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Ultraviolet radiation-induced modifications of the optical and registration properties of a CR-39 nuclear track detector

A.F. Saad [a,b,*], N.M. Al-Faitory [a], M. Hussein [b], R.A. Mohamed [a]

[a] Physics Department, Faculty of Science, University of Benghazi, Benghazi, Libya
[b] Physics Department, Faculty of Science, Zagazig University, Zagazig, Egypt

ABSTRACT

The UV–VIS (ultraviolet–visible) spectra and etching characteristics of poly allyl diglycol carbonate (PADC, a form of the CR-39 polymer) detector films after exposure to UV radiation for various times have been studied. Etching experiments were carried out on the UV-exposed CR-39 detectors after alpha particle and fission-fragment irradiation using a ^{252}Cf source. The bulk and track etch rates were measured using the alpha and fission-fragment track diameters, and the sensitivity and the detection efficiency were also determined. The optical band gap for both indirect and direct transitions was calculated based on the absorption edge of the UV spectra of the pristine and variously UV-exposed detectors. The optical band gap evidently indicates a gradual change in the optical properties of the CR-39 detector that is induced by the UV radiation. This study shows that the UV-exposed CR-39 detectors were demonstrated to be highly sensitive to alpha particles, but proved to be somewhat less sensitive to the fission fragments.

1. Introduction

Radiation-induced modifications of polymers are receiving increasing research attention because of their potential scientific and technological significance. Irradiation with ultraviolet (UV) and high energy photons or with electrons or other particles that do not in themselves make tracks can have significant and sometimes profound effects on the properties of track detectors. The observed effects are confined to plastics, except at extremely high doses [1]. In polymers, the molecular chains can be disengaged by breaking of chemical bonds, which can occur through smaller energy transfers than are typically required for ionization (2–3 eV as opposed to 10–15 eV) [2]. Bulk polymers with lower molecular weights will dissolve more rapidly because of their shorter chain lengths [3], resulting in a region with many chain ends. However, it is well established that polymers can be degraded by UV irradiation, and many previous studies have indicated that UV irradiation will affect the bulk etch and track etch responses and the sensitivity of CR-39 polymeric track detectors [4–14].

The purpose of this work is to investigate the UV–visible spectra of CR-39 polymeric track detectors after exposure to UV radiation using a UV–VIS spectrometer. We extend the analysis performed using this spectroscopic tool to a more reliable microscopic approach to understand how the absorption spectrum of a given material is related to its band structure, and in particular to determine the modifications of the optical properties that are induced by the UV radiation. This approach was readily supported by further studies of the etching properties for comparison. Modifications of the optical band gap energy have been reported along with changes in the registration properties of the charged particles in a CR-39 polymeric track detector.

2. Theoretical approach

The absorption of light by an optical medium is quantified by the medium's absorption coefficient. This is defined as the fraction of the power absorbed in one unit length of the medium. The absorption coefficient $\alpha(h\nu)$ can be calculated from the absorbance (A) using the following formula [15]:

$$\alpha(h\nu) = A/l \tag{1}$$

where l is the sample thickness in cm, and A is defined as, $A = \log(I_o/I)$, where I_o and I are the intensities of the incident and transmitted UV–visible beams, respectively. However, the

* Corresponding author at: Physics Department, Faculty of Science, Zagazig University, Zagazig, Egypt. Tel.: +20 55 2303252, mobile: +20 1016746496, +20 1225307497; fax: +20 55 2308213.
    E-mail address: abdallahsaad56@hotmail.com (A.F. Saad).

absorption coefficient is found to vary exponentially with the photon energy, $(h\nu)$, which follows the Urbach relation [16]

$$\alpha(h\nu) = \alpha_o \exp(h\nu/E_u) \tag{2}$$

where $\alpha(h\nu)$ is the absorption coefficient, which is a function of the photon energy $h\nu$. α_o is a constant and, E_u, which is the Urbach energy, is equal to the inverse logarithmic slope of the absorption coefficient. The previous equation was modified into a more general form by Davis and Mott [17]:

$$\alpha(h\nu) = B(h\nu - E_g)^n/h\nu \tag{3}$$

where $h\nu$ is the energy of the incident photons, the factor B depends on the transition probability and can be assumed to be constant within the optical frequency range, E_g is the energy value of the optical band gap between the valence band and the conduction band, and n is the power that characterizes the electronic transition, regardless of whether it is direct or indirect during the absorption process in K-space. Specifically, n is 2, 3, 1/2 and 3/2 for the indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. The electron wave vector must clearly change significantly when jumping from the valence band to the bottom of the conduction band if the band gap is indirect. It is not possible to make this jump through absorption of a photon alone; the transition must also involve a phonon to conserve momentum. This contrasts with the process for a direct band gap, in which the process can take place without any phonons being involved. The phonon energy ε can be calculated based on the energy difference between the optical band gap energy transitions (direct, E_g^d, and indirect, E_g^{ind}) using the following formula [18]:

$$\varepsilon = E_g^d - E_g^{ind} \tag{4}$$

However, indirect absorption plays a highly significant role in technologically important materials, including some metals and amorphous materials. The treatment of indirect absorption is more complicated than that for direct absorption because of the role played by the phonons [15].

For a linear structure, the number of carbon atoms per conjugation length, N which is known as a cluster [19], is given by

$$N = 2\beta\pi/E_g \tag{5}$$

where N is the number of carbon atoms per conjugation length, and 2β gives the band structure energy of a pair of adjacent π sites. The value of β is assumed to be –2.9 eV because this value is associated with the $\pi \rightarrow \pi^*$ optical transition in the –C=C– structure.

3. Experimental procedures

CR-39 polymer sheets of TASTRAK were produced and provided by Track Analysis Systems Ltd. (TASL), Bristol, UK. A standard thickness of 750 μm was used. The polymeric detector samples were cut to a size of 2×2 cm^2. UV exposure was performed using a UV lamp with a power of 10 W. The UV lamp is switched off automatically for 5 min at 20 min intervals to prevent internal heating of the sample material. The integrated UV exposure times of the samples ranged from 1 to 100 h. The samples were then irradiated (UV exposure, pre-alpha and fission fragment irradiation) in a 2π geometry using a 252Cf radioactive source. A set of detectors was prepared for the exposure experiments; one virgin sample was also retained as a control. After exposure, the detectors were chemically etched in a 6.25 M solution of NaOH at 70 ± 1 °C for an etching time of 4 h. The detectors were then washed in distilled water to stop the chemical reaction and to avoid etching solution contamination on the surfaces of the detectors. The detectors were read and the diameters of the tracks were measured using an

eyepiece micrometer mounted on an optical microscope; the track etching parameters were then estimated accordingly.

A Shimadzu mini 1240 UV–VIS spectrometer was operated in spectrum mode (ABS mode) at a scanning speed of 25 nm/min. The working wave length range of the spectrometer is 190–900 nm.

4. Results and discussion

4.1. Measurement of UV–VIS spectra in UV-radiation exposed CR-39 nuclear track detectors (NTDs)

Optical absorption measurements with the UV–VIS spectrophotometer were carried out on the virgin and irradiated samples of CR-39 after exposure to different doses of UV radiation, and the results are shown in Fig. 1. The absorption peak shifts from the UV region toward the visible region, i.e., toward the higher wavelength, for the exposed samples. This indicates a significant reduction in band gap after UV exposure. We also observed broadening of the absorption peak with increasing exposure time. The broad peaks have a characteristic shoulder shape because of the high dose exposure to UV radiation, as shown in Fig. 1, while in the cases of gamma [20–22], neutron [23] and ionizing particle radiation [18], unlikely shape behavior is shown that depends on the fluence, energy and nature of the radiation itself. The colorless samples become gradually opaque to visible light and the materials of these detectors change from very highly transparent at wavelengths longer than 190 nm to a yellowish color with increasing UV irradiation dose. However, neither the detailed mechanisms nor the specific compounds that are responsible for the yellow coloration have been fully identified to date.

From a systematic study of the spectral behavior of the exposed samples as a function of UV dose, the absorbance values of the exposed samples compared with that of the virgin sample at selected wavelengths of 280, 290, 300, 310 and 320 nm are plotted as a function of the exposure time, as shown in Fig. 2. In this figure, the strongest absorption peak overall was found to be for the UV radiation doses at ~280 nm. The absorbance increased sharply with exposure time up to 40 h, and from 40 to 70 h, there is an insignificant reduction in absorbance; beyond 70 h, the absorbance increases slightly up to 80 h, but decreases slightly thereafter. Thus, it was found that these UV doses seem to be sufficient to induce significant modification of the optical band gap of CR-39 polymeric track detectors. From the UV–VIS absorption spectra, the band gaps of the virgin and exposed detectors were calculated by extrapolation of the plot of $(\alpha h\nu)^{1/n}$ versus $(h\nu)$ on the $h\nu$ axes. To determine the indirect and direct energy band gaps, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ were plotted as a function of the photon energy $(h\nu)$ while taking the linear portion of the fundamental absorption edge of the UV–VIS spectra into account, as shown in Fig. 1. These plots are not presented as part of this report. The variations in the optical band gap energy, the phonon energy, the Urbach energy, and the number of carbon atoms (N) in a cluster of CR-39 polymeric track detectors that have been exposed to UV photons with different exposure times are summarized in Table 1. Note that the band gap energy of the CR-39 detector decreases from 3.50 to 2.70 eV and from 4.88 to 4.64 eV for the indirect and direct transitions, respectively, as a result of the UV exposure. As we increase UV exposure time from 0 to 2 h, the contributions related to phonon absorption gradually increase, and then dose independence of the phonon absorption edge is observed from 5 to 20 h, with a significant gradual increase thereafter. The irregular variations of the phonon energies with UV dose, as shown in Table 1, lead to a characteristic dose dependence of the absorption edge at the lowest and highest UV doses. As previously
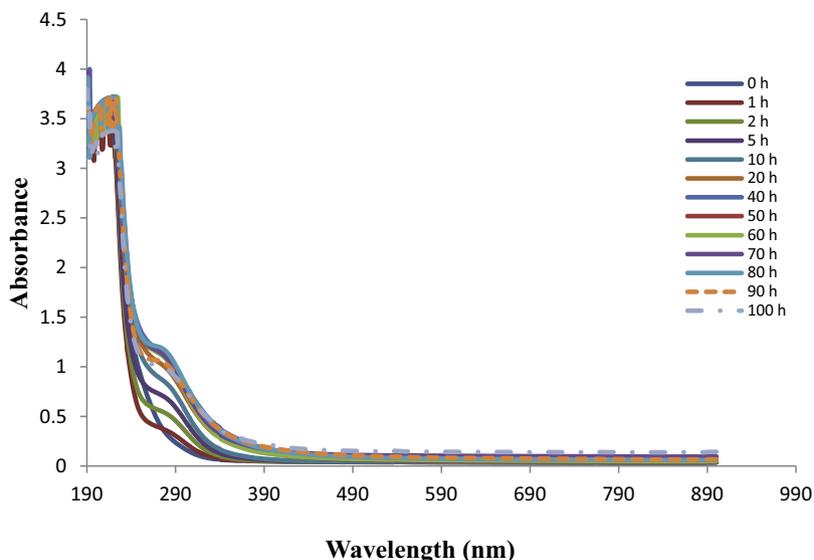
Fig. 1. UV–visible spectra of the virgin and UV-radiation-exposed CR-39 polymer films for exposure periods of 1–100 h.
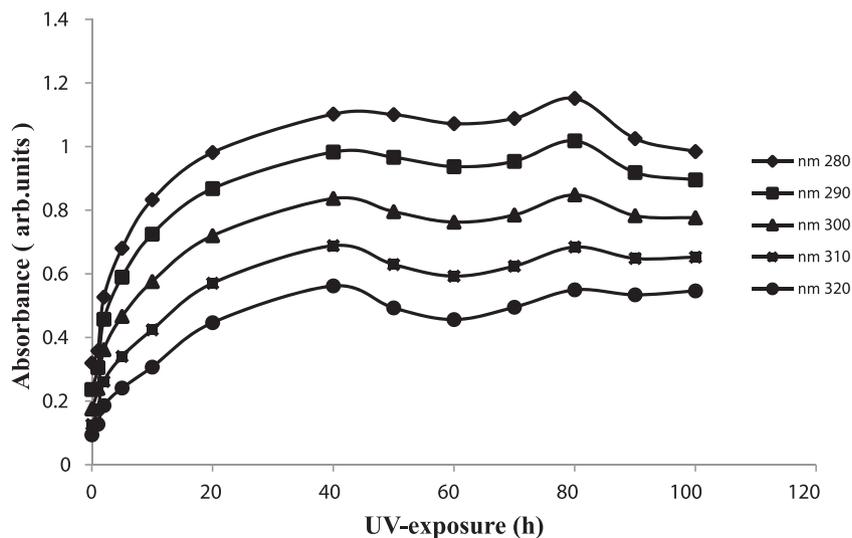
Fig. 2. Plots of absorbance at wavelengths of 280, 290, 300, 310 and 320 nm with UV exposure time.

Table 1
Optical band gap energy, phonon energy, Urbach energy, and carbon atoms (N) in a cluster of PADC polymer-based NTDs exposed to UV photons with different exposure times.

UV-exposure (h)	Band gap energy (eV)		Phonon energy (eV)	Urbach energy (eV)	Carbon atoms (N) in a cluster	
	Indirect	Direct			Indirect	Direct
0	3.50	4.88	1.38	0.55	5	4
1	3.40	4.96	1.56	0.55	5	4
2	3.30	4.96	1.66	0.55	5	4
5	3.20	4.80	1.60	0.53	6	4
10	3.10	4.56	1.46	0.53	6	4
20	3.00	4.56	1.56	0.54	6	4
40	3.00	4.40	1.40	0.54	6	4
50	2.90	4.40	1.50	0.54	6	4
60	2.90	4.40	1.50	0.54	6	4
70	2.80	4.48	1.68	0.63	7	4
80	2.70	4.40	1.62	0.62	7	4
90	2.70	4.48	1.78	0.62	7	4
100	2.70	4.64	1.94	0.62	7	4

mentioned, we observe all phonon energy enhancements at very high doses, because there would be a considerable reduction in the indirect band gap energy, while the corresponding direct gap energy only shows a tiny drop off. This behavior contrasts with that of the indirect gap, in which the absorption edge merely shifts with the band gap as the UV dose is varied. In addition, this decreasing optical band gap trend uses enhancement of the conductivity of the exposed polymers. These changes are attributed to scission of the polymer chains and the formation of cross-linkages. The degradation due to photo-oxidation is a free radical chain mechanism that occurs when the polymer is exposed to UV radiation in the presence of oxygen.

We can see from Table 1 that the Urbach energy does not suffer any change in its value of 0.55 eV with UV exposure times between 0 and 2 h, while there is a slight reduction of 3.6% after exposure for 5 and 10 h. From 10 to 20 h, there is a tiny reduction in the Urbach energy; from 20 to 60 h, the Urbach energy remains constant, whereas from 60 to 70 h, there is a considerable increase in energy of 14.5%, and the energy remains constant thereafter.

On the one hand, the number of carbon atoms (N) per conjugation length in the case of direct transitions remains constant, i.e.,

$N = 4$ carbon atoms in a cluster for virgin and exposed detectors for all doses, as shown in Table 1. On the other hand, in the case of indirect transitions, N per conjugation length increases non-linearly with UV exposure time. Between 0 and 2 h, there is no change in the carbon atoms for $N = 5$ atoms per conjugation length, which corresponds to a constant value of 0.55 eV in terms of Urbach energy. From 2 to 5 h, there is a considerable increase in N to 6 atoms per conjugation length and this remains constant for exposure times up to 60 h, corresponding to more or less constant values of 0.53 and 0.54 eV in terms of Urbach energy. From 60 to 70 h, there is another significant increase in N to 7 atoms per conjugation length, and this remains constant thereafter up to the end of the exposure time at 100 h, which also corresponds to more or less constant values of 0.63 and 0.62 eV in terms of Urbach energy. It is very interesting to note that the number of carbon atoms (N) in a cluster in the direct transition case does not change over the entire exposure time, while in the indirect transition case, the number of carbon atoms gradually and systematically increased over three stages. This behavior is attributed to the transition at the band gap, E_g^{ind}, which is indirect and involves a phonon in the case where the conduction band and the valence band are not parallel to each other. It may be that this phonon energy, as a mechanical energy, can induce thermal vibration in the polymer material network, which causes scission followed by cross-linking to enhance the number of carbon atoms in a cluster or per conjugation length. The Urbach energy, E_u, in the same sense, originates from the thermal vibration in the lattice [16], which produces a correlation trend between E_u and the number of carbon atoms (N) per conjugation length, in the case of an indirect transition.

4.2. Measurement of the registration properties of charged particles in UV-radiation exposed CR-39 NTDs

The optical properties of the detectors have already been investigated, as previously mentioned, and we would like to extend this study to the changes in the registration properties of heavy ions in UV-treated CR-39 polymeric track detectors. Table 2 shows the effects of the UV radiation on the diameters of the alpha and fission fragment tracks, $\frac{D_\alpha}{D_{ff}}$, D^{ff}/D_0^{ff} and D^α/D_0^α, the bulk and track etch rates, V_B and V_T, respectively, the detection efficiency $\eta\% = [1 - (V_B/V_T)]$, the sensitivity S, the critical angle θ_c and the etching behavior of the CR-39 polymeric nuclear track detectors. It should be noted that the UV irradiation significantly enhances the diameters of the alpha particle and fission fragment tracks, but in the case of alpha tracks that were cured using UV radiation, the diameter was approximately 15 times higher than that of the

virgin sample, while this rate was ten times more than that of the virgin sample for the fission fragment tracks. However, the rates of increase in the diameter of the alpha tracks were much higher than that those of the fission fragment tracks that were registered in the CR-39 track detector that was cured using UV radiation. It would seem that the deposited UV energy breaks additional chemical bonds along the tracks of the alpha particles and the fission fragments and these bonds are stabilized by oxidation. These results show, without any doubt, that the response of the UV-treated PADC material to charged particles is highly sensitive to heavy ions with low ionization rates such as alpha particles; the sensitivity to particles with high ionization rates, such as fission fragments, is somewhat lower. This may be because the ionization rates of the alpha particles are considerably lower than that those of the fission fragments, and several methods for particle identification depend upon the quantitative relationship between the track etch rate V_T and the ionization rate. This method works on plastics such as CR-39 high-grade polymer, for which V_T can be strongly increased by application of UV radiation. The processing of CR-39 polymers that have been subjected to a massive dose of UV radiation can be used to identify particles with low ionization rates more effectively than those with higher ionization rates. However, from previous studies, it was noted that the influence of UV effects on a plastic detector such as the Lexan detector for particle identification leads to V_T values that are comparable with the initial value of the pristine sample [24,1], which is consistent with the results of the current study.

UV radiation in the presence of oxygen can greatly enhance the etching rates of the tracks in the CR-39 detector material, where the CR-39 contains oxygen, with very significant enhancement of the bulk etch rate, V_B, as shown in Table 2. The sensitivity S, which in turn involves both the track etch rate and the bulk etch rate, increases with increasing UV exposure time. The track etch rate was found to have changed greatly because of the UV irradiation process, although this change is significantly massive when compared with the change in the bulk etch rate. However, the change in both etch rates is very large. The measurement of this considerable change in etch rates is not difficult, so we have taken the fact that the alpha and fission tracks generally do not overlap each other at the longest exposure times into account. We have plotted the bulk and track etch rates and the sensitivities of the CR-39 NTDs as a function of exposure time, as seen in Fig. 3. The results show quasi-similar behavior, where the variations of the etch rates and the sensitivities of the CR-39 detector with exposure time have four different rates. The observed trend changes for the different exposure time ranges are attributed to the fact that the UV photons are passing through a CR-39 detector medium that produces radiation damage on a continuous basis, whereas this damage is not

Table 2
Etching parameter and diameter ratio values of pristine and UV-cured alpha and fission fragment tracks, $\frac{D_\alpha}{D_{ff}}$, D^{ff}/D_0^{ff}, D^α/D_0^α, V_B, V_T, $\eta\% = [1 - (V_B/V_T)]$, $S = (V_T/V_B)$ and θ_c as functions of UV exposure time for the CR-39 polymeric track detectors.

UV-exposure time (h)	$D_\alpha(\mu m)$	$D_{ff}(\mu m)$	$X = \frac{D_\alpha}{D_{ff}}$	D^{ff}/D_0^{ff}	D^α/D_0^α	$S = \frac{V_T}{V_B}$	$\eta\%$	V_B ($\mu m/h$)	V_T ($\mu m/h$)	θ^c
0	5.0	8.9	0.562	1.0	1.0	1.92	47.89	1.48	2.84	31.38
1	5.8	10.0	0.580	1.12	1.16	2.01	50.30	1.67	3.36	29.83
2	6.5	11.0	0.591	1.24	1.30	2.07	51.72	1.83	3.79	28.88
5	8.0	12.8	0.625	1.44	1.60	2.28	56.17	2.13	4.86	26.01
10	11.3	16.7	0.677	1.88	2.26	2.68	62.68	2.78	7.45	21.90
20	16.5	22.5	0.733	2.53	3.30	3.33	69.98	3.75	12.49	17.47
40	28.0	38.0	0.737	4.27	5.62	3.38	70.41	6.33	21.39	17.20
50	45.0	60.0	0.750	6.76	9.01	3.57	71.99	10.00	35.70	16.26
60	53.0	70.0	0.757	7.87	10.64	3.68	72.83	11.60	42.69	15.76
70	61.0	80.0	0.763	9.01	12.20	3.78	73.54	13.30	50.27	15.34
80	85.0	84.0	0.774	9.43	12.99	3.98	74.87	14.00	55.72	14.55
90	68.0	86.0	0.790	9.71	13.01	4.34	76.96	14.30	62.06	13.32
100	73.0	88.0	0.829	9.90	14.71	5.40	81.48	14.60	78.84	10.67
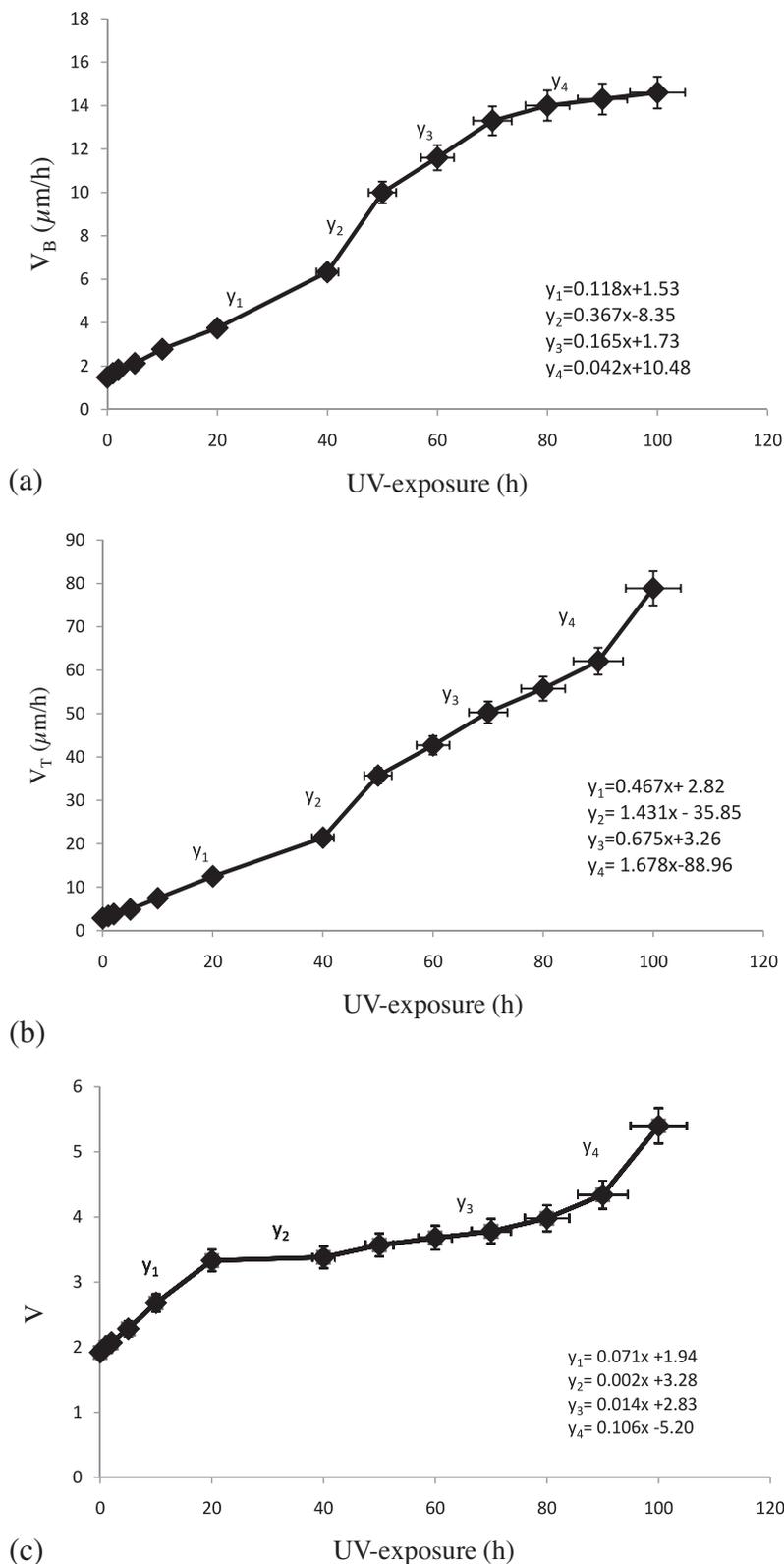
Fig. 3. Plots of (a) bulk and (b) track etch rates and (c) sensitivity of the CR-39 polymer with UV exposure time. The detectors, after UV exposure and subsequent ^{252}Cf irradiation, were chemically etched in a 6.25 M solution of NaOH at 70 ± 1 °C for an etching time of 4 h.

constant along the UV path; consequently, the bulk and track etch rates are also not constant over the exposure time. As shown in Fig. 3(a), the bulk etch rate V_B increases linearly up to 40 h. For the exposure time from 40 to 50 h, the rate of variation becomes fairly large, and for exposure from 50 to 70 h, the rate becomes

slightly greater than that for the first stage, and remains nearly constant thereafter. However, the track etch rate also increases linearly from 0 h (unexposed) up to 40 h, but for exposure between 40 and 50 h, the rate of variation of V_T is rather higher than that for the first stage. For exposure from 50 to 90 h, there is a small

increase in the track etch rate with exposure time, followed by a considerable increase thereafter, as shown in Fig. 3(b). In Fig. 3(c), the sensitivity of the CR-39 detector material is shown to increase non-linearly with exposure time. For exposure of between 0 and 20 h, there is a linear increase in sensitivity, while from 20 to 40 h, the sensitivity remains constant. Beyond 40 h, the sensitivity increases slightly up to 90 h, but shows a significant increase thereafter. In general, it may be that some agents and/or oxygen content in the CR-39 polymer are responsible for actively promoting the UV enhancement of V_T in the material. Exposure to UV radiation can either cut the long chain molecules, thus converting them into shorter and more rapidly etchable materials, or can loosen the chemical bonds of a polymer, and thus greatly increase V_T, as we have observed in the PADC films. Thus, the irradiation effects that have been observed for these PADC films (a form of CR-39) showed that intense radiation equivalent to 100 h of UV exposure would approximately double the detection efficiency and triple the response of the detector material; in addition, this high dose reduces the critical angle to about one third of that of the virgin sample.

5. Conclusions

- UV–VIS spectroscopic studies show that the indirect band gap values in CR-39 polymers are more seriously affected than the corresponding direct band gap values by UV exposure. The number of carbon atoms (N) per conjugation length for indirect transitions increases with increasing UV exposure time, whereas in the case of direct transitions, the number remains constant. The Urbach energy and the phonon energy increase irregularly but significantly; this may be due to the enhancement of the disorder in the CR-39 polymer after UV exposure.
- UV radiation induced considerable positive changes in both the response and the detection efficiency of the CR-39 polymer, whereas the critical angle decreases significantly with increasing UV exposure time.

- The exposed detector material was shown to be highly sensitive to alpha particles, but somewhat less sensitive to fission fragments.
- UV processing of CR-39 polymers for the purpose of particle identification is highly recommended for the fields of nuclear and particle physics.

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