

Indian J. Phys. **83** (7), 921-926 (2009)



Effect of thermal annealing on optical properties of CR-39 polymeric track detector

Nidhi, Renu Gupta, Tanu Sharma, Sanjeev Aggarwal and S Kumar*

Department of Physics, Kurukshetra University,
Kurukshetra-136 119, Haryana, India

E-mail : profshyam@gmail.com

Abstract : The samples of CR-39 polymer (TASTRAK, Bristol, England) were annealed thermally at various temperatures ranging from 100°C to 180°C for 1 hour, in air. FTIR spectroscopy reveals the structural degradation of CR-39 polymer due to thermal annealing above its glass transition temperature. Optical band gap of pristine and thermally annealed samples has been determined using UV-Visible absorption spectra. It has been observed that the optical band gap decreases continuously as a result of annealing.

Keywords : CR-39 polymer, thermal annealing, UV-Visible spectroscopy, optical band gap, FTIR spectroscopy.

PACS Nos. : 78.30.jw, 78.30.-j, 78.40.-q

1. Introduction

It is well known that thermal annealing of polymeric materials changes their morphology at temperatures higher than their corresponding glass transition temperature (T_g). Below T_g , polymeric chains remain almost immobile and retain their original morphology. However, at annealing temperatures above T_g , energy gained by polymeric chains, enhances [1,2] the inter-chain interactions which results [1] in morphological changes in the polymer. These changes inside the annealed polymers lead to alter [3] their electrical, optical, mechanical properties *etc.* A systematic study in this direction is significant for the utilization of polymers in the various scientific and technological applications. Further, the optical performance of a polymer is significant for the applications like optical sensors, LED's, waveguides, antireflective coatings, optical lenses *etc.* [4–6].

CR-39 is high grade amorphous optically transparent plastic and is widely used as a nuclear track detector besides many other applications [7,8]. The chemical structure of

* Corresponding Author

repeating unit of CR-39 is shown in Figure 1.

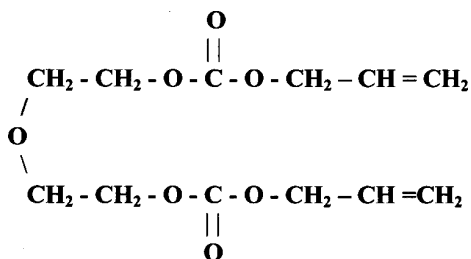


Figure 1. Monomer structure of CR-39 polymer.

In the present work, the effect of thermal annealing on the absorption and structural behaviour of CR-39 polymer has been studied through UV-Visible and FTIR spectroscopy. Such studies may contribute towards the better understanding of track formation process.

2. Experimental details

Samples of CR-39 polymer (TASTRAK, Bristol, England) were cut from a flat polished sheet of thickness 1 mm. The heat treatment was carried out at varying temperatures ranging from 100°C to 180°C in air on different specimens of CR-39 for one hour each. Virgin and heat treated CR-29 samples were subjected to spectral studies in the ultraviolet and visible region. These studies were carried out by using Shimadzu Double beam Double Monochromator UV-Visible Spectrophotometer (UV-2550) in the wavelength range of 190–900 nm with resolution of 0.5 nm. All the spectra were recorded by mounting the samples in the integrating sphere assembly ISR-240A attached with the Spectrophotometer, keeping air as reference. The Fourier transform infrared spectroscopy was performed in the transmission mode using Abb Bomen FTIR Spectrometer in the range 2000–600 cm^{-1} .

3. Results and discussions

Figure 2 presents the UV-Visible absorption spectra of CR-39 virgin and thermally annealed samples at different temperatures ranging from 100–180°C for 1 hour.

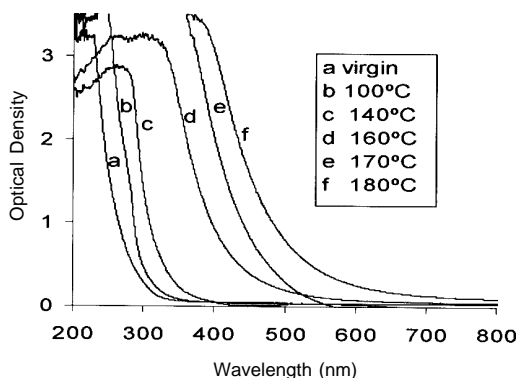


Figure 2. UV-Visible absorption spectra of CR-39 polymer : (a) virgin and thermally annealed at (b) 100°C, (c) 140°C, (d) 160°C, (e) 170°C and (f) 180°C.

It is obvious from Figure 2 (curves 'a' to 'f') that thermal annealing results in the shifting of absorption edge in virgin CR-39 polymer towards higher wavelengths. Such a red shift may be attributed to the fact that due to thermal annealing, energy gained by the host polymer changes the polymer morphology. Thermal treatment at temperatures above T_g , results [9–13] in bond rupture, reorientation of dipole moments, cross-linking, steric rearrangement of polymer chains *etc.* All these processes are responsible [13,14] for the red shift of absorption edge. Another possibility for red shift may be the increase in conjugation [14] with increasing annealing temperature resulting in a decreased HOMO-LUMO gap.

3.1. Determination of optical band gap :

From the UV-Visible absorption spectra, the optical band gap of virgin and thermally annealed CR-39 polymer has been determined. For this purpose, the values of $(\alpha h\nu)^{1/2}$ were plotted as a function of photon energy ($h\nu$) [4,15], taking into account the data corresponding to the linear portion of the fundamental absorption edge of the UV-Visible absorption spectra. Optical band gap has been determined from the fundamental absorption edge of the absorption spectra using the relation [6–8] :

$$(\alpha h\nu)^{1/2} \sim (h\nu - E_g) \quad (1)$$

where $h\nu$ is the incident photon energy, α is absorption coefficient, and E_g is the optical band gap.

Figure 3 presents these plots for virgin and thermally annealed CR-39 samples. From the intercept of the best fit lines on $h\nu$ axis, optical band gap has been determined and the results are presented in Table 1.

Table 1. Optical band gap values for virgin and thermally annealed CR-39 polymer.

Sl. No.	Temperature	Optical band gap (eV)	Regression coefficient 'R'
1.	Virgin	3.81	0.99
2.	100°C	3.64	0.99
3.	140°C	3.53	0.99
4.	160°C	2.50	0.99
5.	170°C	2.25	0.99
6.	180°C	2.01	0.99

The regression coefficients have been found to be nearly 0.99 for the fitted straight lines. From the repeated measurements, the standard error in the quoted values of optical band gap has been estimated to be less than 3%.

It is obvious from Table 1 that the optical band gap goes on decreasing continuously from 3.81 eV in virgin CR-39 sample to 2.01 eV in thermally annealed sample at 180°C. Such a lowering in optical band gap may be correlated to the morphological changes in the polymeric sample as a result of thermal annealing.

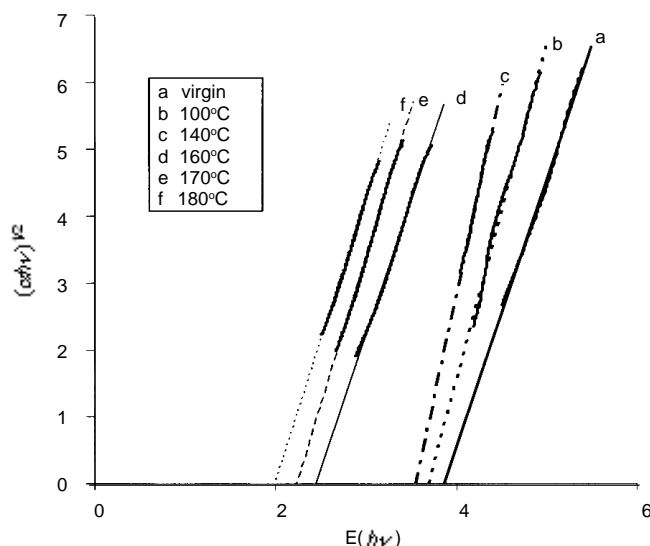


Figure 3. Plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for optical band gap (eV) in CR-39 polymer : (a) virgin and thermally annealed at (b) 100°C, (c) 140°C, (d) 160°C, (e) 170°C and (f) 180°C.

FTIR spectra of virgin and thermally annealed CR-39 samples have been shown in Figure 4. In virgin CR-39 samples (curve 'a', Figure 4) a number of sharp intense bands at 783, 1227 and 1734 cm^{-1} have been observed confirming its monomer structure [16]. The strongest intensity band at 1227 cm^{-1} is due to C-O-C stretching, whereas other strong intensity bands at 783 and 1734 cm^{-1} can be attributed to the =C-H bending and C=O stretching vibrations. The other small intensity bands at 1450 and 1398 cm^{-1} originates from C-H bending mode whereas the band at 1136, 1091 and 1021 cm^{-1} are due to C-O stretching mode vibrations and the bands at 955 and 870 cm^{-1} are due to =C-H out of plane bending mode vibrations.

After thermal annealing at 100°C (curve 'b', Figure 4), it is clearly seen that the intensities of the transmission bands at 783, 870, 955, 1021, 1091, 1136, 1227, 1398, 1450, 1734 cm^{-1} have been increased. This clearly indicates that reduction in the absorption intensities of these bands. The reduction reveals that the sample undergoes serious degradation under thermal annealing [17]. On further annealing upto 170°C (curve 'c', Figure 4), the band at 850 and 955 and 1091 cm^{-1} are nearly eliminated. This might be attributed to breakage of chemical bonds and the formation/emission of low molecular gases and radicals due to thermal annealing indicating the change in chemical structure of CR-39 due to thermal annealing [18]. The transmission intensities of the bands 783, 1227 and 1734

cm^{-1} is further increased indicating reduction in the absorption of these bands which leads to the amorphisation of the specimen.

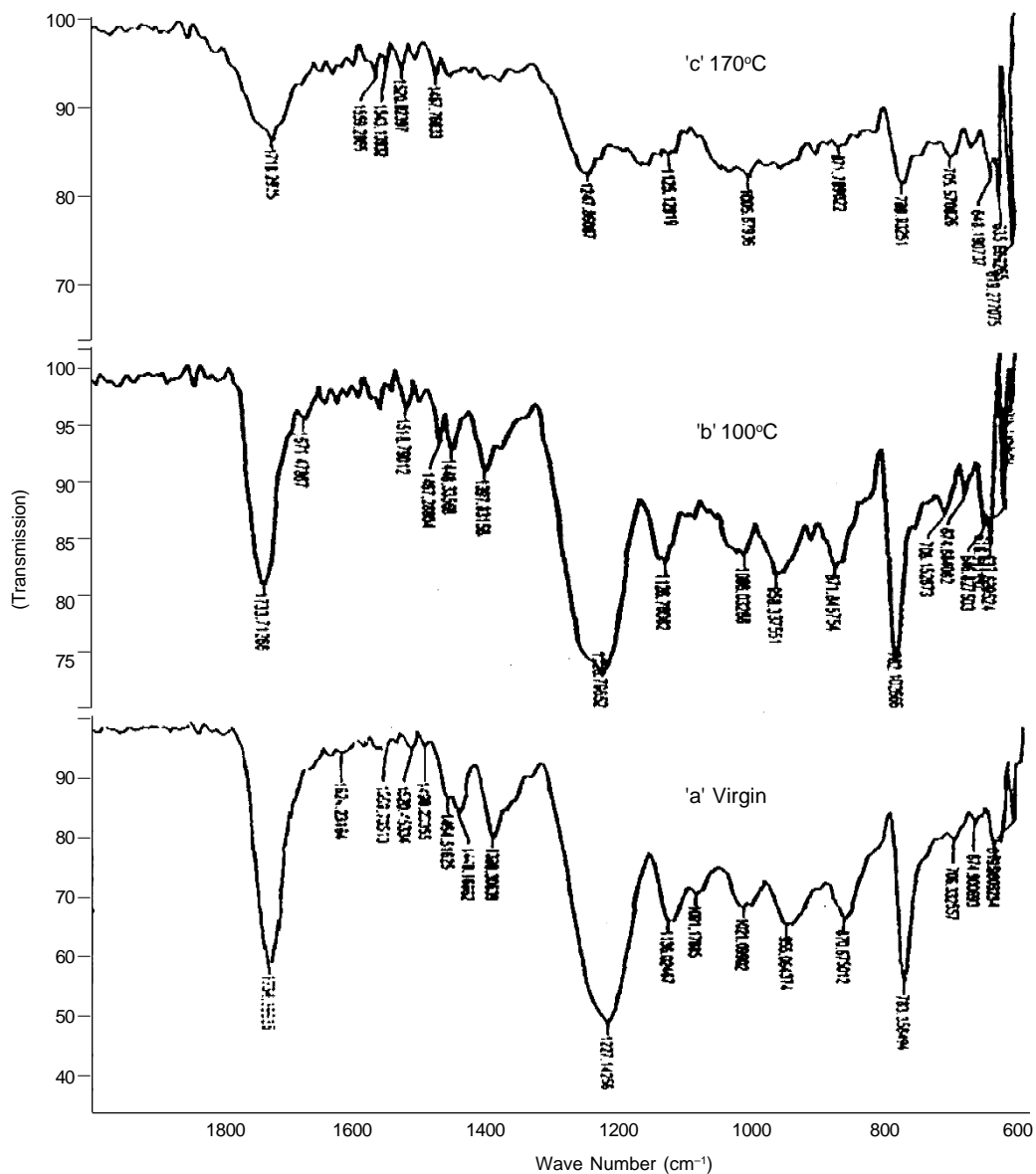


Figure 4. FTIR spectra of CR-39 polymer : (a) virgin and thermally annealed at (b) 100°C, (c) 170°C.

Hence the amorphisation and degradation resulted due to thermal annealing in the CR-39 polymer samples as revealed by FTIR above may be responsible for the reduction in band gap. The decrease in optical band gap as a result of thermal annealing has also been quoted by several other groups in different polymers [2,11,14,19].

4. Conclusions

It is concluded that there is a decrease in optical band gap in CR-39 polymer as a result of thermal annealing at temperatures above T_g . This decrease in optical band gap can be correlated with the changes in the structure of CR-39 as seen using FTIR studies.

References

- [1] H H Jellinek (ed.) *Aspects of Degradation and Stabilization of Polymers* (New York : Elsevier Scientific Publishing Company) (1978)
- [2] M A El-Shahawy *Poly. Degr. Stab.* **57** 157 (1997)
- [3] A Tager *Physical Chemistry of Polymers* (Moscow : Mir Publishers) (1978)
- [4] C J Mathai, S Saravanan, M R Anantharaman, S Venkitachalam and S Jayalekshmi *J. Phys. D : Appl. Phys.* **35** 2206 (2002)
- [5] K Nagagawa *J. Appl. Polymer Sci.* **41** 2049 (1990)
- [6] Y Koike, E Nihei, N Tanio and Y Ohtsuka *Appl. Opt.* **29** 2686 (1990)
- [7] D L Henshaw *Physics in Technology* **13** 266 (1982)
- [8] S A Najjar, R K Bull and S A Durrani *Nucl. Tracks.* **3** 169 (1979)
- [9] Anupam, S Kumar and N Lal *Nucl. Tracks Radiat. Meas.* **18** 335 (1991)
- [10] F Yakaphanoglu, M Arslam, M Kucukislamoglu and M Zengin *Solar Energy* **79** 96 (2005)
- [11] R Singh, J Kumar, R K Singh, A Kaur, K N Sood and R C Rastogi *Polymer* **46** 9126 (2005)
- [12] W Lincoln Hawkins (ed.) *Polymer Stabilization* (USA : Wiley Interscience) (1972)
- [13] J Liu, T F Guo and Y Yang *J. Appl. Phys.* **91** 1595 (2002)
- [14] J Hou, C Yan, C He and Y Li *Chem. Commun.* **8** 71 (2006)
- [15] T Sharma, S Aggarwal, S Kumar, V K Mittal, P C Kalsi and V K Manchanda *J. Mat. Sci.* **42** 1127 (2007)
- [16] D L Pavia, G M Lampman and G S Kriz *Introduction to Spectroscopy* 2nd ed. (New York : Harcourt Brace College Publishers) (1994)
- [17] Youmei Sun, Zhiyong Zhu, Zhiguang Wang, Yunfan Jin, Jie Liu, Mingdong Hou and Qinxiang Zhang *Nucl. Instr. Meth.* **B209** 188 (2003)
- [18] N L Singh, A Sharma and D K Avasthi *Nucl. Instr. Meth. Phys. Res.* **B206** 1120 (2003)
- [19] K Bhowmick and J R White *J. Mat. Sci.* **37** 5141 (2002)