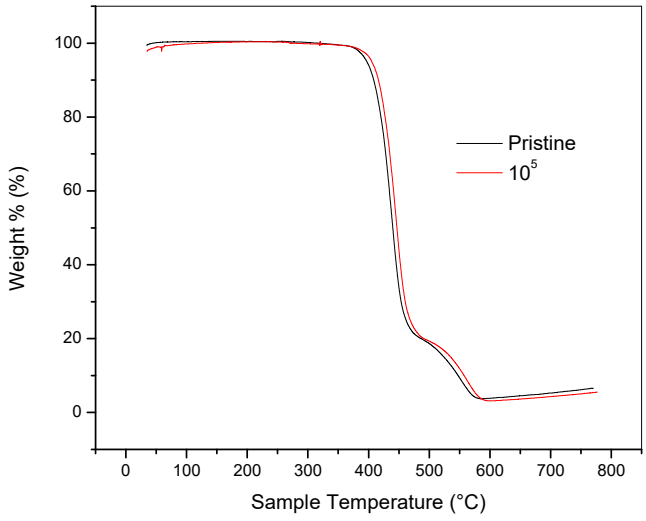


Fig 4: TGA Curve of pristine and irradiated PET

2. Study the modifications in track properties due to gamma irradiation

IR studies for Polycarbonate

Figure 3 shows the comparative IR spectra for pristine and irradiated at a dose of 10^6Gy. From the spectra, it seems like the peak at 3118 cm^{-1} (C-H stretching for benzene group) is not present at the dose of 10^6Gy. Again the peak at 2863 cm^{-1} (C-H stretching for CH_3 group), which was present for the pristine polymer is almost disappearing at 10^6Gy of radiation. It is also observed that one new peak has appeared at a frequency of 2200 cm^{-1} for the irradiated polymer. This peak at 2200 cm^{-1} might be due to the formation of some triple bonds in the polymer matrix. From this above observations in the IR results, some probable explanation about the structural modifications might be as follows : due to gamma irradiation, scissioning of C-H bond for both CH_3 group as well as aromatic group took place.

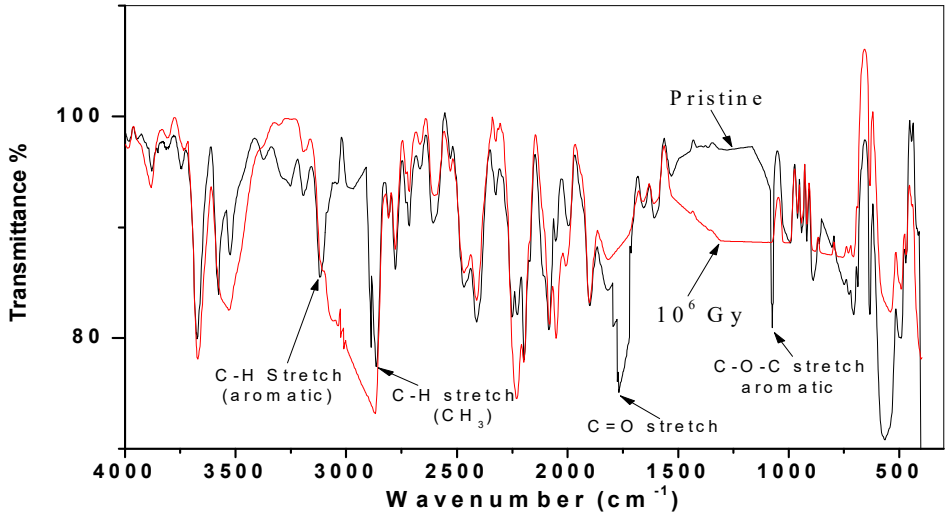


Fig 5: FT-IR spectra of Pristine and irradiated (10^6 Gy) of Polycarbonte Polymer

Also Scissioning of C-H bond for aromatic group lead to formation of aryne group in the polymer. Further it is also observed there is a disappearance of the carbonyl peak at 1768 cm^{-1} in the irradiated polycarbonate. Also due to gamma irradiation, a peak at around 3531cm^{-1} appears and this might be due O-H stretching. Thus it is probable that occurrence of O-H stretching is

due to the formation of a phenolic group in the polymer matrix due to the breakage of ester group. Scissioning of ester linkage leads to the formation of oxygen radicals which easily combine with hydrogen radicals and forms phenolic groups.

Other studied that had being done is that of FT-IR studies of PET as given below inFigure 6:

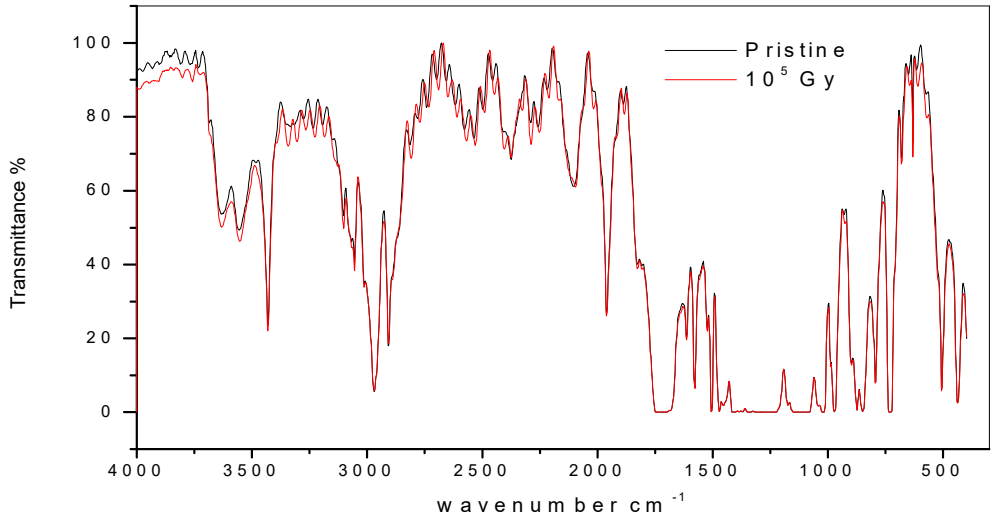


Fig6: FT-IR spectra of pristine and Irradiated PET

Functional group of Kapton polymer was also investigated and is shown in Figure 7

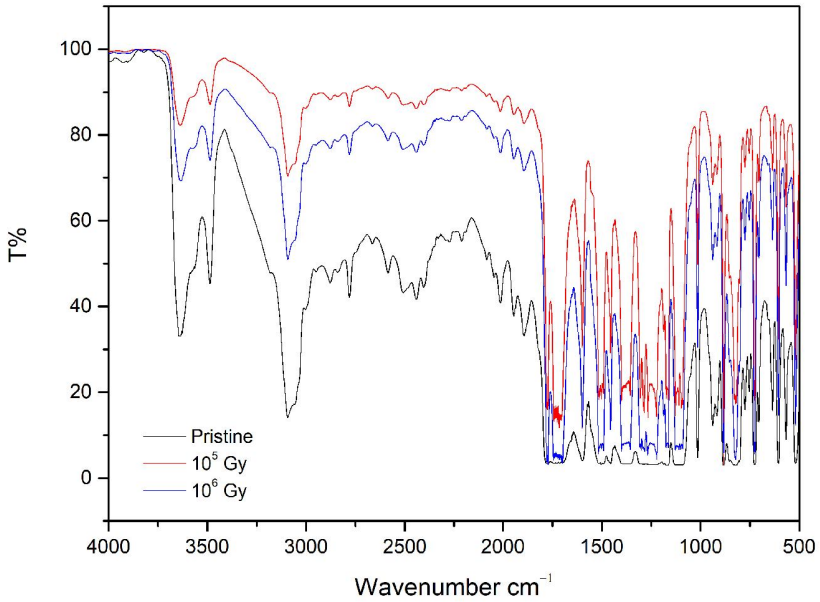


Fig. 7. IR-Spectra of pristine and irradiated Kapton polymer

3. Gamma irradiation effect on electrical properties of polymeric track detectors

Dielectric studies for Polyacetate and polycarbonate

Due to gamma exposure the dielectric constant of the polyacetate polymer increases at a dose higher than 10^4Gy .The increase is visible in the lower frequency region i.e. in the range of 42-1000Hz. The increase in dielectric constant value is probably due to irregularity in the polymer chains caused by irradiation. This irregularity gives rise to a hopping mechanism which enhances the polarization in the polymer matrix at a dose higher than 10^4Gy On the basis of the study the following conclusions were made; Due to gamma exposure the dielectric constant of the polyacetate polymer increases at a dose higher than 10^4Gy; The increase is visible in the lower frequency region i.e. in the range of 42-1000Hz; The increase in dielectric constant value is probably due to irregularity in the polymer chains caused by irradiation. This irregularity give rise to a hopping mechanism which enhances the polarization in the polymer matrix at a dose higher than 10^4Gy.(figure 8)

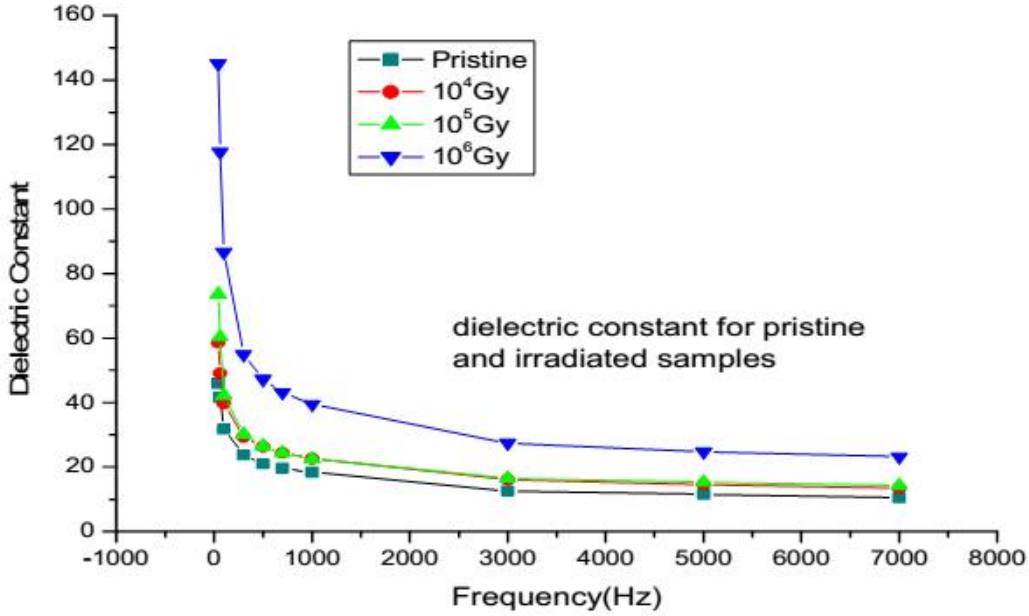


Fig8: A comparison of dielectric constant value ofpristine and Irradiated sample at different frequencies

Another work is on dielectric studies of polycarbonate

When irradiated with gamma radiation, it is observed that the dielectric constant increases which signifies that polarization in the polymer increases with gamma exposure. The increase in the dielectric constant due to irradiation is probably due to increase in carrier polarization indicating that charge carriers move by discontinuous hopping movements between localized sites. The irregularity in the polymer chains due to irradiation give rise to a hopping mechanism which will enhance the polarization in the polymer matrix. It is apparent from figure 9 that dielectric constant increases with irradiation and this increase is apparent at a dose of higher than 10^4Gy. Also it is observed that dielectric constant becomes almost constant at a frequency of 300Hz and higher. It is found that Dielectric constant increases with gamma exposure.

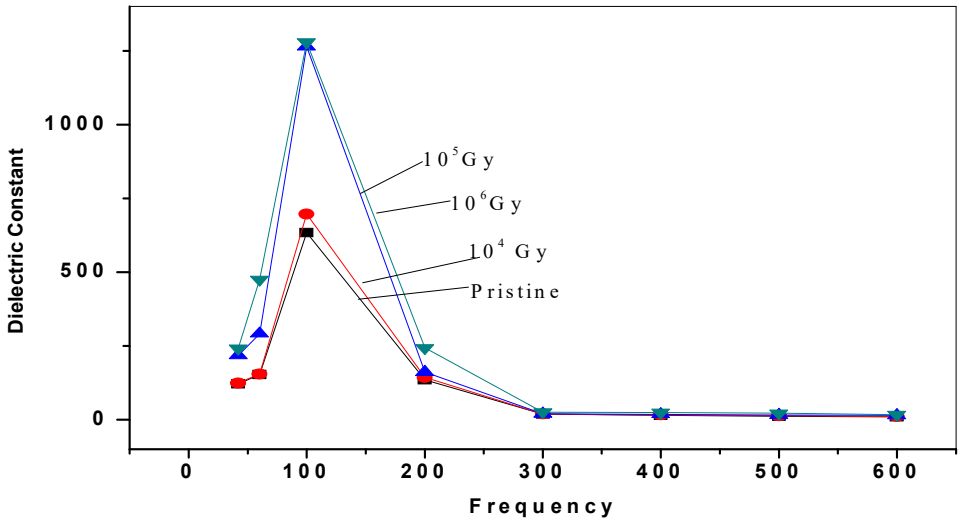


Fig. 9: Comparison of dielectric constant of polycarbonate polymer irradiated at different doses

4. Gamma irradiation effect on optical propertiesproperties of polymeric track detectors

The optical absorption spectra in the wavelength region of 200-800 nm. The optical band gap of the material was determined from the UV-Vis spectra using the Tauc's ex-pression.

$$\omega^2 \varepsilon_2 = \left\{\left(\frac{h}{2\pi}\right)\omega - E_g\right\}^2$$

whereε_2 is the optical absorbance at wavelength λ The values of $\sqrt{\varepsilon_{2/\lambda}}$ are to be plotted against 1/λ to find out the gap wavelength (λ_g). The gap wavelength can be found out from the intersection of the extrapo-lated curve on the abscissa. The band gap is then de-rived by the relation

$$E_g = hc/\lambda_g.$$

The UV-Vis spectra of non-irradiated and irradiated samples show an increase in the absorption with the increase in the radiation dose towards the longer wavelength

region. Figure10 shows the UV-visible spectra recorded for gamma irradiated CR-39 samples at different doses by using the UV-visible spectrophotometer.

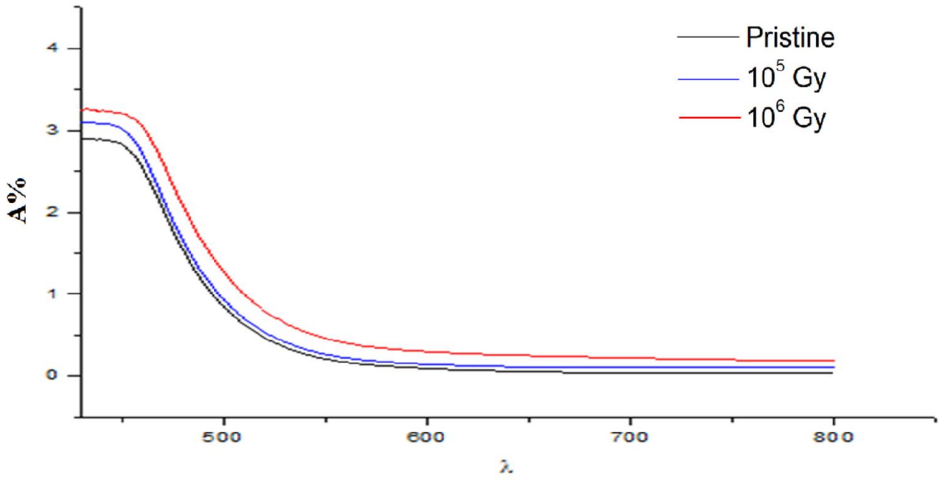


Fig.10: UV-Vis Spectra of pristine and gamma irradiated CR-39