ELSEVIER

Polymer 40 (1999) 1903–1909

polymer

Polymer Communication

Radiation dose effects in chlorinated polyvinyl chloride

M.E. Bassiouni*, F. El-Shamy

Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Received 16 October 1997; revised 6 May 1998; accepted 6 May 1998

Abstract

The optical properties have been studied in chlorinated polyvinyl chloride (CPVC) film in the wavelength range from 200 to 500 nm using UV-160 Shimadzu spectrophotometer. The irradiated samples of different energies (5, 9 and 13 MeV), as well as different radiation doses were studied. This investigation were carried out to determine the optical parameters, optical energy gap (ΔE), absorption coefficient (α) and the energy of direct and indirect transition $E_{(opt)1}$ and $E_{(opt)2}$. The results show that both direct and indirect transition exist in CPVC and highly sensitive to electron irradiation doses and energies. The variation of optical energy gap with electron irradiation energies and doses can be explained as the change in the degree of disorder and the optical band energy is dose and energy dependent.

Keywords: Chlorinated polyvinyl chloride; Radiation dose effects; Optical properties

1. Introduction

Microlithography is the process of transferring a mask pattern to a radiation sensitive polymer system (resist). Resist materials play an essential role in fabricating bags for medical devices, sterilization and pasteurization of food.

Irradiation is known to induce lattice defects, e.g. color center in polymeric materials. The action of ionizing radiation on polymers results in the following fundamental processes: cross-linking of the molecular chains, degradation of macromolecules, changes in the number and nature of the double bonds. These processes can take place simultaneously, controlled by the chemical nature of the polymer [1].

Vinylidene polymers $(\text{-}CH_2\text{-}CX_2\text{-})_n$ are of great interest in a conformational sense. In contrast to their vinyl ($\text{-}CH_2$-CHX) counterpart, they are sterically in all conformations. A combination of techniques has been employed in an attempt to elucidate the preferred conformation of CPVC, and a chain-conformational model is favored [2]. From a structural point of view, CPVC has a low glass transition temperature in spite of its steric crowding.

Disordered CPVC showed strength enhancement at moderately high strain rates [3]. A modified CPVC films exhibit stable optical properties, while stored in air, in contrast to the oxidative instability of pure polyacetylene [4]. Due to the polar nature of CPVC, it is difficult to calculate its conformation energy [5–7].

Most amorphous materials show exponential absorption edges [8–11]. An attempt will be made to explain the exact nature of the physical origin of this origin. The changes in properties of polymeric materials that occur when they are subjected to high energy including γ rays and electron beam as a result of chemical reaction initiate by radiation.

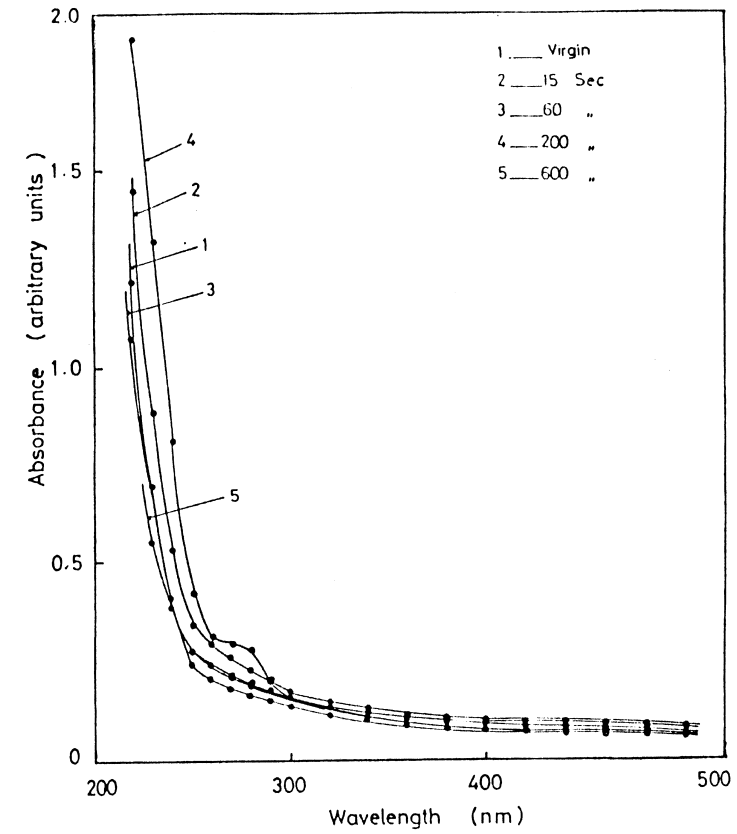
2. Experimental

CPVC films (thickness of 12.5 μm) produced by Goodfellow, Cambridge, UK, have been used in this investigation. The CPVC films were irradiated in linear accelerator type Mevatron 74 (7445). It is a compact device which is capable of producing X-ray energy (10 MeV) and up to six nominal electron energies (between 5 and 13 MeV). The accelerating waveguide uses microwave field to accelerate low energy electrons to high energy levels. The radiofrequency (RFD) system contains an automatic frequency control power source used for acceleration. The RFD system produces up to 2.5 MW of pulsed power. This power is transmitted to the accelerating waveguide through the RF transmission waveguide, where it is used to accelerate electrons to the required energy levels. The electron gun (injector) is the source of electrons, from an indirectly heated barium oxide impregnated cathode of pierce design. The stream of electrons is focused into a

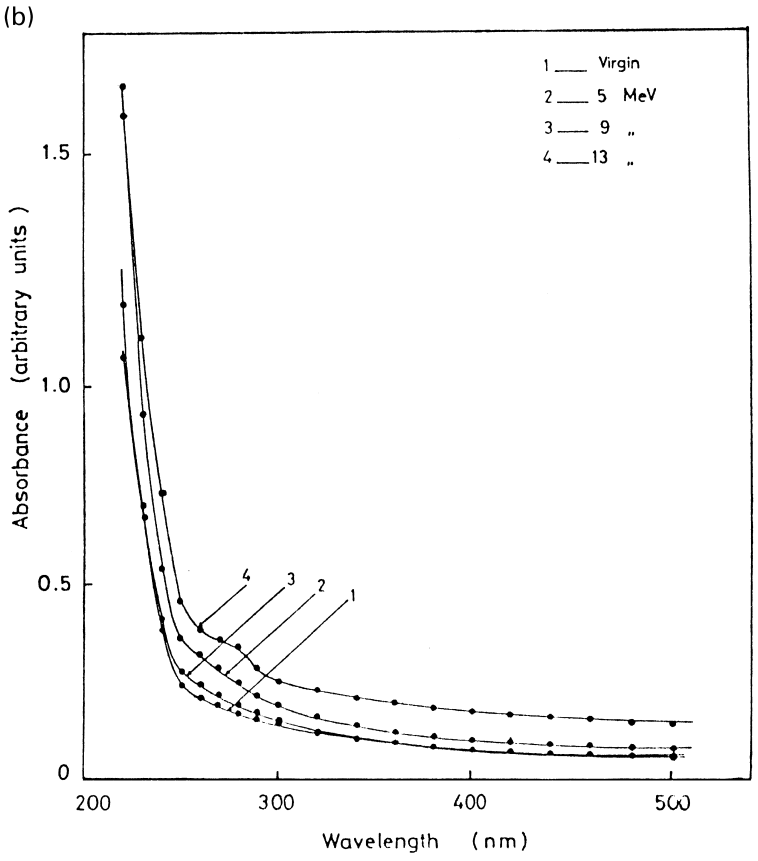
* Corresponding author.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00351-6

(a)


1 ___ Virgin
2 ___ 15 Sec
3 ___ 60 „
4 ___ 200 „
5 ___ 600 „
Absorbance (arbitrary units)
Wavelength (nm)
2.0
1.5
1.0
0.5
0
200
300
400
500

(b)


1 ___ Virgin
2 ___ 5 MeV
3 ___ 9 „
4 ___ 13 „
Absorbance (arbitrary units)
Wavelength (nm)
1.5
1.0
0.5
0
200
300
400
500

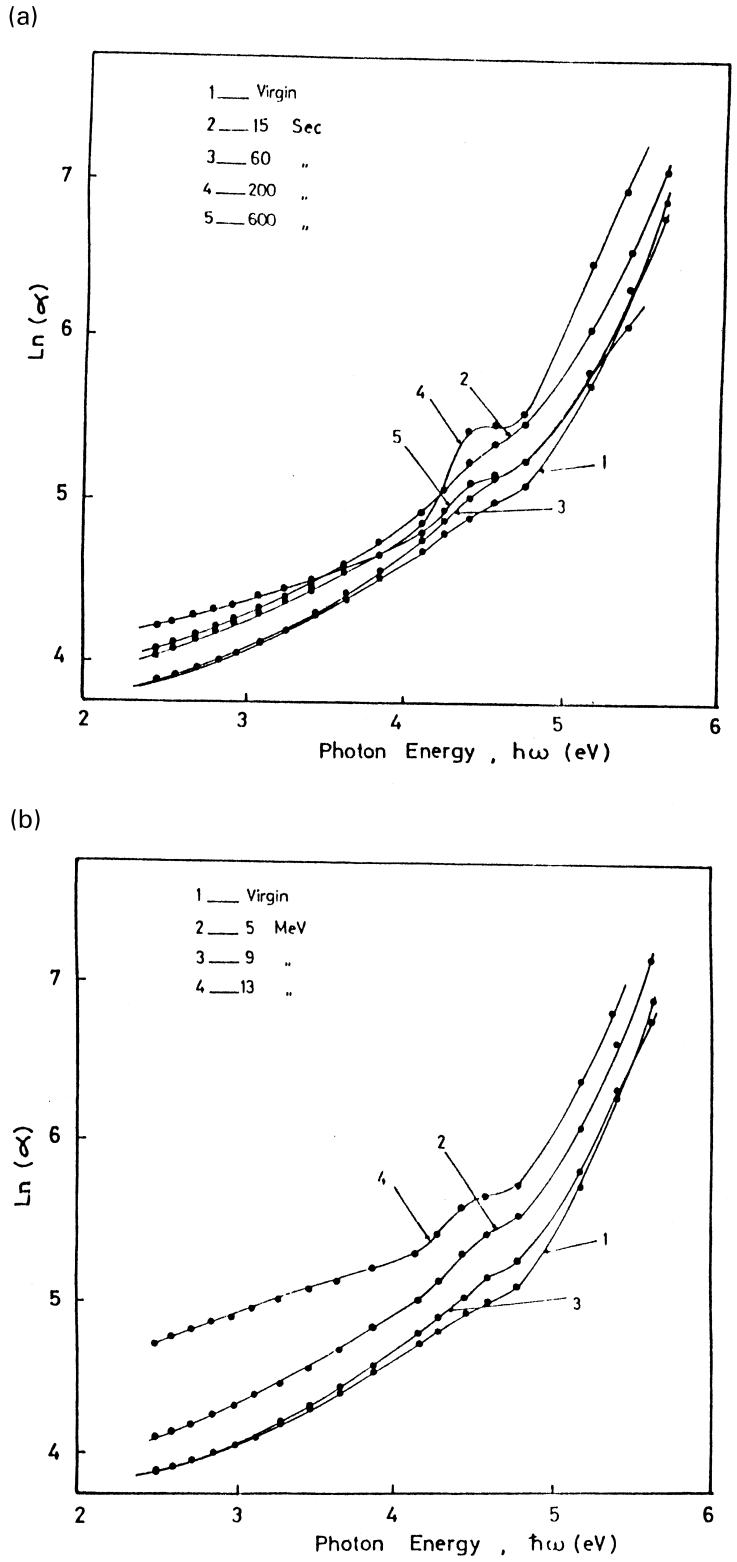


Fig. 2. (a) Dependence of (lnα) on the photon energy ($\hbar\omega$) for virgin and irradiated CPVC samples at different doses with energy 9 MeV. (b) Dependence of (lnα) on the photon energy ($\hbar\omega$) for virgin samples and samples subjected to dose 60 s at different energies (5, 9 and 13 MeV).

Fig. 1. (a) Optical spectral distribution for virgin and irradiated CPVC samples at different doses, with energy 9 MeV. (b) Optical spectral distribution for virgin and samples subjected to dose 60 s at different energies (5, 9 and 13 MeV).

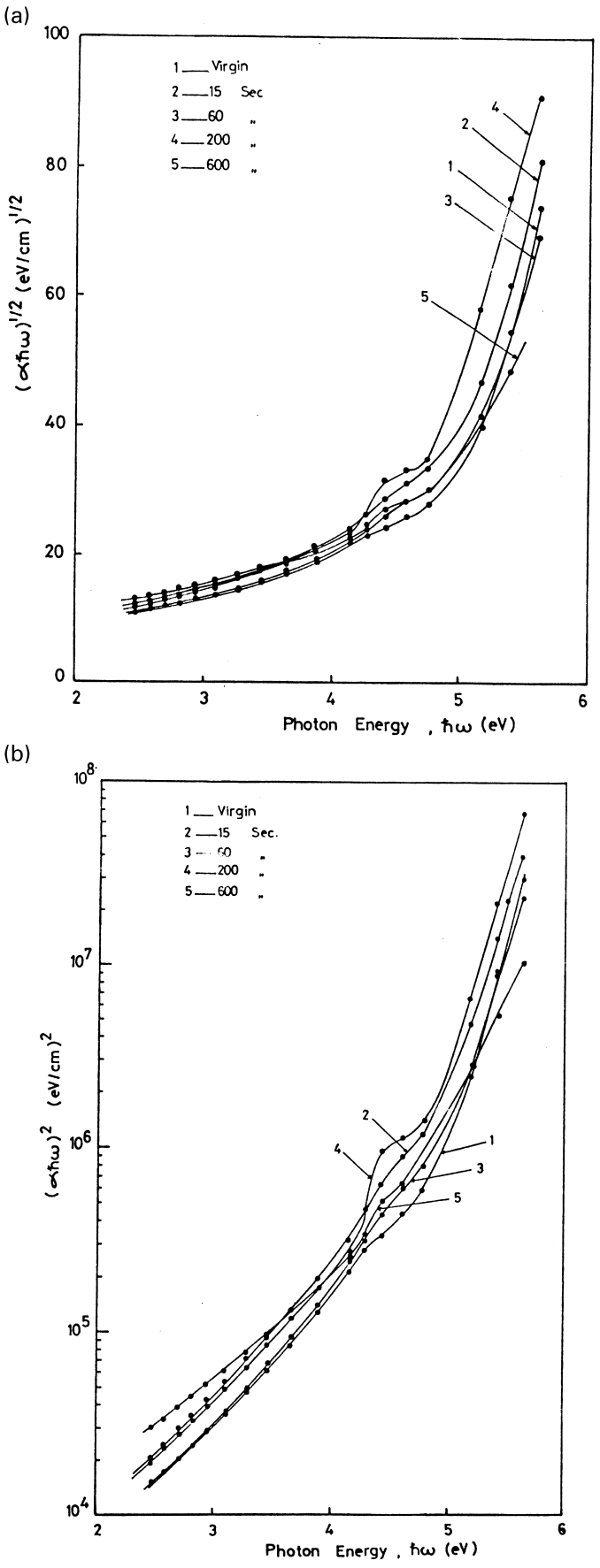


Fig. 3. Variation of $(\alpha\hbar\omega)^n$ with the photon energy ($\hbar\omega$) for virgin and irradiated CPVC samples at different doses with energy 9 MeV. (a) $n = 1/2$; (b) $n = 2$.

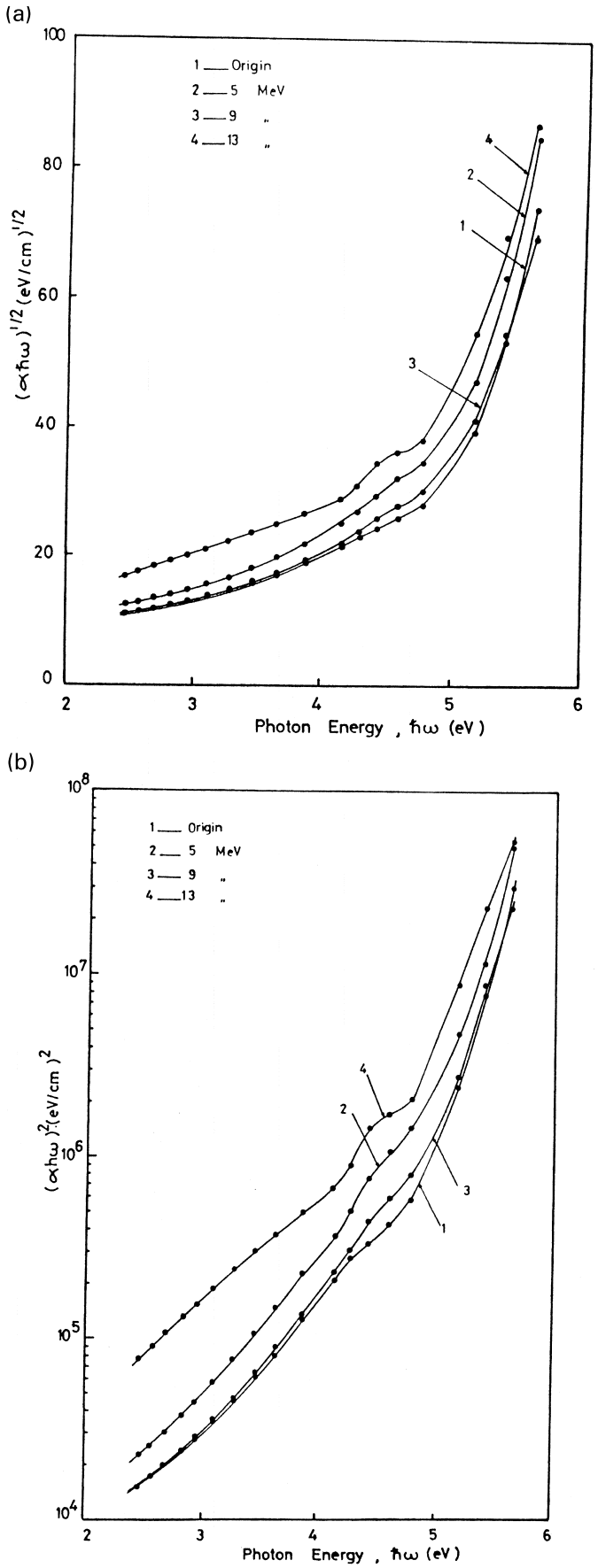


Fig. 4. Variation of $(\alpha\hbar\omega)^n$ with the photon energy ($\hbar\omega$) for virgin and samples subjected to dose 60 s at different energies (5, 9 and 13 MeV). (a) $n = 1/2$; (b) $n = 2$.

Table 1
Variation of E_{opt} and ΔE with different doses at energy of 9 MeV

Exposure time (s)	ΔE (eV)	$E_{(opy)1}$ (eV)	$E_{(opt)2}$ (eV)
Virgin	0.36	4.83	4.18
15	0.44	4.48	3.97
60	0.49	4.60	3.92
200	0.42	4.35	3.80
600	0.71	4.00	3.44

tightly packed beam and injected into the accelerating waveguide. All experiments were performed at the same electron beam current. The only variable were the energy of electrons and the irradiation time.

3. UV measurement

The absorption spectra of the virgin as well as irradiated samples were measured by UV-160 Shimadzu spectrometer in the wavelength range 200–500 nm. A perfectly flat piece of CPVC thin sheet has been placed vertically in the path of the sample beam, while the reference beam reach directly to the detector. So, the obtained spectra data are of absolute values.

4. Results and discussion

Electron irradiation affects quantitatively on the optical properties of CPVC film in the same way as other kinds of irradiation [12]. Fig. 1a shows the absorption spectra of the virgin as well as irradiated samples at different electron irradiation doses. The energy of the electron beam was kept constant at 9 MeV. It is evident that the optical absorption spectral distribution is sensitive to the irradiation dose. The sharp absorption band edge shifts towards a higher value of the wavelength, except at 600 s, as the irradiation dose is increased.

Spectra of virgin and samples subjected to dose 60 s at different electron irradiation energies are shown in Fig. 1b. The band edge shifts to a higher wavelength. This behavior can be attributed to dipole of the irradiated sample.

The absorption coefficient $\alpha\omega$ for many amorphous materials behaves exponentially as a function of photo energy $\hbar\omega$:

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{\Delta E}\right) \quad (1)$$

where α_0 is a constant, $\hbar$ is the reduced Planck's constant, and ΔE is the width of the band tails of the localized states in the normally forbidden band gap associated with the amorphous nature of the materials. Fig. 2a and b show the variation of the absorption coefficient, α, with the photon energy $\hbar\omega$ at different electron irradiation doses and energies. A sharp increase in α can be seen at a particular photon energy. This sharp increase is followed by a flattening out at a higher photon energies depending on the exposure time and electron energy.

Table 2
Variation of E_{opt} and ΔE with different electron irradiation energy (5, 9 and 13 MeV) at exposure time 60 s

Irradiation energy (MeV)	ΔE (eV)	$E_{(opt)1}$ (eV)	$E_{(opt)2}$ (eV)
Virgin	0.36	4.83	4.18
5	0.42	4.73	3.95
9	0.49	4.60	3.92
13	0.45	4.43	3.47

The optical energy gap for each samples is calculated from the Mott and Davis relationship for indirect optical transition [13]:

$$\alpha\hbar\omega = B(\hbar\omega - E_{opt})^n \quad (2)$$

where B is a constant, E_{opt} is the optical energy gap, and n is an index determined by the nature of the electronic transitions during the absorption processes.

To find out an experimental value for the optical energy gap, E_{opt}, we have applied Eq. (2). Values of E_{opt} are obtained by extrapolating the straight portions of the curve to $(\alpha\hbar\omega)^{1/n} = 0$. A best fit of the experimental data is obtained if the exponent n is chosen to be 0.5 and 2. Such a behavior is assigned for systems with indirect and direct optical energy gap of transition [13].

Fig. 3a and b depict a plot of $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ at different doses at beam energy 9 MeV. Fig. 4a and b show the same plots for different energies (5, 9 and 13 MeV) at electron exposure time 60 s. The obtained $E_{(opt)1}$ and $E_{(opt)2}$ at different doses and energies are summarized in Tables 1 and 2, respectively. Obviously, as the electron irradiation dose or energy increases, the crystalline structure, if any, of CPVC is assumed to be perturbed and leading to an increase in the degree of disorder. This behavior can be explained as follows: the interaction of an electron with the polymer molecule will result an excited state and lead to ionization [14]. Most probably a Cl^- will be formed and react with the nearest H and form HCl leaving C=C double bond on the polymer chain. The process would continue with irradiation until all the chlorine is removed.

From the density-of-state model it is known that E_{opt} decreases with increasing the degree of disorder of the amorphous phase [8]. At this stage one may expect that a band tail is, probably, created due to irradiation. The decrease in E_{opt} leads to the shift of the band tail ΔE towards the higher energy region and hence the value of ΔE calculated by Eq. (1) is expected to increase as the radiation dose or energy is increased. The decrease in ΔE at energy 13 MeV of electron beam (cf. Table 2) is due to production of X-ray together with electrons.

In conclusion, the interaction of high energy electrons with CPVC polymeric materials leads to an increase of

the energy band gap ΔE. This increase makes it a resist system responsive to radiation and used in application.

References

[1] Clegg DW, Collyer AA. Irradiation effects on polymers. London: Elsever Applied Science, 1991.
[2] Wu MS, Painter PC, Coleman MM. J Polymer Sci Phys 1980;18 (1):95.
[3] Wu JBC, Brown N. J Mater Sci Engng 1980;44 (1):121.
[4] Ankele B, Leising G, Kahlert H. J Solid State Commun 1987;62 (4):245.
[5] Bayd RH, Kesner LJ. J Polym Sci, Polym Phys 1981;19:393.
[6] Bayed RH, Kesner LJ. Chem Phys 1980;72:2179.
[7] Bayd RH, Kesner LJ. J Polym Sci, Polym Phys Edn 1980;19:375.
[8] Kurik MV. Phys Stat Sol 1971;8 (a):9.
[9] Down JD, Redfield D. Phys Rev 1972;B5:594.
[10] Madi NK, Abou Taleb WM, Abdel-Rehim N, Kassem ME. Rad Effects Defects Solids 1994;129:345.
[11] Moridi GR, Hogarth CA. Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977:688.
[12] Kassem ME, El-Khatib A, Ammar EA, Hamed AE. Radiat Effects Defects Solids 1993;127:198.
[13] Davis EA, Mott NF. Phil Mag 1970;22:903.
[14] O'Donnell JH. In: Clough RL, Shalaby W., editors. Radiation effects on polymers. ACS Symposium series 475. Washington, DC: ACS, 26–31 August 1990:405.