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## Effect of $\gamma$ - irradiation on thermal stability of CR-39 polymer

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### ABSTRACT

The thermal behavior of pristine and  $\gamma$ -irradiated CR-39 polymer (upto a maximum dose of 1800 kGy) has been studied using Thermogrametric analysis. The changes in degradation activation energy, frequency factor, entropy of activation, free energy of decomposition and rate coefficient have been analyzed as a consequence of  $\gamma$ -irradiation. The results clearly indicate the lowering of thermal stability of CR-39 as an effect of  $\gamma$ -irradiation. Such a reduction in thermal stability has been tried to be correlated with the induced structural changes as revealed by FTIR spectroscopy.

**Keywords:** CR-39, TGA,  $\gamma$ -irradiation, activation energy, FTIR spectroscopy.

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### INTRODUCTION

The polymers, now days, have gained interest of researchers worldwide in various fields of science and technology. The reason being, besides having excellent inherent properties[1], their characteristics can be altered to suit specific requirements by various treatments e.g. chemical doping, heat treatment, ion implantation[2-4] etc. In addition,  $\gamma$ -irradiation has been proved to be a significant tool [5] for such modifications. It is well known that  $\gamma$ -irradiation can amend the electrical, optical, thermal properties etc of the polymeric materials by changing their morphology through various processes of chain scissioning and cross linking [6-8].

CR-39 (monomer composition:  $C_{12}H_{18}O_7$ ) is a high grade amorphous optically transparent polymer widely used as nuclear track detector. Besides many other applications in optical devices etc., it finds significant applicability in fission related studies. In such studies, the

polymer gets exposed to high doses of neutrons, beta and gamma radiations [9-10]. Thermal behavioral analysis of CR-39 as an effect of  $\gamma$ -irradiation is an important study in this direction.

## MATERIALS AND METHODS

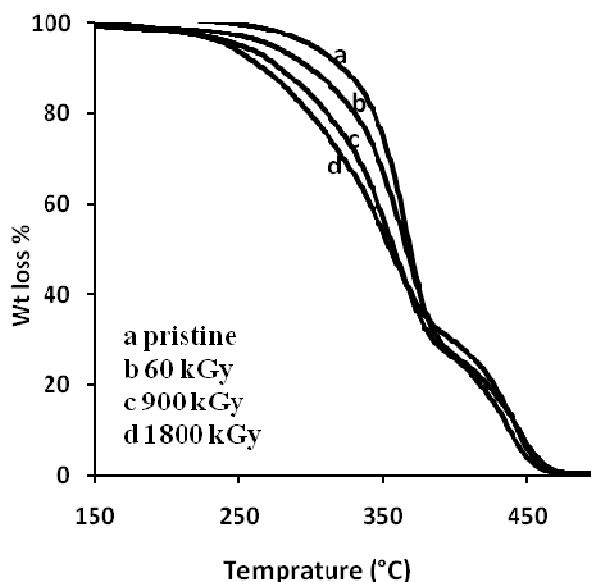
The samples (1cm x 1cm) were cut from 1000  $\mu\text{m}$  thick sheet of CR-39 (TASTRAK, Bristol, England). The irradiation to these samples was carried out at a dose rate of 1.5 kGy per hour using  $^{60}\text{Co}$  gamma source in air for different times to achieve the total doses of 60, 900 and 1800 kGy respectively, utilizing the exposure facility available at Bhabha Atomic Research Centre (BARC), Mumbai, India. Thermograms for the pristine as well as irradiated samples were recorded at a linear heating rate of  $10^\circ\text{C}/\text{min}$ , in the temperature range  $\sim 30\text{-}600^\circ\text{C}$  using Q600 TA Instruments. The ATR-FTIR spectra were recorded in the absorption mode using Bruker Model Vertex 70 with ZnSe crystal, in the wave number range  $\sim 600\text{-}2000\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### 3.1. Thermogravimetric analysis

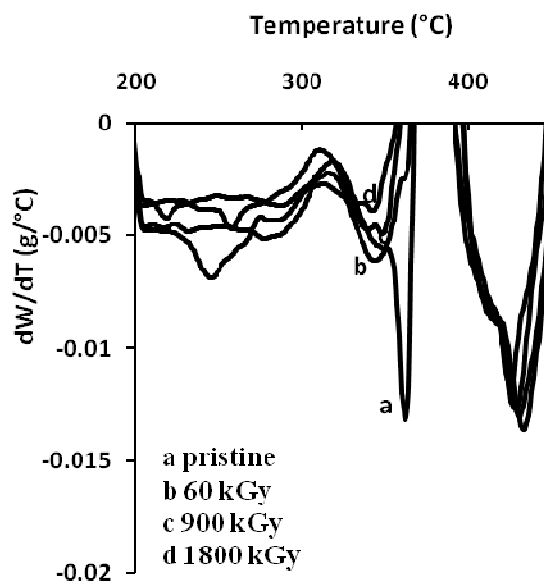
Thermal degradation is a very important process which helps in determining the influence of the polymer morphology on the thermal stability, the optimum temperature of operation and the activation energies related to the degradation processes [11-12]. Thermogravimetric analysis (TGA) has been proved to be reasonably rapid and precise method for the determination of such kinetic parameters related to the degradation processes [13].

In order to study the effect of  $\gamma$ -irradiation on these kinetic parameters, TGA thermograms of pristine and gamma irradiated samples of CR-39 at different doses have been recorded and are presented in Figure1.



.Figure 1: TGA thermograms for pristine and  $\gamma$ -irradiated samples of CR-39 polymer

The corresponding DTG thermograms have been presented in Figure 2.



**Figure 2:** DTG thermograms for pristine and  $\gamma$ -irradiated samples of CR-39 polymer

Figure 1 clearly indicates that degradation process for pristine as well as  $\gamma$ -irradiated CR-39 polymer proceeds in three steps which is again supported by the occurrence of three peaks in the corresponding DTG thermograms presented in figure 2.

From TGA thermograms, various kinetic parameters of degradation reaction have been determined by adopting most commonly used method of Horowitz –Metzger [9, 10, 12-15].

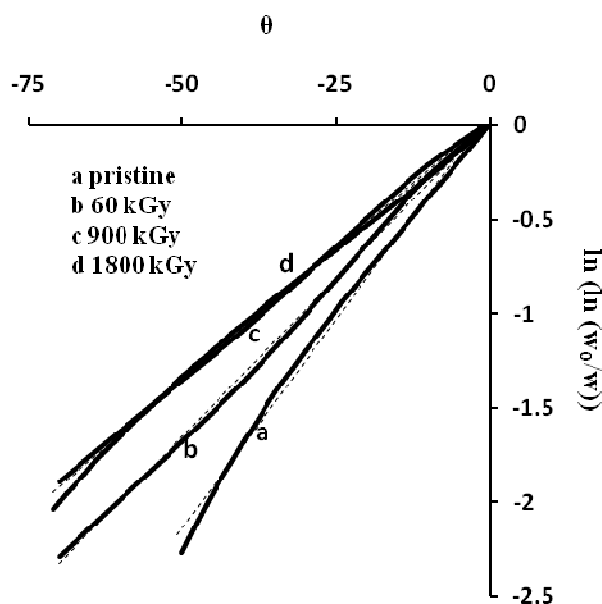
### 3.1.1. Determination of activation energy

The activation energies of virgin and  $\gamma$ -irradiated samples of CR-39 corresponding to the major degradation process (1<sup>st</sup> step) have been deduced using the expression [15]

$$\ln\left(\ln\left(\frac{W_0}{W}\right)\right) = \frac{E_a \theta}{RT_s^2} \dots\dots\dots (1)$$

where  $W_0$  is the initial weight,  $W$  is the remaining weight at temperature  $T$ ,  $E_a$  is the activation energy,  $R$  is gas constant and  $\theta = T - T_s$  with  $T_s$  as the reference temperature corresponding to  $W/W_0 = 1/e$ .

In the light of the equation(1), the activation energy  $E_a$  can be calculated from the slope of the linear fitted line between  $\ln(\ln(W_0 / W))$  and  $\theta$  as illustrated in Figure 3, for virgin and  $\gamma$  irradiated samples at doses 60, 900 and 1800kGy.



**Figure 3: Plots of  $\ln(\ln(W_0/W))$  vs.  $\theta$  for pristine and  $\gamma$ -irradiated samples of CR-39 polymer**

The values of activation energies so determined for pristine as well as  $\gamma$ -irradiated samples have been enlisted in Table I. There is a clear cut decrease in the values of activation energy with the increasing irradiation dose. Such a decrease may be attributed to the initialization of chain scissioning, possible evaporation of volatile side groups resulting in significant reduction of packing density, reorganization of molecular arrangements etc. in the polymeric sample which signifies the decrease in thermal stability of the polymer [9-10, 16]

*3.1.2. Determination of frequency factor*

The corresponding values of frequency factor for the virgin and the  $\gamma$ -irradiated samples of CR-39 have been determined by substituting the values of activation energies in the expression [15]

$$1 = -\frac{A RT_s^2}{\beta E_a} \exp\left(-\frac{E_a}{RT_s}\right) \dots \dots \dots (2)$$

where A is the frequency factor and  $\beta$  is the constant rate of heating.

The values of frequency factor so determined are listed in Table I. It is apparent from table I that corresponding to the decrease in values of activation energy, the values of frequency factor also decreases. Such a decrease in the frequency factor signifies the decrease in the rate of reaction. This may be due to the scissioning of the polymeric chains destructing the interstates which slows down the reaction as a result of  $\gamma$ -irradiation [16].

*3.1.3. Determination of entropy of activation*

The difference between the entropy of the transition state and the sum of the entropies of the reactants is called entropy of activation ( $\Delta S$ ) and is calculated as [12]

$$\Delta S = 2.303R \log \left( \frac{Ah}{kT_s} \right) \dots \dots \dots (3)$$

where h is Planck's constant and k is Boltzmann constant.

The calculated values of entropy of activation ( $\Delta S$ ) are listed in Table 1. The evident decrease in the values of entropy of activation with the increase in the  $\gamma$  dose again supports the relative slow nature of reaction [16].

### 3.1.4. Determination of free energy of change of decomposition:

Free energy of change of decomposition ( $\Delta G$ ) is given as the difference between the enthalpy of the transition state and the sum of the enthalpies of the reactants in the ground state. It may be considered to be the driving force of a chemical reaction.  $\Delta G$  determines the spontaneity of the reaction. The values of  $\Delta G$  are calculated using the expression [12]

$$\Delta G = E_a - T_s \Delta S \dots \dots \dots (4)$$

The values so obtained are listed in Table 1. The positive values of  $\Delta G$  signify the non spontaneity of the degradation reaction [16].

### 3.1.5. Determination of rate coefficient

The rate coefficient (K) can be calculated using Arrhenius equation [12]

$$K = A \exp \left( -\frac{E_a}{RT_s} \right) \dots \dots \dots (5)$$

The calculated values of rate coefficients are listed in Table 1. The decreasing trend in these values again confirms the slow nature of reaction with increasing  $\gamma$  dose [16].

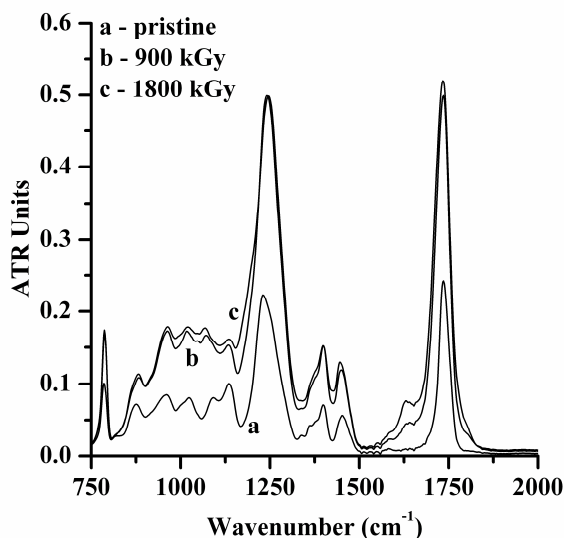
S.No.	Gamma dose (kGy)	$E_a$ (kJ/mol)	A ( $s^{-1}$ )	$\Delta S$ (J/mol/K)	$\Delta G$ (kJ/mol)	K ( $s^{-1}$ )
1.	Pristine	142.7	9.6E10	-41.2	169.7	0.40
2.	60	116.9	7.5E8	-81.5	170.2	0.33
3.	900	95.7	1.2E7	-115.7	171.3	0.27
4.	1800	83.8	3.9E6	-124.6	159.9	0.27

**Table 1: Values of various kinetic parameters for virgin and  $\gamma$  irradiated CR-39 polymer**

### 3.2. FTIR Analysis

FTIR-ATR spectra of pristine and  $\gamma$ -irradiated CR-39 polymer are presented in figure 4. A number of sharp intense bands at 785, 1240 and 1739  $cm^{-1}$  have been observed in the spectrum of pristine CR-39 polymer. These bands correspond to =C-H bending, C-O-O stretching and C=O stretching respectively. The other small intensity bands at 1395 and 1460  $cm^{-1}$  originates from C-H bending modes while the bands in the region 1000-1200  $cm^{-1}$  are due to C-O stretching

mode vibrations whereas the band at  $937\text{ cm}^{-1}$  corresponds to  $=\text{C-H}$  out of plane bending mode vibrations. The occurrence of these bands confirms the monomer structure of CR-39 polymer [17].



**Figure 4:** FTIR-ATR spectra of virgin and  $\gamma$ - irradiated samples of CR-39 polymer

It is clearly evident from figure 4 that the peaks in the region  $935\text{-}1200\text{ cm}^{-1}$  start broadening with increasing dose of  $\gamma$ -irradiation. This may be attributed to the breakage of chemical bonds and the possible elimination of low molecular gases and volatile radicals as an effect of  $\gamma$ -irradiation [18]. This signifies the initialization of chain scissioning in CR-39 polymeric samples which becomes more and more prominent corresponding to the increase in  $\gamma$ -dose. This may be responsible for the reduction in thermal stability as a consequence of  $\gamma$ -irradiation [9, 18].

## CONCLUSION

The decrease in activation energies for thermal degradation and other related kinetic parameters like the frequency factor, entropy of activation and rate coefficient with the increasing dose of  $\gamma$ -irradiation clearly indicates the reduction in thermal stability of CR-39 as an effect of  $\gamma$ -irradiation. The reduction in thermal stability may be correlated with the morphological changes induced in the polymeric sample as a consequence of  $\gamma$ -irradiation as confirmed using ATR-FTIR spectra.

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## REFERENCES

- [1] F. W. Billmeyer *Textbook of Polymer Science*, Wiley Interscience Publications, New York, **2005**, pp 261-330.
- [2] V. Kumar, P. K. Goyal, S. Mahendia, R. Gupta, T. Sharma, S. Kumar *Rad. Effects and defects in Solids* 166, 2, **2011**, pp 109-113.
- [3] A. M. Visco, L. Torrisi, N Campo, A. Picciotto *International J. Polym. Anal. And Character.* **2010**, 15(2), 73-86.
- [4] R. Gupta, V. Kumar, P. K. Goyal, S. Kumar *J. Chem. Pharm. Res* 2, 4, **2010**, pp 629-634.
- [5] D. Fink (Ed.). *Fundamentals of Ion-Irradiated Polymers*; Springer- Verlag Berlin Heidelberg: Germany, **2004**, pp 7-84.
- [6] T. Sharma, S. Aggarwal, S. Kumar, V. K. Mittal, P. C. Kalsi, V. K. Manchanda *J. Mat. Sci.* 42, **2007**, pp1127.
- [7] A. A. Abiona, A. G. Osinkolu *Inter. J. Phys. Sci.* 5, 7, **2010**, pp. 960-967.
- [8] M. F. Zaki, *Brazilian J. Phys.* 38, 4, **2008**, pp558-562.
- [9] S. A. Nouh, M. R. Atta, W. M. El-Melleegy *Rad. Effects and Defects in Solids*, **2004**, 159(8), 461-474.
- [10] P. C. Kalsi, K. D. S. Mudher, A. K. Pandey, R.H. Iyer *Thermochimica Acta* **1995**, 254, 331-336.
- [11] J. H. Flynn, L.A. Wall *J. Research of NBS-A Phy. and Chem.* 1966, 70A(6), 487-523.
- [12] K. G. Mallikarjun *E-Journal of Chem.* **2004**, 1(2), 105-109.
- [13] H. H. G. Jellinek *Aspects of Degradation and Stabilization of Polymers*; Elsevier Scientific Publishing Company : New York, 1978.
- [14] B. K. Singh, P. Kumari, A. Prakash, D. Adhikari *Nature and Science* **2009**, 7(7), 73-78.
- [15] H. H. Horowitz, G. Metzger *Anal. Chem.* 1963, 35(10), 1464-1468.
- [16] E. V. Anslyn, D. A. Dougherty *Modern Physical Organic Chemistry*; Edwards Brothers, Inc. USA, 2006.
- [17] D. L. Pavia, G. M. Lampman, G. S. Kriz *Introduction to Spectroscopy 2<sup>nd</sup> ed.* New York, Harcourt Brace College Publishers, **1994**.
- [18] N. L. Singh, A. Sharma, D. K. Avasthi *Nucl. Instr. Meth. Phys. Res. B* 206, **2003**, pp 1120.